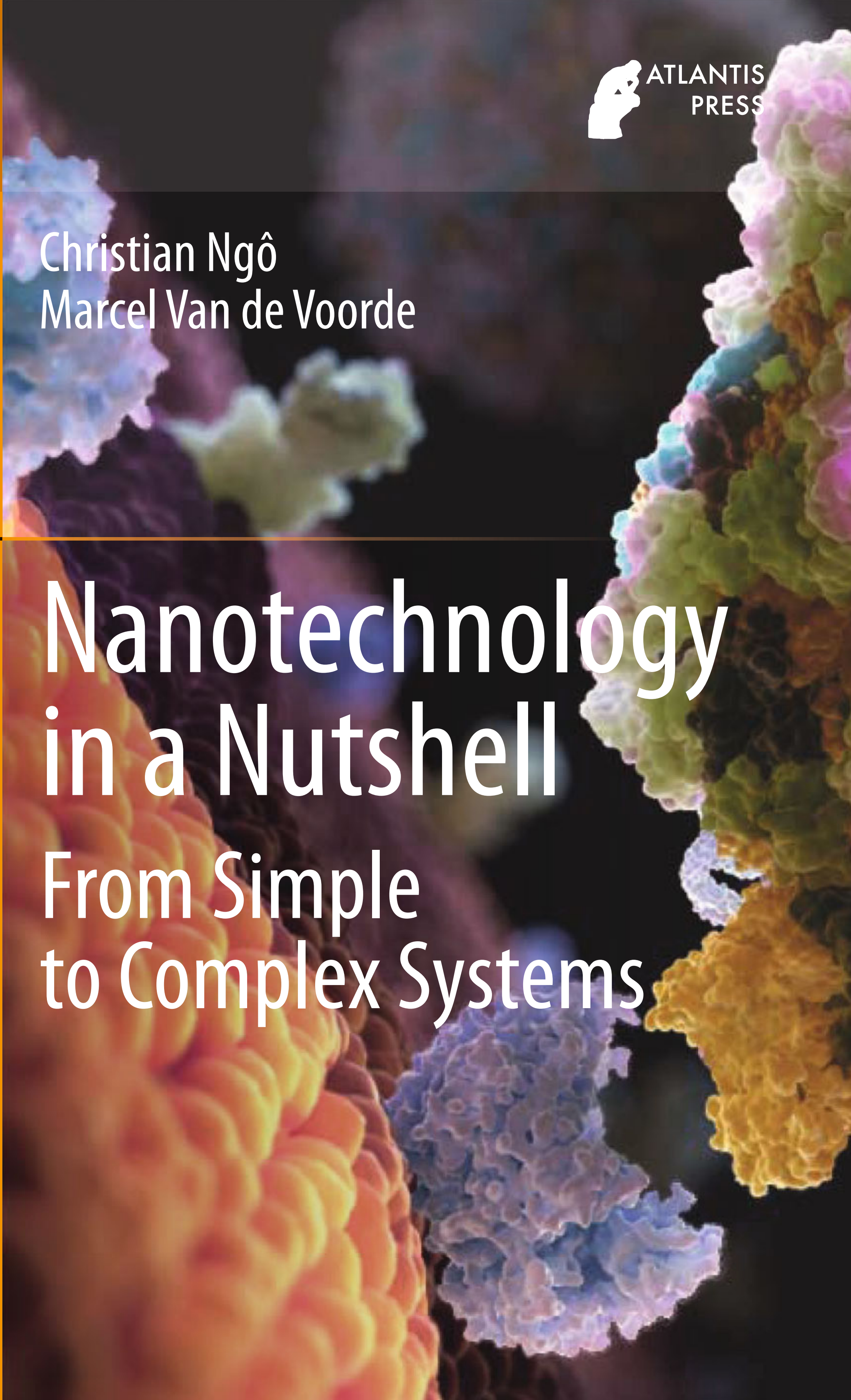

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Christian Ngô
Marcel Van de Voorde

Nanotechnology in a Nutshell

From Simple to Complex Systems

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Christian Ngô · Marcel Van de Voorde

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Christian Ngô
Edmonium
Saint-Rémy-lès-Chevreuse
France

Marcel Van de Voorde
Faculty of Applied Sciences
DELFT University of Technology
The Netherlands

Image Courtesy H. DAWSON, Ch. ABERG, M. MONOPOLI, University College Dublin (Ireland). The picture on the cover page of the book represent: Nanoparticle protein corona engaging with a cellular receptor.

ISBN 978-94-6239-011-9 ISBN 978-94-6239-012-6 (eBook)
DOI 10.2991/978-94-6239-012-6

Library of Congress Control Number: 2013953213

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Foreword

Science and technology are engines of progress in society. They are also of increasing interest to the general public, consumers, and policy makers, in addition to scientists and economists. New ground for science policy was broken in January 2000, when the then President Clinton announced the National Nanotechnology Initiative driven by a 20-year vision. Nanotechnology currently is well recognized as a science and technology megatrend for the beginning of the twenty-first century. This book aims to show where nanotechnology is now—transitioning to complex systems and fundamentally new products—and communicates the societal promise of nanotechnology to specialists and the public.

All materials we see around us have a nanostructure that determines their behavior. Because of nanotechnology—control of matter at the atomic, molecular, and macromolecular levels where specific phenomena enable novel applications—major industries and medicine are changing. Advances at the nanoscale are leading to new understanding of nature and manmade things, and an increased ability to restructure matter at the atomic and molecular levels. The multidisciplinary field of nanotechnology has been expanding since 2000 in large public and private programs around the world, reaching an annual global investment in 2012 of approximately $20 billion.

Most of what has already made it into the marketplace is in the form of "First Generation" products (passive nanostructures with steady behavior, such as coatings, nanoparticles, nanowires, and bulk nanostructured materials). Many small and large companies have "Second Generation" products (active nanostructures with changing behavior during use, illustrated by transistors, amplifiers, targeted drugs and chemicals, sensors, actuators, and adaptive structures) and embryonic "Third Generation" products (nanosystems, including three-dimensional nanosystems using various synthesis and assembling techniques such as bio-assembling; nanoscale robotics; networking at the nanoscale and multiscale architectures; after 2010) in the pipeline. Concepts for "Fourth Generation" products, including heterogeneous molecular nanosystems, are only in research. Each generation of new products is expected to include, at least partially as components, products from previous generation. The labor and markets are estimated to double every 3 years, reaching a $3 trillion market encompassing 6 million jobs by 2020 if one assumes that the rates of increase in the last 12 years would continue. Nanotechnology has the promise to create a basic understanding and a general purpose technology with mass and sustainable use by 2020 ("Nanotechnology Research Directions for Societal Needs in 2020", Springer, 2011, www.wtec.org/nano2/).

While expectations from nanotechnology may have been overestimated in the short term, the long-term implications on health care, productivity, and the environment appear to be underestimated. This volume will stimulate further interest and bring faster societal recognition to nanotechnology and overall to emerging technologies.

Mihail C. Roco
Senior Advisor for Nanotechnology
National Science Foundation
Arlington
USA

Reference

M. C. Roco, C. A. Mirkin, and M. C. Hersam, "Nanotechnology research and directions for societal needs in 2020", Springer, 2011

Presentation of the Book

It is rare for a new technology to transform all aspects of human activity. In history, one can identify agriculture, the industrial revolution, and the advent of personal computing as truly unprecedented advances.

In the twenty-first century, nanotechnology is predicted to provide the next revolution. Nanotechnology spans all of our human activity, from agriculture, medicine and food to clothing, from transport to industrial processes. It is not just about the ability to understand and manipulate material at the nanoscale, it is the way in which a new technology will be used to change the way products are made and to provide a step change in the functionality that they provide.

Nanotechnology has been a part of many commonplace products for hundreds of years. Steel, concrete, adhesives, and cosmetics have all used nanoscale mechanisms to achieve their properties, but developments have historically been through craft skills and trial-and-error rather than through science and engineering. Recent developments in experimental techniques that allow the study and manipulation of materials at the nanoscale, coupled with novel manufacturing techniques, mean that we are poised to be able to realize new properties and functions that previously could not be achieved.

One nanometer (nm) is one millionth of a millimeter (mm) or/and a billionth of a meter. As a matter of comparison, ants range in size from 2 to 25 mm and a red blood cell has a size around 6,000–8,000 nm. Ultimately, all living and inert matter is made of atoms, which have a dimension well below the nanometer range, typically a diameter between 0.1 and 0.65 nm = 100 and 650 pm (1 pm = picometer). An atom is made of electrons surrounding a nucleus whose diameter is even smaller: its size is about 1.8–15 millionths of a nanometer depending upon the element (1.8–18 fm)! Table 1 recalls the different subunits used as we go from the visible macroscopic world to the microscopic world.

A nanometer is quite a small length scale. In order to imagine a 1 nm compared to 1 m (= 10^9 nanometers) which is a billion larger, let us consider two large distances in our solar system: the distance from the earth to the moon ($\sim$360,000 km) and the distance to the sun ($\sim$150 millions of km). If we shrink these distances by a factor of 10^9 we get 36 cm for the first distance and 150 m for the second one. The radius of the sun ($\sim$696,000 km) becomes 69.6 cm and that of the earth (6,400 km) becomes equal to 6.4 mm. These comparisons show that a

Table 1 Units and subunits

Unit	Value in meter	Value in meter
1 m (meter)	1 m	10^{0} m
1 centimeter (cm)	0.01 m	10^{-2} m
1 millimeter (mm)	0.001 m	10^{-3} m
1 micrometer or micron (μm)	0.000 001	10^{-6} m
1 nanometer (nm)	0.000 000 001	10^{-9} m
1 picometer (pm)	0.000 000 000 001	10^{-12} m
1 femtometer (fm)	0.000 000 000 000 001	10^{-15} m

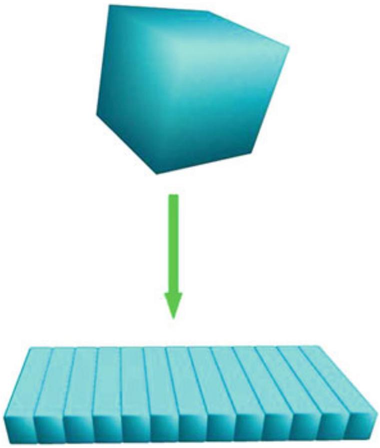

Fig. 1 Dividing a cube into nanocubes increases the total surface of the system a lot

nanometer distance is quite a small distance compared to those we are faced at the macroscopic level.

Compared with macroscopic systems, surface effects are very important at the nanoscale. The reason for this can be illustrated by considering a cube of side 1 cm, as shown in Fig. 1. The total surface area of this cube is six faces each of dimensions 1 × 1 cm, making a total of 6 cm^2. Suppose we divide this cube into small cubes of side 1 nm (Fig. 1). This gives the incredible number of 10^{21} nanocubes each with a tiny surface area of 6×10^{-14} cm^2. However, the total area of these nanocubes amounts to 6,000 meters squared! This corresponds to the surface area of 60 houses of 100 m^2. This demonstrates the power of surfaces at the nanoscale.

Strictly speaking, nanotechnology should concern building objects from the bottom-up using atoms or molecules. It also makes possible a top-down approach of reducing size and organization from the macroscopic scale. However this vision is extended to a broader domain where it is possible to observe, see, detect, move, and manufacture objects with dimensions in the range of 1–100 nm. This is much less restrictive and opens a wide field of applications, some of them being already on the market.

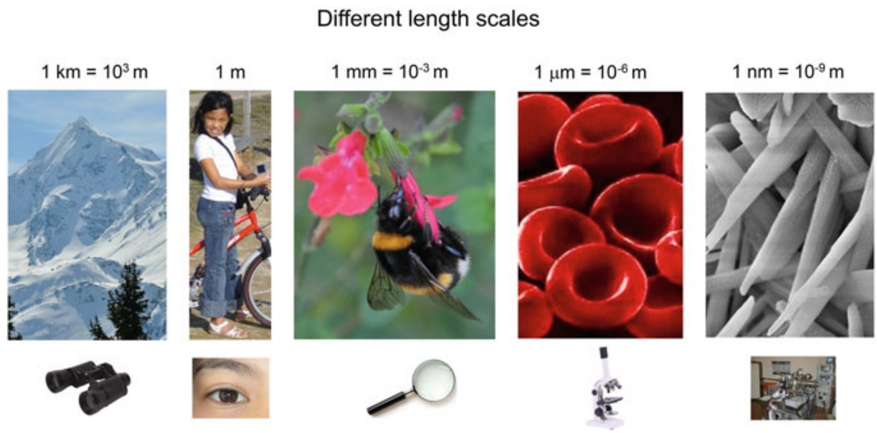

Fig. 2 Illustration with objects of different length scale and instruments that can be used to observe them

On the other hand, "nanomaterials" is a term used to describe a broad and disparate range of materials containing characteristic features with dimensions below 100 nm. It is the properties of these individual nanoscale features and their organization both at the nanoscale and up to the macroscale that will define the properties of nanomaterial. These features can be organized in random or well-ordered patterns. Confusingly, a "nanomaterial" can be of macroscopic size containing many nano-objects but it can also be an individual object investigated as a material at the nanoscale. A nanomaterial can be a thin film, a thin wire, or a collection of nanoparticles, for example. A nanomaterial is often characterized by a dimension linked either to the dimension of the salient nanofeatures making up the material or to their organization. When some interesting property of a material emerges from this organization or pattern, the combined material may be referred to as a "nanostructure" or a "nanostructured material".

The term "nanomaterials" is used to describe objects that have at least one of their dimensions below 100 nm. Nanomaterials encompass a very broad and disparate range of natural and artificial materials. In practice, they can have the form of a thin film, cylinder, or particle. Neither a single human hair, which looks like a cylinder but has a diameter of about 80,000 nm, nor a red cell, can be called nano-objects, even though they look very small.

Figure 2 shows different length scales, each separated by a factor of 1,000, with different objects and the instruments that can be used to see details of the object. For example, the size of mountains is of the order of several kilometers and, if we are far away, we use binoculars to observe their details. Most humans have a height below 2 m and we can see them just with our eyes if we are close by. Insects can have a size of a few millimeters or centimeters: they can be observed with a magnifying glass. Red blood cells have a size of a few thousands nanometers and can be observed with a light microscope. Finally, silicon wires of an integrated

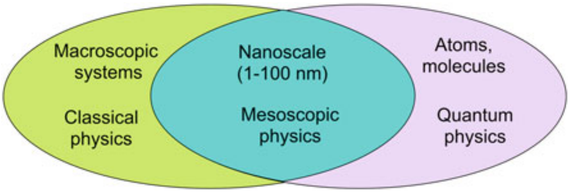

Fig. 3 Nanotechnology deals with nanoscale dimensions (1–100 nm). It is a domain at the crossroads between the macroscopic domain governed by classical physics, and the microscopic domain governed by quantum physics

circuit (IC) with a transversal size of several nanometers can be seen with a scanning tunneling microscope. Indeed, to emphasize how the instruments for observing nanomaterials get large and complicated but are becoming more available, so it will revolutionize the field.

Objects with a size greater than about 100 nm are currently observed and have been studied for decades. Atoms and molecules with dimensions well below a single nanometer are investigated, but indirectly by means of their interactions with other objects. It is only recently that scientists have had the tools to move and manufacture nano-objects in the range of 1–100 nm. The interesting thing is that at this length scale, we are at a crossroads between classical and quantum physics (Fig. 3). Compared with macroscopic objects that have a behavior governed mostly by the classical laws of physics, quantum effects can appear at the nanoscale and are able to completely change some of the properties of objects that we are used to.

A direct consequence of such a surface increase is that if we paint an object with a coating containing nanoparticles, the opacity is greatly enhanced; meaning that less paint is needed for a given area. This is also good for the environment because it reduces pollution and the quantity of raw materials needed to manufacture paint. The same is also true when pesticides are applied in agriculture, for example.

Another feature occurring as the dimension of a system that reaches the nanoscale domain is the appearance of quantum effects that change some physical effects. The drawback is that it may happen that the function of a device can no longer be performed as the dimensions of the components are now too small. However, the good thing is an opening up of other fields of applications and functionalities such as electron transistors, Coulomb blockade, and quantum cryptography, with new phenomena.

Working with nanomaterials and nanocomponents demands for high expertise and complex and expensive equipment. Figure 4 shows the infrastructure of a nanoelectronics laboratory.

The twenty-first century will see huge developments in the nanotechnology domain and a large number of applications will be evident in the marketplace. This development is likely to be ongoing, proceeding by steps. Predicted generational steps in the development of nanotechnology are displayed in Fig. 5.

Fig. 4 This figure gives an idea of a laboratory working in nanoelectronics, namely a lithography tool from the ASML company. Image courtesy of IMEC (Belgium)

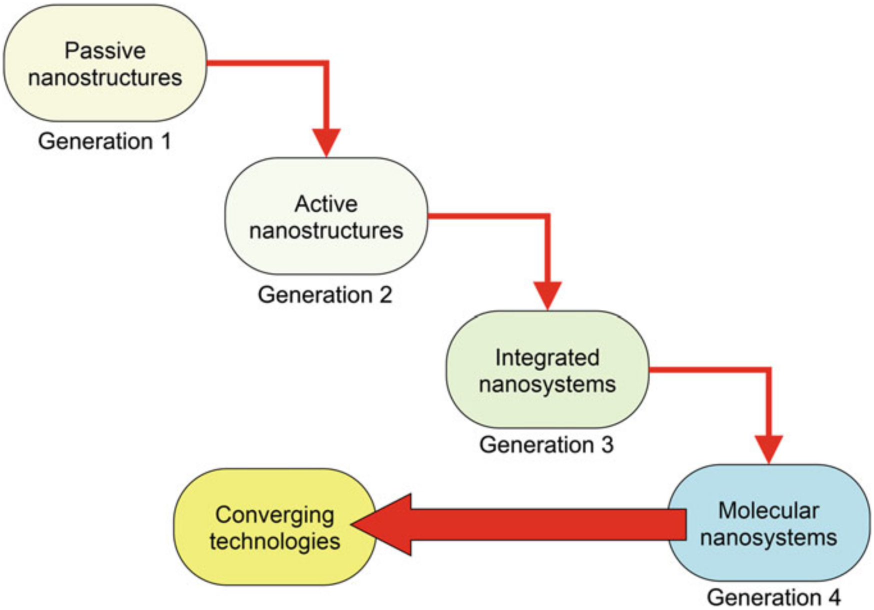

Fig. 5 Different generations of products coming from nanotechnology according to the classification of M. C. Roco, C. A. Mirkin, and M. C. Hersam, "Nanotechnology research and directions for societal needs in 2020", Springer, 2011

The First Generation corresponds to passive nanostructures, such as coatings made of nanomaterials or containing embedded nanoparticles. The Second Generation, which is presently in progress at both research and industrial stages, is about active nanostructures such as those made for drug delivery or nanotransistors. Generation Three will deal with more complex structures with several functions, such as nanorobots, for example. Generation Four is devoted to nanosystems built from atoms and molecules. This is a difficult area of research and, in most of the cases, we are far from mass production capability. The final goal is to build systems incorporating nanotechnology in other technologies to produce powerful and cheap devices useful in daily life.

This book provides an overview of the many areas where nanotechnology can make a contribution, in sectors as diverse as health care, building construction, security, or energy. Nanotechnology can provide smart coatings for buildings that provide self-cleaning using the same technologies already being applied in sunscreens. Technologies used today for odor prevention in clothing will be further developed using nanotechnology to fabricate bandages that disinfect and protect a wound. Networks of sensors will be available for monitoring the environment and for providing security in public places.

It is accepted that there has been adverse publicity about nanotechnology, based on a lack of understanding of what they are, what benefits they provide, and what risks they may pose to our health, and to our environment. Many nanotechnologies will be as safe in application as concrete, steel, and the nanoengineered microprocessors used in our laptop computers. Nevertheless, on the basis of the precautionary principle, technologies using nanomaterials—do need to be carefully assessed for their toxicity, with the same stringent standards of testing and regulation applied to these nanomaterials as to any other new product. In order to ensure the optimum exploitation of nanomaterials, authorities need to work with the industry to develop robust methodologies that secure the confidence of the public. Education about nanomaterials is a prerequisite to a high-value, knowledge-based economy.

The book is divided into ten parts; each part is subdivided into chapters (Fig. 6).

Nanotechnology consists in exploring and working in the nanoworld. Part I is a basic introduction to this nanoworld. In Chap. 1 we show that it is now possible to see and move atoms and, in Chap. 2, that scientists are able to make nano-objects using different techniques. Since quantum phenomena can emerge at the nanoscale, we introduce, in Chap. 3, a few ideas allowing understanding of this new behavior and the new physics.

Nanomaterials have been used for a long time, in coatings, for example, but it is now possible to design them with properties on demand. Part II is devoted to this subject. Chapter 4 describes how using nanomaterials provides better performance and function with less material. This is clearly a priority in a sustainable developmental approach to use materials. Carbon plays a very specific role in the advancement of nanotechnology through fullerenes, carbon nanotubes, and graphene. Chapter 5 is devoted to this subject. Manufacturing nanomaterials on

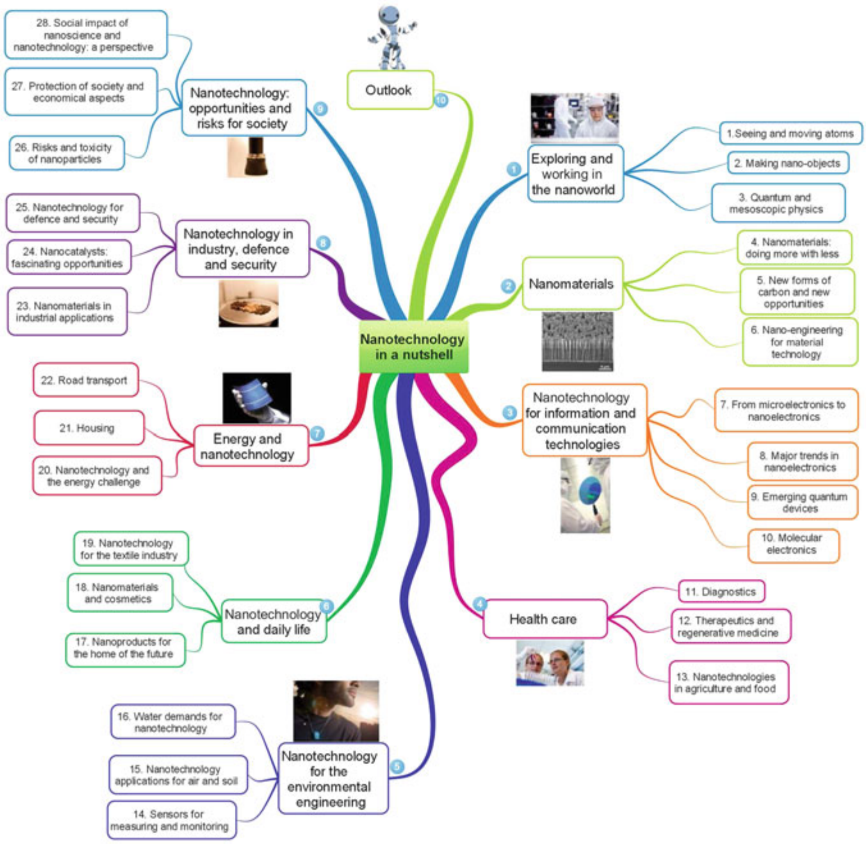

Fig. 6 Plan of the book

demand with specific properties is the role of nanoengineering. Chapter 6 treats this important aspect.

Part III covers a broad and important subject: the applications of nanotechnology to information and communication technologies. There is already today an evolution of microelectronics at the nanometer domain. Many of the integrated circuits we are using are now manufactured using technologies where silicon is engraved with features below 100 nm. Chapter 7 addresses this subject. In Chap. 8 we describe the major trends in nanoelectronics while in Chap. 9 we present some emerging quantum devices. Finally, Chap. 10 is devoted to the basic ideas of molecular electronics where nanodevices are built from atoms or molecules in a bottom-up approach.

Health is an important subject for all people. We have devoted Part IV to health care and to some of the possibilities of nanotechnology in this domain. The goal in medicine is to “better see,” “better treat,” and “better repair.” Along these lines, Chaps. 11 and 12 treat diagnostics, therapeutics, and regenerative medicine.

Connected to health is the question of applications of nanotechnology in the domain of agriculture and food treated in Chap. 13.

The environment is today an important item in many societies and this is discussed in Part V. Measuring pollution is an important issue. Chapter 14 introduces sensors for measuring and monitoring chemical or biological products present in the environment. Humans are in constant interaction with air, water, and soil and Chaps. 15 and 16 introduce the contributions which are expected to these sectors by nanotechnology. The question of climate change is also briefly addressed.

Part VI addresses the domain of daily life and the impact of nanotechnology in this area. This is relative to the products used at home in daily life (Chap. 17) including cosmetics (Chap. 18) and textiles (Chap. 19). The number of such products exploiting nanomaterials will increase significantly in the near future.

Energy is an essential consideration and Part VII is devoted to this subject. It concerns the production of energy, Chap. 20, and also the role of nanotechnology in the use of energy: in housing (Chap. 21) and in road transport (Chap. 22).

Industry, defense, and security are also concerned with nanotechnology. Nanomaterials have many industrial applications (Chap. 23) and nanocatalysis allows for more efficient industrial processes (Chap. 24). Issues related to defense and security are important in democratic societies to prevent threats. Chapter 25 deals with these aspects.

If nanotechnology provides opportunities for society it has also some risks. This is the subject of Part IX in which we address the problem of risk and toxicity of nanoparticles (Chap. 26), the protection of society and economical aspects enabled by nanotechnology (Chap. 27) and the social impact of nanoscience and nanotechnology (Chap. 28).

Finally, Part X draws some conclusions and perspectives on nanotechnology.

This book is intended to give a flavor of nanotechnology and its applications. It will swiftly go through different domains where nanotechnology can have present or future applications. Although we did our best to cover the whole subject of nanotechnology, this book is not an encyclopedia. Many things are missing and we merely gave a short introduction of the different subjects without entering into the technical details. There are many books and review articles devoted to specific areas of nanotechnologies where the reader can find more details.

We have chosen to address to a wide audience of people interested in science and technology. As far as nanotechnology is concerned, we have focused attention mostly on "how it can be used" rather than "how it works." The reason is that nanotechnology will be found in a very large number of applications and everybody will be faced with it one day in one form or another. A basic understanding of the domain is therefore helpful. We have enjoyed writing this book and hope that the reader will enjoy reading it.

Acknowledgments

The Authors wish to thank all the colleagues, institutes, and companies that have made contributions toward the publication of this book. It would not have been possible without their efforts. The support of the CEA (Commissariat à l'énergie atomique et aux energies energies alternatives) in providing permission to reproduce many of the diagrams and pictures is greatly acknowledged. We are deeply indebted to Professor Michael Fitzpatrick, the Lloyd's Register Foundation Chair in Materials Fabrication and Engineering at The Open University, UK, for his work throughout the book in technical and academic editing to ensure a consistent style and accessibility of the book for a non-specialist reader, as well as for numerous technical contributions.

One of us (C. N.) is especially grateful to all colleagues from the CEA who helped him to learn the vast domain of nanotechnology. It was a real pleasure to have discussions with them and a privilege to benefit from their experience.

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About the Authors

Christian Ngô, ScD, was formely Executive General Manager of ECRIN (Echange et Coordination Recherche-industrie) and Scientific Director of the Atomic Energy High Commission Office. In 2008, he founded EDMONIUM, a consulting company. He has worked in fundamental research for 20 years, and has published approximately 200 papers in the field. In the 1990's, he moved to applied research and took three patents before holding several management positions such as advisor to the CEA's CEO, Scientific Director of the Direction of Technology Research and so on. Dr. Ngô is author or co-author of 12 books (11 in French and one in English) and has contributed to several collective books. His main interest today in EDMONIUM relates to energy and nanotechnology.

Marcel Van de Voorde, Dr. ir.ing, Dr. h.c., 40 years experience in European Research Organisations including CERN; European Commission research centres. Member of numerous Councils and Governing Boards of Research Institutions across Europe, the US and Japan. Emeritus Professorship at the University of Technology, Delft, The Netherlands, and a number of Visiting Professorships in Europe and worldwide. Member of the Science and Technology Office of the French National Assembly/Senate in Paris, Executive Advisor to the IMEC CEO—President for European Programmes in Belgium.

Part I
Exploring and Working in the Nanoworld

Introduction

The nanotechnology revolution has been possible because scientists are able to explore and work at the nanoscale, a scale corresponding to dimensions between 1 and 100 nm.

In Chap. 1 we describe how it is possible to see and move atoms and more generally to characterize materials at the nanoscale (Fig. I.1).

In Chap. 2 we describe how to make nanoscale objects, either by starting from macroscopic objects and carving or modifying them precisely, or by building them from atoms or molecules. Clever manufacturing methods have been developed and some of them are briefly reviewed.

The physics at the level of atoms and molecules (the microscopic world) is dominated by quantum effects while the macroscopic world where we live is mostly determined by classical physics. As we go to the nanoscale, quantum phenomena become more and more important and at the same time classical

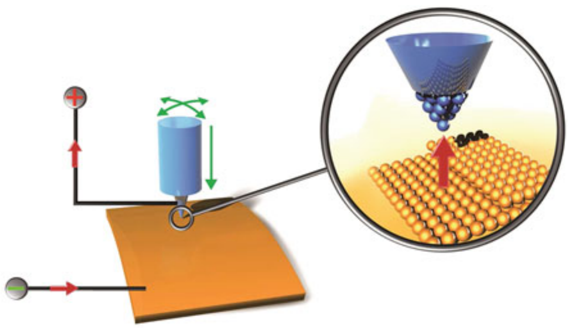


Fig. I.1 Artist's impression of the principle of a scanning tunnel microscope. Image courtesy of CEA/LETI (France) effects disappear in some cases. Chapter 3 introduces some basic physics necessary to understand what is going on at the nanoscale. It is between the microscopic and the macroscopic world (which can be called the mesoscopic world). Several phenomena at these dimensions can be described by semiclassical physics where classical descriptions are modified by some quantum features.

Chapter 1
Seeing and Moving Atoms

Matter is made up of atoms. Their existence has been proved less than two centuries ago. Although it was not possible to see individual "atoms", it was possible to indirectly demonstrate their existence and measure their properties.

Half a century ago, nobody would believe that a scientist could ever see and move individual atoms. This was a wrong idea and it is now possible, since 1981, when G. Binnig and H. Rohrer invented the scanning tunneling microscope (STM). They were able to map a gold surface at the atomic scale with the STM, and later a silicon surface. This new device was really a breakthrough for exploring and interacting with the nanoworld.

In 1986, G. Binnig developed a new microscope: the atomic force microscope (AFM) which is able to image, at the atomic scale, all kinds of surfaces: insulators, semiconductors, or conductors. The van der Waals forces, which are very weak atomic forces, are involved in the interaction between the tip of the AFM and the surface of the sample. They are very small, of the order of $\approx 10^{-9}$ N, corresponding to a mass of about 10^{-10} g or 0.1 ng.

1.1 Atoms Can Be Seen

The scanning tunneling and atomic force microscopes belong to a family of instruments, the *scanning probe microscopes*, allowing study of the properties of material surfaces at the atomic scale.

An STM can be used in many environmental conditions: vacuum, air, water, different gases, from very low temperatures to temperatures of a few hundred degrees. This characterization is extremely useful both in research laboratories and in the industry. An STM can give images of metal surfaces allowing measurement of physical properties such as the surface roughness, or identifying surface defects and aggregates or molecules located at the surface, or the geometry of defects, etc.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_1,

Fig. 1.1 Principle of a scanning tunneling microscope (STM)

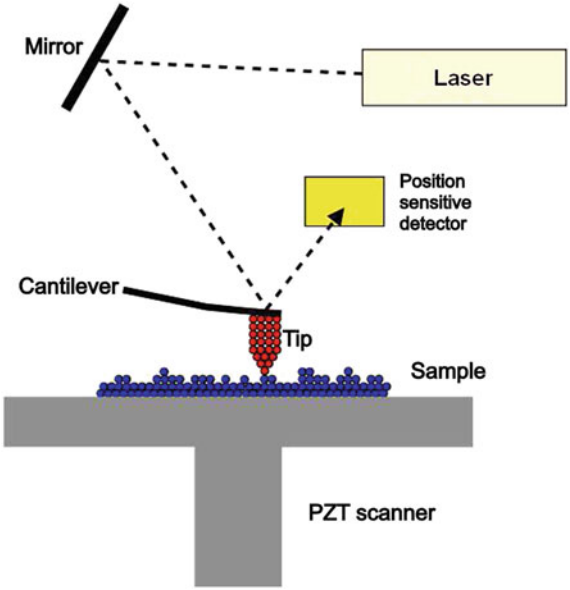
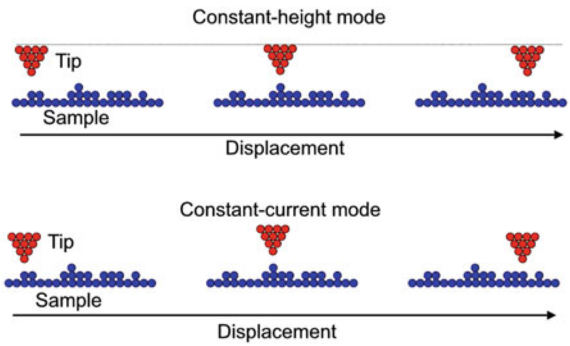


Fig. 1.2 Schematic illustration of the two operating modes of the STM: the constant-height mode and the constant-current mode



The principle of an STM is shown in Fig. I.1 and in Fig. 1.1 of the general introduction. A sharpened conducting tip with only one atom at the end is brought to a distance of about 1 nm from the surface of the sample. The tip and the sample are generally a conductor or semiconductor. At such a small distance, electrons from the sample tunnel to the tip, and vice versa, depending upon the sign of the voltage applied between them. The tunneling current decays exponentially as the distance between the tip and the sample increases. Typically, a 10 % change in the distance (about 0.1 nm or 1 Å) makes a change of about one order of magnitude in the tunneling current. This strong dependence gives the STM a high sensitivity in the vertical direction of about 0.01 nm.

An STM can be operated in two modes (Fig. 1.2): constant-height mode or constant-current mode.

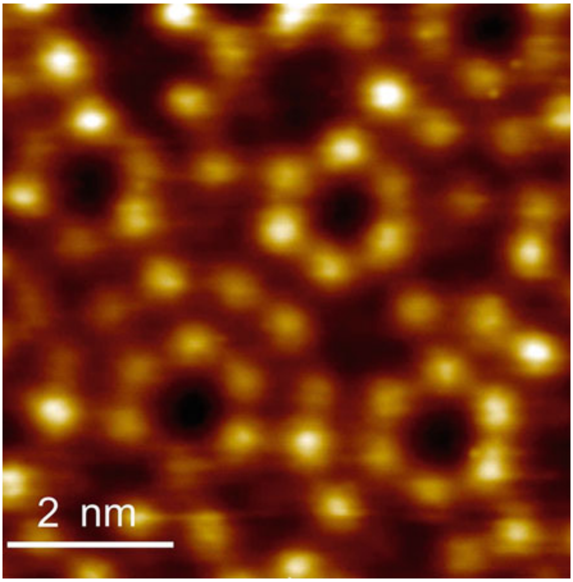


Fig. 1.3 STM image of a silicon surface when the crystal is oriented along the (111) plane, *bright dots* correspond to surface Si-atoms. Image courtesy of CEA/LETI (France)

- In the constant-height mode, the tip scans the sample while staying in a horizontal plane. The tunneling current varies according to the topography of the surface. This mode allows fast measurements but a smooth surface is needed.
- In the constant-current mode, feedback is used to adjust continuously the distance between the tip and the sample in order to keep the tunneling current constant. This movement is done using piezoelectric crystals. The constant-current mode is slower than the constant-height mode but it can be used to investigate irregular surfaces.

An STM maps the topography of the surface but the tunneling current gives also information about the electronic density of states at the surface. The spatial resolution of an STM in the horizontal plane is about 0.2 nm.

Figure 1.3 shows an image, taken with a STM by the CEA/LETI, of the surface of a silicon crystal oriented along a particular crystallographic plane. The image is slightly fuzzy but atoms are clearly distinguished. High-end STMs can have lateral resolution of about 0.1 nm and a depth resolution of 0.01 nm.

With the atomic force microscope, the sample does not need to be a conductor: it can be an insulator or a semiconductor. A sharp tip is still mounted at the free end of a cantilever (Fig. 1.4). Forces between the tip and the sample surface (essentially van der Waals forces) bend the cantilever and the bending angle is measured, using, for example, laser beams reflecting on the cantilever.

Van der Waals forces are involved in measurements on insulating material. These forces are attractive at long distance and repulsive at short distances. If the tip is very close to the sample's surface, the interaction is repulsive while it is attractive if it is located at a larger distance, typically a few nanometers.

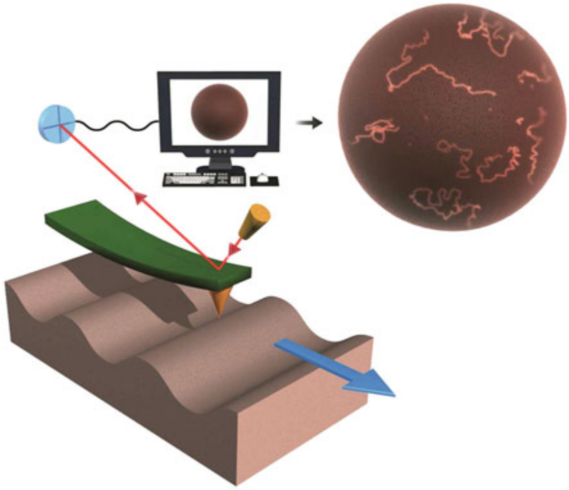


Fig. 1.4 Artist's impression view of the principle of an atomic force microscope (AFM). Image Courtesy CEA/LETI (France)

There are essentially two basic modes of operation of an AFM: the static mode and the dynamic mode.

In the static mode the tip is moved across the surface of the sample. The shape of the surface is measured by the deflection of the cantilever, which provides a feedback to the system that keeps constant the distance between the tip of the AFM and the surface. In the contact-mode, in addition to the repulsive part of the van der Waals forces, other interactions can be involved, such as capillary forces, because there is often a thin film of water originating from humidity of the atmosphere at ambient conditions, as well as electrostatic forces, etc. The sign and the magnitude of the cantilever force depend upon the bending. It can be viewed as a spring exercising either a compressive or an attractive force on the surface of the material.

In the dynamic mode, the cantilever is oscillated around its fundamental or harmonic resonance frequencies (between about 20 and 200 kHz). The tip is not in contact with the surface of the sample and oscillates with an amplitude of the order of a few nanometers. The van der Waals forces are effective and strong in the range of 1–10 nm but other long-range forces may also be present depending upon the nature of the sample. These forces decrease the resonance frequency of the cantilever and this property is used in a feedback system to maintain the frequency by changing the distance from the tip to the cantilever. The distance between the tip and the sample surface allows reconstruction of the topographic image of the surface of the sample. The dynamic mode is a noncontact mode allowing nondestructive measurement of the local surface sample and no damage to the tip.

The intermittent contact mode, or tapping mode, is an extension of the usual dynamical mode where an intermittent contact with the sample surface is driven by an external oscillation of the cantilever. Compared to the noncontact mode presented just above, the oscillation amplitude is larger, typically between 100 and 200 nm.

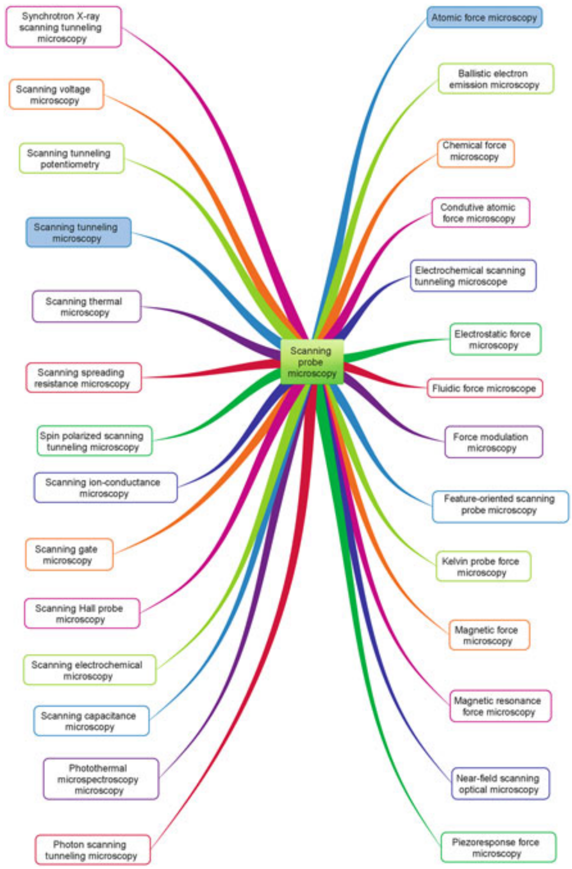


Fig. 1.5 Compilation from http://en.wikipedia.org/wiki/Scanning_probe_microscopy of scanning probe microscopy techniques

Tapping mode is, for example, used to image samples where a liquid layer has developed due to the environmental conditions.

STM and AFM belong to a wider family of probing devices that are able to scan samples. This family belongs to a branch of microscopy called *microscopy scanning probe*. An image of the surface is made by moving the probe (a tip) in a raster scan that is line-by-line, like in CRT screens used in old TV sets. Close to 30 different scanning probe microscopes have been developed so far. Figure 1.5 shows a compilation made by Wikipedia of the existing scanning probe microscopies existing around the world. The best known are STM and AFM. Several of the other microscopes are just derived from these. The purpose of the figure is not to quote every existing scanning probe microscopy but to show that this characterization domain is very active in several areas of nanotechnology.

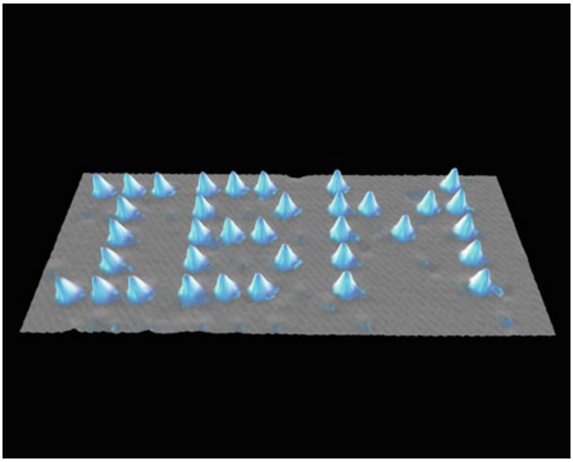


Fig. 1.6 Atoms of xenon moved on the surface of a nickel crystal and arranged in order that IBM, the name of the Company, appears to be written. Courtesy of IBM company (www.almaden.ibm.com)

1.2 Atoms Can Be Moved

In 1989, D. Eigler and his team from IBM have moved 35 xenon atoms using a scanning probe microscope (Fig. 1.6). By moving the tip of the microscope close to an atom they could drag it to another place and write the logo IBM. To perform this operation the sample was cooled down to very low temperature, close to absolute zero, in order to reduce the thermal motion of the atoms. Such an operation is possible if the surface of the material is smooth enough and the sample is kept under high vacuum. Some atoms are easier to move than others. This is the case of xenon atoms because they are only weakly bound to the surface.

More complicated structures have been made such as quantum coral where atoms are arranged to make a closed structure (Fig. 1.7). Inside the coral a particle can be trapped and, because of the very small size of the coral, quantum effects can be observed.

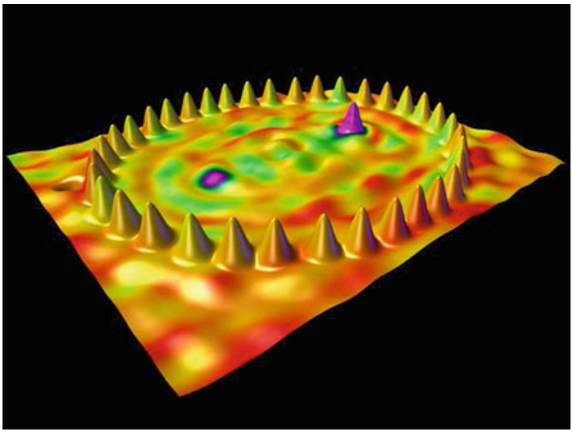


Fig. 1.7 Quantum coral. An STM was used to place 36 cobalt atoms to form an elliptical coral on a copper substrate. The small purple spot is just a mirage revealed by the interaction of electron waves moving in the copper substrate. Inside the coral, a cobalt atom is located at the foci of the ellipse (the *purple cone*). Courtesy of IBM Company (www.almaden.ibm.com)

1.3 Microscopy

Microscopy allows seeing small three-dimensional objects to the unaided eye. The oldest technique is optical microscopy, using visible light. The first optical microscopes were developed at the beginning of the seventeenth century. Great improvements have been made since that time. Microscopy can basically be classified into three main families: optical microscopy, electron microscopy, and scanning probe microscopy as just presented.

Optical and electron microscopy use scattering, diffraction, or inelastic interaction phenomena of a beam (usually photons or electrons) that interacts with the sample. They work by irradiating the whole sample, a large area of it (wide-field microscopy), or by scanning the sample with a narrow beam as a probe.

A large number of optical microscopy techniques have been developed. The simplest one is bright field microscopy. A thin sample is illuminated from below and observed from above with microscope optics. In other techniques, the incident light is reflected by the sample. The image which is obtained can be observed directly by the eye, imaged using a photographic plate or detected using a Charge-Coupled Device (CCD) camera. Diffraction limits the resolution that can be obtained using optical microscopy to about 0.2 μm, a dimension far above the resolution needed in nanotechnologies. However the evolution or transformation of living systems incorporating nanosystems, or which have been in interaction with nanosized systems, can be observed with optical microscopy techniques.

There are basically two main techniques of electron microscopy (plus some additional ones dedicated for special high-resolution problems): transmission electron microscopy where a well-focused electron beam goes through a very thin sample; and scanning electron microscopy where a well-focused electron beam scans a small area of the sample in raster mode.

In Fig. 1.8 we display the basic principles of three microscopes extensively used in micro- and nanotechnology studies. A transmission electron microscope is similar to an optical microscope except for the fact that electrons instead of photons are used to probe the sample. The first optical microscope was made in 1605, while the first transmission electron microscope dates back to 1931. The principle (left part in Fig. 1.8) is that an electron beam is focused (with electrostatic and magnetic lenses) on the sample. After interacting with the sample, it is magnified with lenses before it reaches the detector.

In scanning electron microscopy an accelerated electron beam is focused with electrostatic and electromagnetic lenses into a fine probe, to image a sample by scanning in raster mode a small rectangular area of it. The first electron microscope was made in 1931 by E. Ruska and M. Knoll, in Germany. In an electron microscope, the energy of the electrons ranges typically between 20 and 30 keV. The higher the energy of the electrons, the smaller the de Broglie wavelength and the better the spatial resolution. At 60 keV, for example, the de Broglie wavelength is 0.005 nm and the diffraction limit, which gives the smallest dimension which can be resolved,

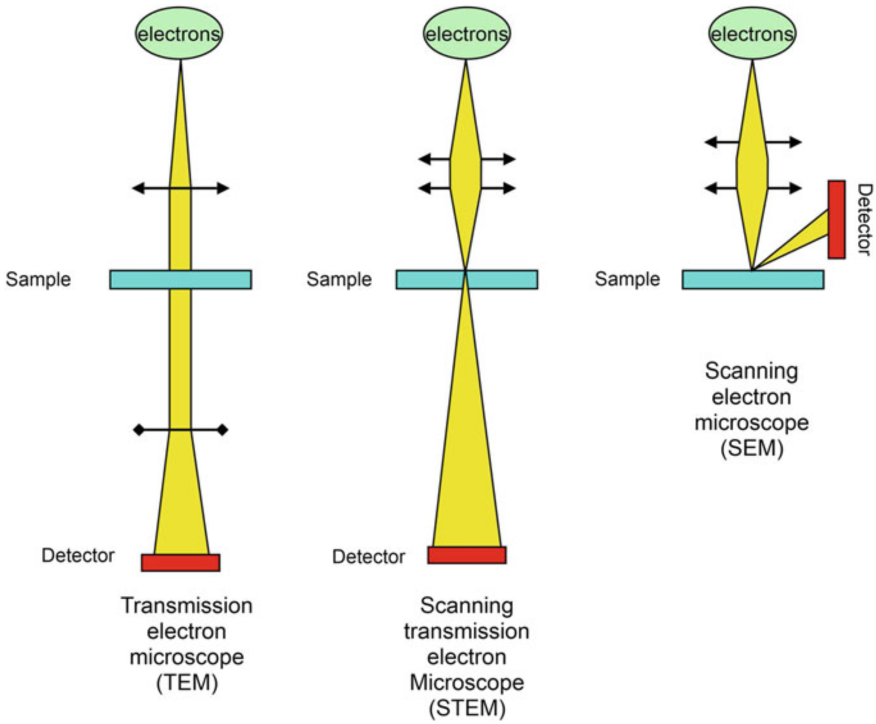


Fig. 1.8 Principle (simplified) of transmission and scanning electron microscopes

is about 0.25 nm. A lateral resolution between 1 and 50 nm can be obtained in secondary electron mode.

Scanning electron microscopes can be used in transmission mode where incident beam is detected after interacting with the sample (Fig. 1.8 in the center); or in reflection mode where the reflected beam is used to image the sample (right part of Fig. 1.8).

1.3.1 Transmission Electron Microscopy

Since the 1970s, transmission electron microscopes have been extensively used in the domain of materials and in particular in microelectronics. A thin sample (less than about 200 nm thick) is bombarded in vacuum with a well-focused beam of electrons with a single defined energy. They allow a direct imaging of the arrangement of atoms in a material, but require thin samples and computer calculations to properly reconstruct images. This technique has several limitations but, thanks to computer simulations, it is a basic characterization tool for materials at the micro- and nanoscopic scale, providing useful information about the atomic structure organization. For example, carbon nanotubes were discovered in 1991 by S. Iijima using this device. Lateral resolutions better than 0.2 nm can be obtained on some instruments. Resolutions better than 0.05 nm are obtained in modern high-resolution electron transmission microscopes with aberration correction systems. Figure 1.9 shows a most modern microscope with the following characteristics:

- Point resolution in Transmission Electron Microscopy (TEM) mode of 0.05 nm.
- Point resolution in Scanning Tunneling Electron Microscopy (STEM) mode of 0.08 nm.
- Voltage variables from 300 to 60 kV; the latter is especially important for studies of beam sensitive materials as graphene or nanotubes.
- Correction of the spherical aberration in TEM mode as in STEM mode.
- Electron Energy Loss Spectroscopy (EELS) resolution to 0.2 eV.
- EELS voltage and Energy Dispersive X-rays (EDX) mapping till an atomic scale.

Several other techniques based on a transmission electron have been developed allowing detection of defects in crystal structures, and making local chemical analysis by direct imaging or scanning. Figure 1.10 shows various transmission electron microscopy techniques.

To illustrate the kind of image that can be obtained, Fig. 1.11 shows a high-resolution image of a palladium catalyst deposited on the membrane of amorphous carbon.

In any given research study, several characterization techniques are typically used. They complement each other and allow the relevant information at the nanoscale to be obtained. An example of this is shown in Fig. 1.12 showing where a multiwall carbon nanotube is anchored on a reduced iron oxide catalyst.

Microscopy can also give more information than just a high-resolution image of the sample. A local chemical analysis can be performed by direct imaging or by scanning. An example of such an application is shown in Fig. 1.13 where the aim is to study the diffusion of Ti out of a thin film of TiN of 8 nm thickness. The chemical elements have been mapped in different views and superimposed in the upper figure. The map corresponding to Ti is shown in the bottom of Fig. 1.13.

Another example is shown in Fig. 1.14. The chemical mapping of small magnetic particles of FeNi is built from three chemical images corresponding to Ni (green), Ni (red), and Fe (blue) respectively. Chemical images are taken with a transmission electron microscope equipped with a graded interference filter spectrometer. In the image, the oxide layer is clearly seen at the surface of the magnetic particles.

Figures 1.15 and 1.16 show individual atoms in a gold nanoparticle (in Fig. 1.15 a particle with fivefold symmetry and in Fig. 1.15 a nanobar). The clear points correspond with the positions of the atoms. Gold nanoparticles have multiple applications in catalysis, nanoelectronics, and in cancer treatments.

Figure 1.17 shows a nanobar where the nucleus and the exterior (coating) consist of different materials. On the right-hand side the nucleus is presented in three dimensions. This is possible via a technique called "electron tomography". As it can be seen in the figure, individual atoms can be observed with this technique.

Fig. 1.9 Schematic representation of a most modern microscope, Image courtesy of G. Van Tendeloo, UIA Antwerp, (Belgium)

Figure 1.18 shows a collection of semiconductor nanoparticles which can be used for developments in optoelectronics applications. The different nanoparticles grow together and form chains.

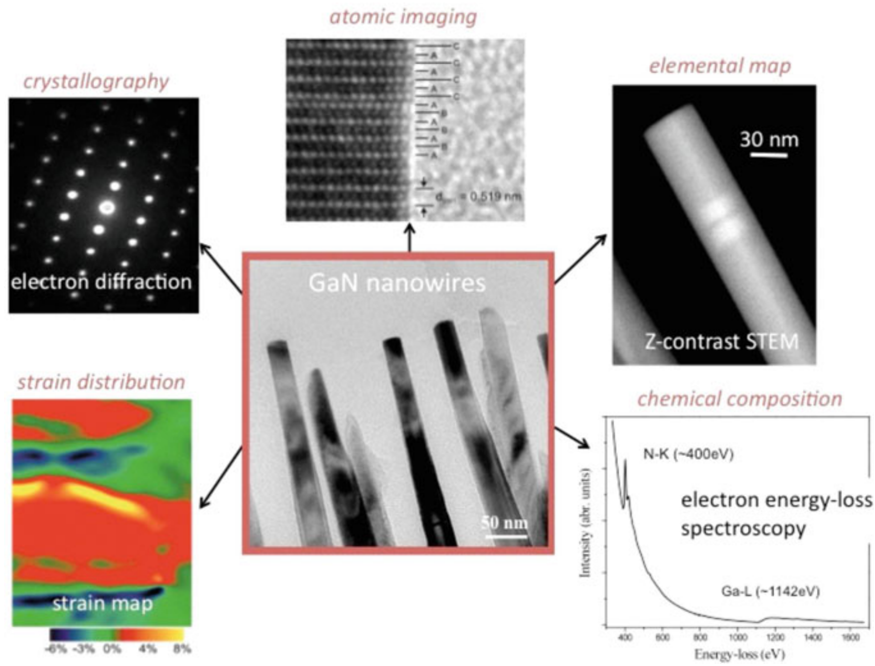


Fig. 1.10 Applications of transmission electron microscopy *(TEM)*. Courtesy of Paul Drude Institute, Berlin

1.4 Synchrotron and Neutron Facilities

The development of nanomaterials and nanotechnologies depends very much on a good knowledge of matter at the nanoscale which can be obtained only with efficient characterization methods. Many characterization methods exist, based on different probes, but, in most of the cases, it is necessary to use simultaneously several methods to obtain the required information about the nanomaterial or nanosystem. It is important to be able to make measurements at different length scales, and also to be able to access dynamic processes, which means measurements at different timescales to follow kinetic processes. It is preferred to make nondestructive or minimally invasive measurements on the sample.

Although it is sometimes possible to have information about a system by just detecting what is coming out (for example, in the case of a radioactive sample), in most cases a probe is needed to obtain information about the sample. This probe can be electromagnetic radiation or particles like neutrons. X-rays and neutrons are probes used to obtain details of the structure and dynamics of matter at the atomic scale.

Laboratories working in nanotechnology usually have numerous characterization techniques at hand but cannot afford to have large and expensive facilities for

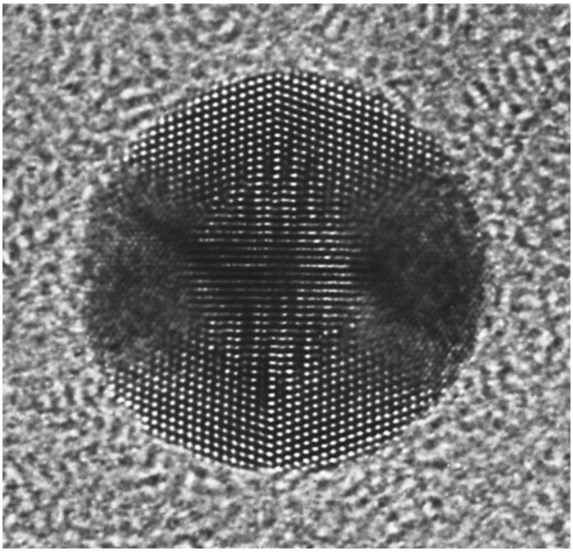


Fig. 1.11 High-resolution image of a palladium catalyst deposited onto a membrane of amorphous carbon membrane. The icosahedral particle has a diameter of about 10 nm. Each white point represents a column of about 10 atoms aligned along the electron beam of the microscope. From Clef CEA n°52. Image courtesy of CEA/LETI (France)

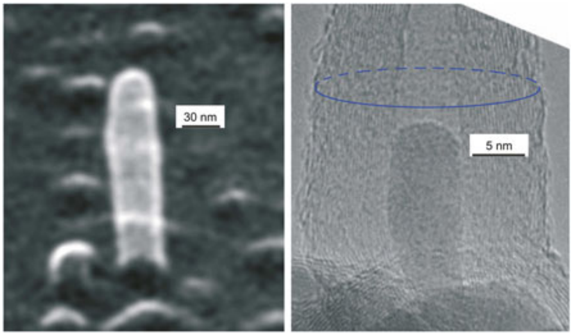


Fig. 1.12 Multiwall carbon nanotube grown on an iron oxide catalyst. On the *left-hand side* a scanning microscope image is shown and on the *right-hand side* a high-resolution electron microscope image. Published in "Clef CEA n°52", Image courtesy of CEA/LETI (France)

synchrotron radiation or neutrons. However, such facilities offer unique characterization tools that give a strong scientific competitive advantage to scientists using them. These facilities are usually financed and used at the national level. This is for example the case of the SOLEIL facility, in Saclay (France) or of the ESRF at Grenoble at the European level, both for synchrotron radiation.

Synchrotron radiation facilities deliver photons. Neutrons are produced either in nuclear reactors or in nuclear spallation sources. Photons and neutrons are complementary probes to study materials at the micro- and nanoscale. The main interaction of X-rays is with the electron cloud of the atoms while neutrons interact with the nucleus of atoms.

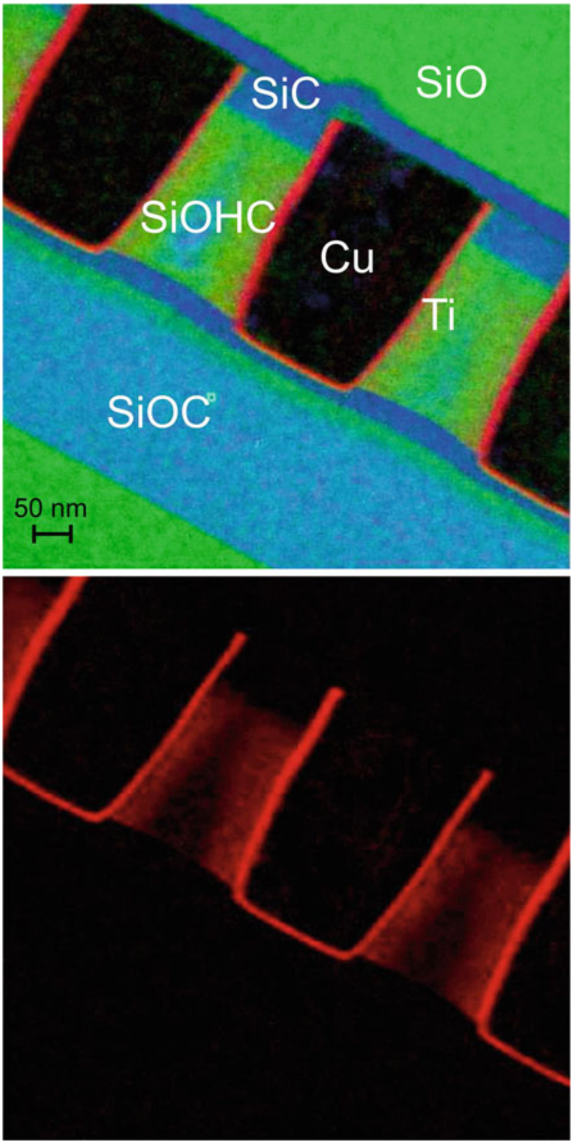


Fig. 1.13 Chemical image of interconnections in an integrated circuit made at CEA/LETI. The *bottom* part of the figure is the map of Ti while the *upper* part is a superimposition of maps of Ti, O, and C. Published in "Clef CEA n°52", Image courtesy of CEA/LETI (France)

1.4.1 Synchrotron Radiation

Electromagnetic radiation (photons) is widely used to probe a sample. The main advantage is that it is possible to use photons over a very wide range of frequencies and wavelengths.

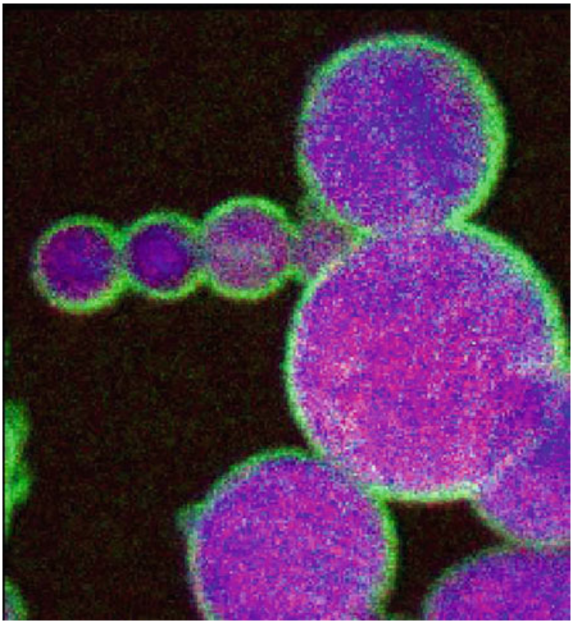


Fig. 1.14 Chemical mapping of small magnetic particles of FeNi constructed from three chemical images. Oxygen (O) is in *green*, nickel (Ni) in *red*, and iron (Fe) in *blue*. Published in "Clef CEA n°52", Image courtesy of CEA/LETI (France)

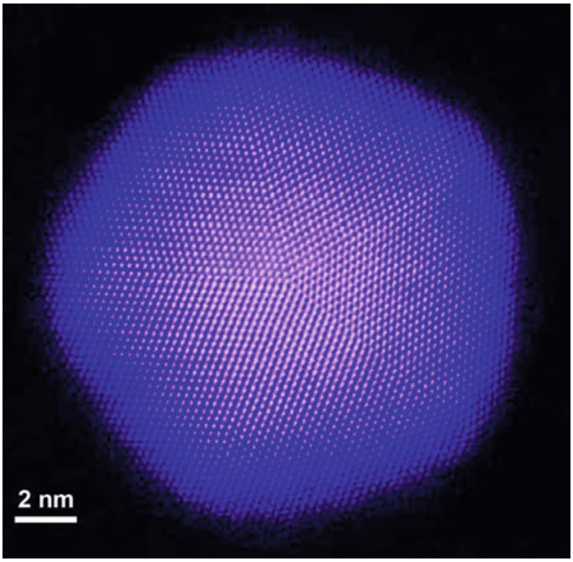


Fig. 1.15 Individual atoms in a gold nanoparticle with fivefold symmetry. Image courtesy of G. Van Tendeloo UIA Antwerp (Belgium)

Synchrotron facilities produce intense and focused beams of light going from hard X-rays to ultraviolet and, in some facilities like SOLEIL in France, in the infrared region.

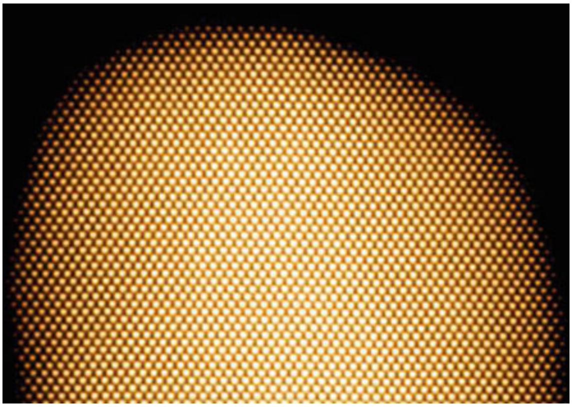


Fig. 1.16 Individual atoms in a *gold* nanobar. Image courtesy of G. Van Tendeloo UIA Antwerp (Belgium)

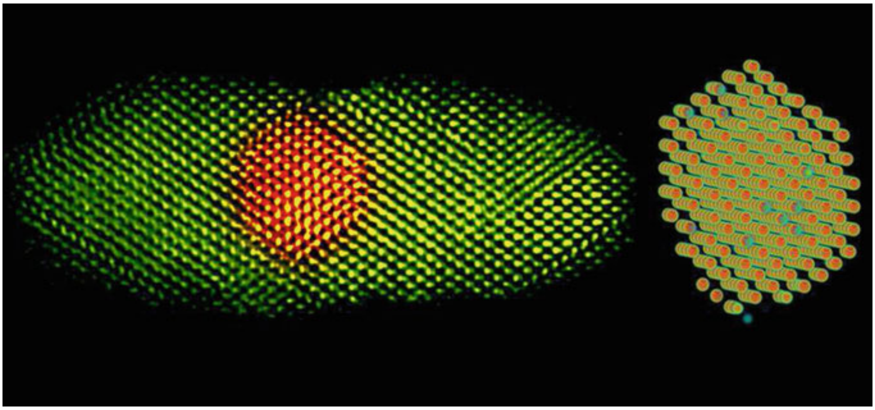


Fig. 1.17 Nanobar where the nucleus and the exterior (coating) consist of different materials. Image courtesy of G. Van Tendeloo UIA Antwerp (Belgium)

Accelerated electrons at a speed close to the speed of light radiate electromagnetic radiation in a narrow cone in their direction of motion. This is called *Bremsstrahlung* radiation. Synchrotron machines accelerate electrons at ultra-relativistic energies. These electrons are stored in storage rings and different methods are used to produce high intensity photon beams by synchrotron radiation by changing their trajectory (bending magnets, wigglers, and undulators). There are presently more than 10 dedicated facilities devoted to synchrotron radiation in Europe. They complement other probes such as conventional microscopy techniques. Synchrotron radiation is used in several fields of physics, chemistry, biology, and engineering.

The main qualities of synchrotron radiation are summarized in Fig. 1.19. Compared to standard laboratory X-rays, synchrotron machines provide exceptionally

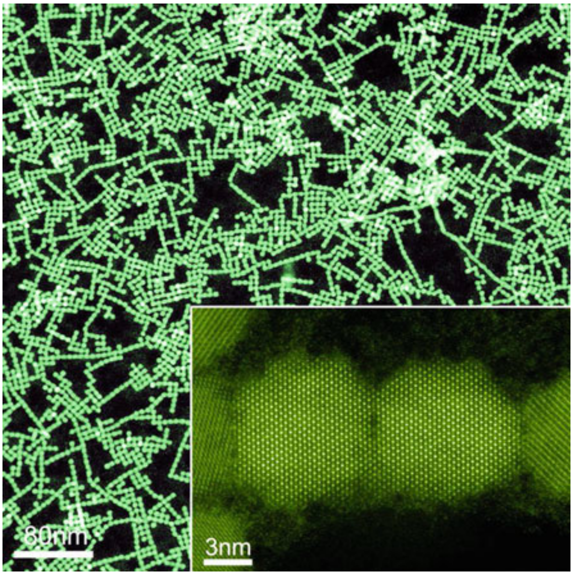


Fig. 1.18 Collection of semiconductor nanoparticles forming chains. Image courtesy of G. Van Tendeloo UIA Antwerp (Belgium)

high intensity, several orders of magnitude larger than conventional X-rays sources. Furthermore, the beam is well collimated, thanks to the ultra-relativistic energy of the electrons producing *Bremsstrahlung* radiation.

A continuous wavelength spectrum is obtained going from hard X-rays to even infrared radiation. This allows covering a large set of atomic or molecular excitations. The time structure of the beam allows making real-time measurements of processes and is an important tool to study dynamic processes. Finally, it is possible to have a circular or linear polarization of the synchrotron radiation allowing investigation of magnetic materials.

X-rays can be used to measure structural parameters of nanoparticles, nanocomposites, macromolecules, etc. Elemental composition as well as bonding states at surfaces and interfaces can be characterized. Information about catalytic activity and growth processes can also be obtained. Depending upon the technique used, different information can be gleaned. The most widely used synchrotron techniques and the type of information obtained are summarized in Fig. 1.20.

1.4.2 Neutron Probes

Neutrons are uncharged particles having a number of interesting properties for probing nanosystems and nanomaterials, one of which is that they can penetrate deep into a thick sample. Because a neutron has an intrinsic magnetic moment which can couple to the magnetization of materials at the atomic scale, neutrons are useful to study magnetic materials.

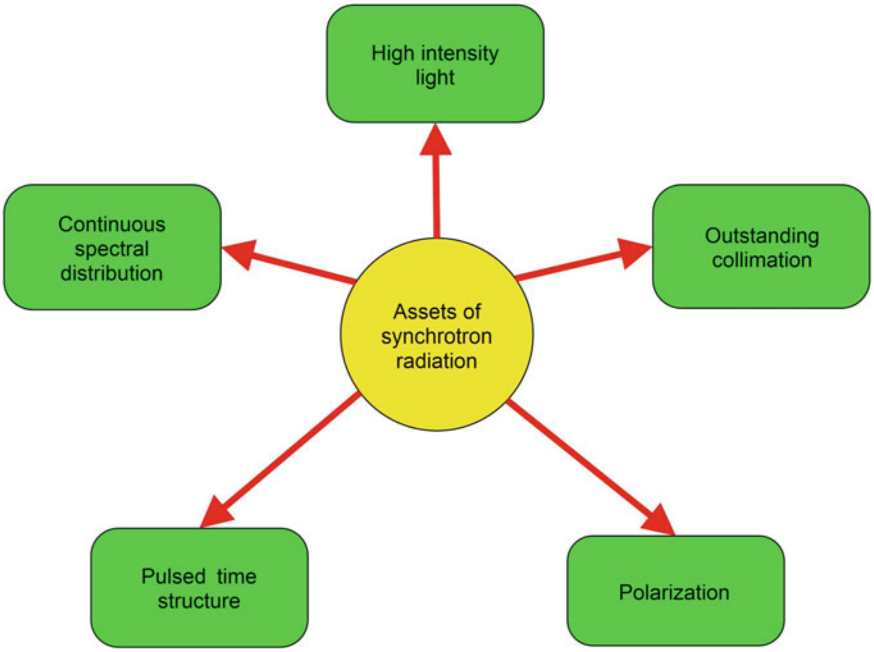
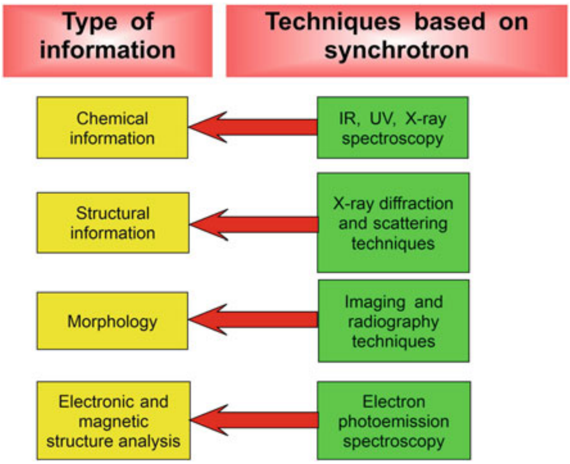


Fig. 1.19 Main advantages of synchrotron radiation sources

Fig. 1.20 Main techniques using synchrotron radiation and the type of information that can be obtained



Measurements are made using neutron beams that are produced in dedicated nuclear reactors or by spallation sources.

In the first case, neutrons are produced by nuclear fission in the core of the nuclear reactor. In the second case, an intense high-energy proton beam, produced in a particle accelerator, bombards a thick target of a heavy metal. About 20–30 neutrons are

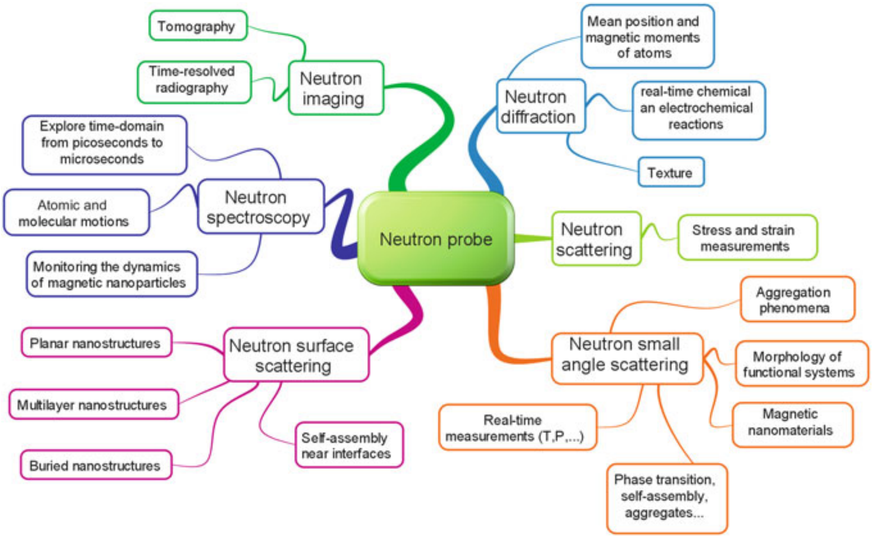


Fig. 1.21 Some applications of neutrons to nanoscale analysis

"spalled" from the nuclei of the target by each of the protons in the incident pulse (spallation process). The neutrons are then moderated in energy to an appropriate range for the desired experiments using moderator reflector assemblies. Nuclear reactors operate in continuous mode providing high fluxes of cold or thermal neutrons for scattering experiments. Spallation sources are generally used in pulsed mode allowing time-of-flight scattering measurements that can offer greater information from a single experiment. In Europe, more than eight facilities are dedicated to neutron production for material analysis. The kinetic energy of the neutrons allows information to be obtained in a range of length scales going from 0.1 to 10,000 nm.

An advantage of neutrons is that they can penetrate deeply into the matter thanks to their uncharged nature and to the fact that they interact mainly by nuclear forces which are of short range (the range is typically of the order of the fm (1 fm $= 10^{-15}$ m $= 10^{-6}$ nm). Because neutrons are uncharged there is no coulomb interaction after they have interacted with the nuclei of the sample, making interpretation of the data, and any comparison with theoretical calculations easier.

Neutrons can be used in several techniques to get information about the sample. Besides the fact that they can penetrate deeply into the sample, another advantage of neutrons is that they provide a nondestructive analysis. Some uses of neutrons as probes are shown in Fig. 1.21.

Diffraction of neutrons allows locating the mean position of atoms in a sample and can give a measure of their magnetic moment. Neutrons are useful probes to measure kinetic reactions in rather large volumes because they are able to penetrate deeply into the sample compared to other probes. Real-time diffraction is helpful in many studies such as in battery investigations. Information about the nanotexture of a material can also be obtained by measuring the number of neutrons reflected by the different atomic planes.

Neutron scattering gives the ability to measure the internal stress and strain into materials such as steel, aluminum, etc. Internal strains are deduced from the measurement of tiny changes occurring in the interatomic spacing. This has been used to study safety-critical components for the aerospace and nuclear power industries.

Small angle scattering is an efficient technique allowing to study structures having length scales in the range of 1–100 nm. It enables, for example, to study aggregation phenomena in various materials such as amorphous solids, porous materials, nanostructured materials, colloidal particles, etc. Using polarized neutrons it is even possible to get information about static and dynamic properties of materials.

Thin multilayer structures can be probed by neutron surface scattering, for example, by specular reflection but other methods have been developed as well.

In addition to elastic scattering, neutron inelastic scattering can be used to explore the time domain between the microsecond (10^{-6} s) and the picosecond (10^{-12} s). Using time-of-flight techniques, backscattering, and neutron spin echo spectrometers, it is possible, using the correlation existing with time and length scale, to differentiate the size of atomic and nanostructures.

Neutron imaging is also possible over large volumes because neutrons are able to penetrate deeply into matter. Neutron radiography, which is extensively used in the industry to study materials can be extended to smaller scales and neutron tomography, which is a 3D-imaging technique, can be used to study and image materials with a special emphasis on the hydrogen content in the material. Furthermore, time-resolved radiography allows the evolution of dynamical processes, such as the reaction in a fuel cell, to be followed.

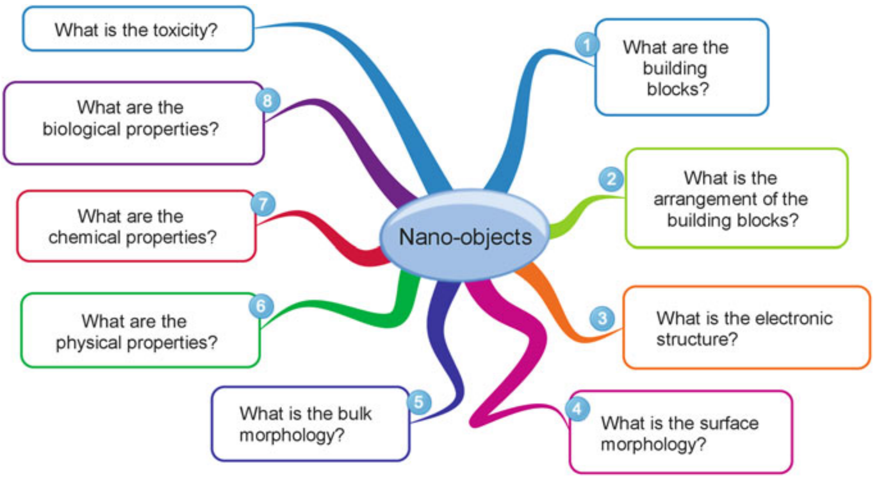


Fig. 1.22 Main questions that should be asked in studying nano-objects

1.5 Conclusion

Characterization tools are essential to study the nanoworld. It has been a revolution to be able to see and move atoms and this is due to the possibility of observing and working at the nanometer scale. A large number of techniques have been and continue to be developed and are more and more efficient to work at the level of the nanoworld. Some of these techniques are daily used in university and industry laboratories but others require huge investment and need skilled people/experts to be operated. It is the case for neutron and synchrotron radiation facilities for materials analysis. Central laboratories, at the national or international level, are needed to increase the efficiency of research in nanotechnology.

A number of questions must be answered on nano-objects that are manufactured or synthesized in the laboratory concerning physical, chemical, and biological properties or morphology and three-dimensional arrangement. Different (complementary) tools are needed for measuring different characteristics. Some of these questions are shown in Fig. 1.22.

Chapter 2
Making Nano-Objects

Making nano-objects is a big challenge and the main goal is to manufacture them at low cost, with a good yield, using the simplest and most efficient technology possible. There are two ways to tackle the problem:

1. The *top-down* approach consists in starting from macroscopic materials such as a wafer of silicon. They are "carved" and modified to produce nanoscale objects. Several techniques are used to build pieces of nanometer-size in one or more dimensions: evaporation techniques to manufacture thin films of thickness smaller than 100 nm is one example of this. The most used top-down approach is to extrapolate microtechnology techniques to smaller dimensions. This is what is presently done to manufacture microprocessors with patterns below 100 nm. It should be noted that films with a thickness smaller than 100 nm have been made for a long time by evaporation, molecular beam epitaxy, or similar techniques.
2. The *bottom-up* approach is where atomic and molecular units are assembled to form molecular structures ranging from atomic dimensions to structures in the nanometer size or above. Making macromolecules (polymers) from one or several monomers is an example of the bottom-up approach. Nature uses this route to build up complex structures, but *nature is cleverer* than humans. Erosion is the top-down approach of nature to carve macroscopic objects like rocks, for example. Chemistry and biology are the sciences involved in the bottom-up approach. Furthermore, time and control are essential aspects to be considered in any bottom-up approach used for manufacturing nano-objects.

Figure 2.1 schematically shows the basic difference between the top-down approach and the bottom-up approach.

The present challenge is to merge the *top-down* and *bottom-up approaches* to develop a toolbox allowing the creation of low-cost complex nanoscale structures. Lithography techniques (top-down) can produce nano-objects and their functionalization can be achieved using chemistry or biological sciences (bottom-up).

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_2, © Atlantis Press and the authors 2014

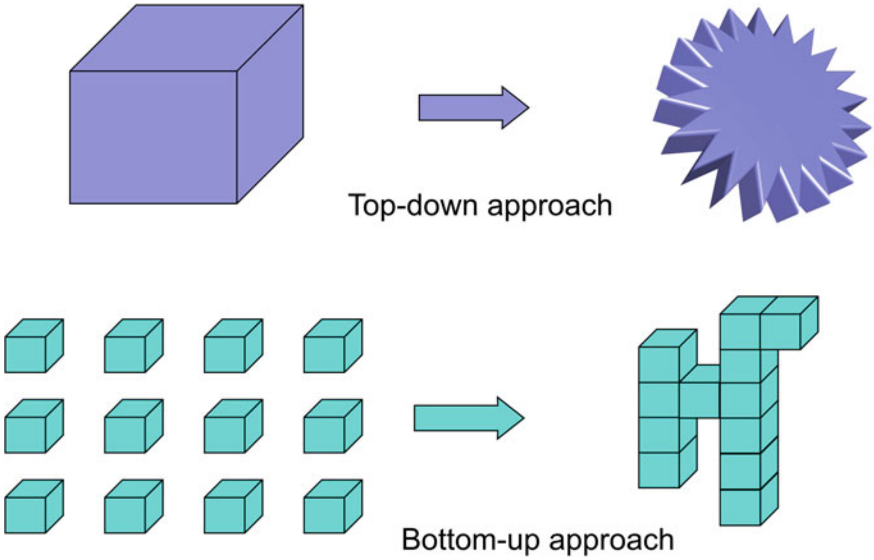


Fig. 2.1 Difference between a *top-down* and a *bottom-up* approach

2.1 The Top-Down Approach

While small systems (cm or mm-size) can be manufactured by precision mechanics with lathes, saws, and sanders, microchips or microsystems are made using planar technology. A disk of silicon or glass, called a *wafer*, is used as a substrate to build up complex microchips or microsystems. Lithography techniques are used to modify the surface of the substrate either by etching or building up new layers.

In microtechnology, lithography is a technique allowing transfer of a pattern to a photosensitive material (called *photoresist* or *resist*) by a selective exposure to light (ultraviolet or X-rays) or particles (electrons or ions). In microelectronics, silicon wafers are mostly used. An image of the pattern is projected, using a reduction lens onto a silicon wafer coated with a thin layer of photoresist, usually deposed by spin coating. Depending upon the nature of the photoresist, the exposed part can become soluble in the developer liquid used after exposure, or it can become insoluble, depending on the method used. An image of the mask pattern is obtained on the wafer after etching by the developer.

The principle of lithography (there are several steps, called *masks levels* in the manufacturing of integrated circuits) is shown in Fig. 2.2. The different stages are schematically displayed. A masking level starts by depositing a thin layer of photoresist (resin) by spin coating (the wafer is made to rotate at high speed while the dissolved photoresist is poured onto the wafer), making in this way a homogeneous thin layer of photoresist (steps 1–2). The pattern of the mask is then projected using a reduction optics system (step-and-repeat exposure) (3). After exposure, the

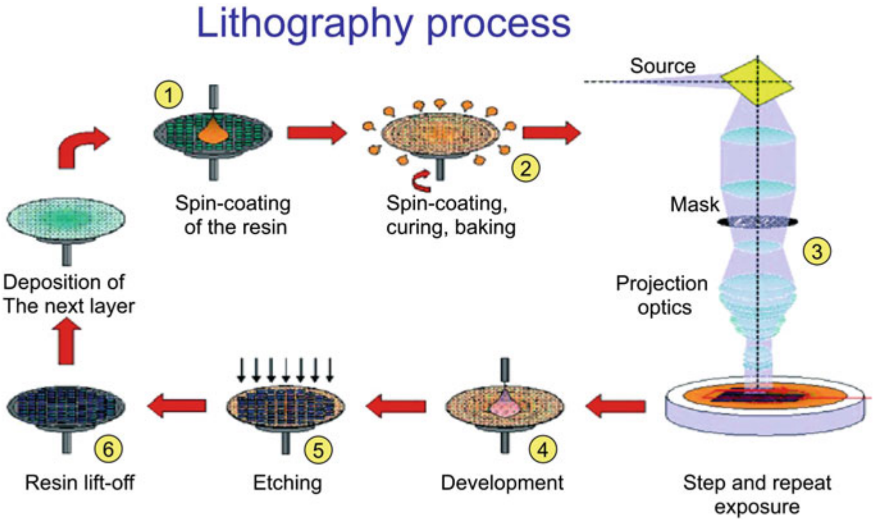


Fig. 2.2 Different stages in a lithography process during one masking level. Clef CEA n° 52. Image courtesy of CEA/LETI (France)

photoresist is developed (4) and the parts of the resin which are removed after development are selectively etched (5). The remaining part of the resin is then lifted-off (6) before deposition of the following layer.

2.1.1 Photoresists

Most lithography techniques used in micro and nanoelectronics are based on planar technology. A photoresist layer is used to image the pattern of a mask in a positive or negative manner (like in photography for negatives or slides) onto the resist. After developing, the positive or negative image of the mask pattern is reproduced onto the resist, which in turn, can be used as a mask for the wafer. The principle of positive or negative resist processes is shown in Fig. 2.3.

Most of the photoresists used in micro and nanoelectronics are based on organic polymers deposited in a very thin layer by spin coating onto the wafer. The resist is chosen in such a way that its solubility in a particular solvent changes after it has been exposed to radiation. (light or electrons, for example). If the change is a higher solubility we have a positive resist. If, on the contrary, the change is a lower solubility we have a negative resist. A good resist should produce steep edges after development in order to make very small, well-defined structures. A small change in the radiation dose must induce a big change in solubility. Many other properties and constraints for the resist are required and they are a key element in micro- and nanosystems manufacturing. The demand is even more stringent for nanotechnologies compared to microtechnologies because a higher accuracy is required.

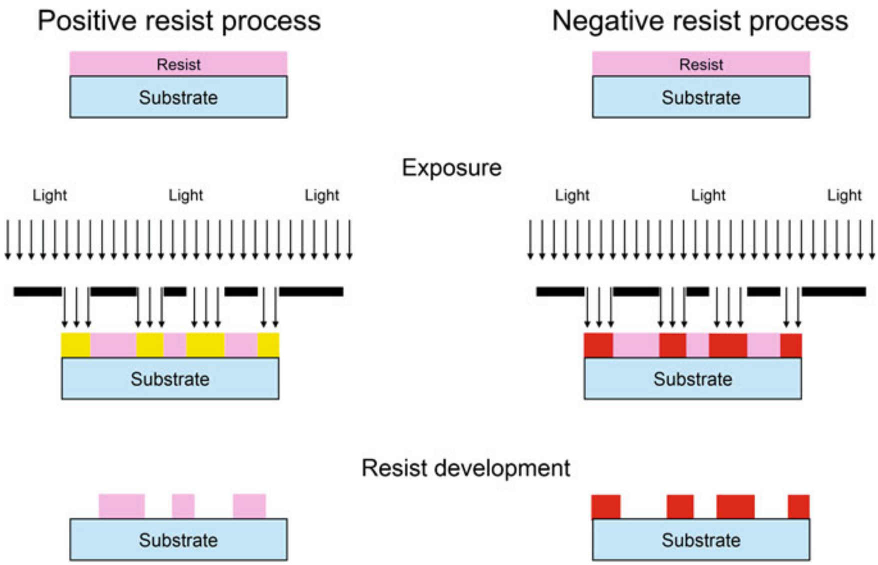


Fig. 2.3 Principle of lithography using a positive and a negative photoresist

Lithography for chips (such as memory chips or microprocessors) demands extremely high-performance processes:

- The spatial resolution is more and more precise; printing lines of 45 or 30 nm are nowadays currently used in the manufacturing of chips. The 22 nm lithography technology is now commercially used, for example, to manufacture the "Sandy Bridge" Intel microprocessors.
- The pattern that has to be transferred onto the wafer is extremely complex. For example, with a 30 nm printing line resolution, assuming that we create square pixels of 100 nm on a surface of 25 mm^2 (square of 5 mm on each side), there would be 2.5 billion of pixels. This is much higher than HD video pixel density (1080p $=$ 1920 $\times$ 1080 pixels) which has "only" 2.07 million pixels. Even the ultra-high video definition format which is under preparation (4320p $=$ 7680 $\times$ 4320 pixels) has only 33.18 million pixels on a much larger area. Any error in one pixel makes the chip nonfunctional and must be rejected in the manufacturing process.
- Integrated circuits are manufactured with successive layers obtained by transferring a pattern to the wafer. The number of mask layers is large, typically between 15 and 25. Each layer must be aligned with respect to the previously patterned layers with an accuracy which is a fraction of the linewidth resolution. This is similar, in principle but not in accuracy, to the way a color picture is produced in a sublimation printer where the three colors (cyan, yellow, and magenta) must be precisely overcoated.

Table 2.1 The number of transistors, the accuracy of the lithographic process, the area and transistor density are shown for different microprocessors which have been put on the market over the last two decades

Year	Microprocessor	Number of transistors (millions)	Process (nm)	Area (mm^2)	Density (millions of transistors/cm^2)
1993	AMD 486	1.2	350	35	3.4
1995	AMD K6 III	9	250	78	11.5
1998	AMD Athlon	37	180	120	30.8
2003	AMD Opteron	100	130	193	51.8
2005	AMD Dual Core Opteron	233	90	199	117.1
2009	AMD Six-core Opteron 2400	904	45	377	239.8

As an illustration of the progress in making micro- and nanoscale objects, Table 2.1 shows the evolution of the density of transistors among different generations of microprocessors and the accuracy of the printing line. In parallel, the cost of a transistor has dramatically reduced.

Light sources used in lithography processes correspond to given wavelengths. Above 100 nm processes, the g-line (436 nm) and the i-line (365 nm) of mercury lamps have been used. To have smaller wavelength, excimer laser are utilized (KrF at 248 nm and ArF at 193 nm). To go down to smaller dimensions, extreme ultraviolet lithography (EUVL) uses light of very short wavelength (13.5 nm) allowing manufacturing features for the 32 nm process. Because conventional optics no longer works, mirrors and reflective masks are required to image patterns on the silicon wafers.

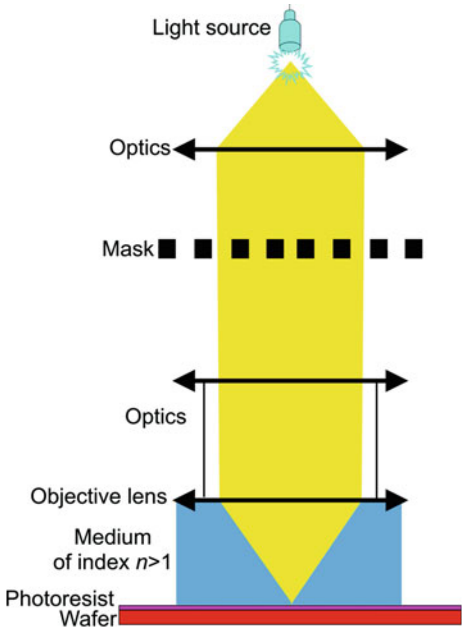
In order to increase the resolution, new techniques are developed such as immersion lithography where the air gap between the final lens of the optical device is replaced by a liquid with a refractive index greater than one (Fig. 2.4). The gain in resolution is equal to the refractive index.

2.1.2 e-Beam Lithography

Electron beam (*e*-beam) lithography uses a beam of electrons to pattern a resist deposited on a substrate. Depending upon the nature of the resist, the irradiated zones can be etched or not etched after chemical treatment. The main quality of *e*-beam lithography is that a resolution of a few nanometers can be routinely obtained. No mask is required during the irradiation, which is performed in raster mode: the electron beam scans point-by-point the substrate area to form the pattern.

One drawback of *e*-beam lithography is that it takes a long time to expose the whole substrate because this is done point-by-point. Light (UV or X-rays) illuminates

Fig. 2.4 Principle of immersion lithography



the whole substrate at once allowing to proceed much more swiftly. Because of this extremely slow speed, *e*-beam lithography is mostly used in research and development laboratories or for low-volume production of semiconductors.

2.1.3 Block Copolymer Nanolithography

A homopolymer is made by polymerization of a single type of monomer. A copolymer is a polymer obtained by polymerization of two or more different monomers. A block copolymer consists of two or more subunits of homopolymer (blocks) linked by covalent bonds. Block copolymers are used to manufacture nanoscale periodic structures. During solidification, phase separation takes place and distinct periodic nanostructures are formed. Depending upon the relative volume structure, spherical, cylindrical, lamellar, or more complex periodic structures can be made. In the case of lamellar structures, for example, lamellae can be oriented parallel or perpendicular to the surface with a period ranging between 10 and 100 nm. More generally, directed block copolymer self-assembly allows making periodic nanostructures with long- range order such as high density nodes or pores arrays. This technology is relevant for magnetic data storage, semiconductor devices, nanophotonics, etc. Nanoparticle-block copolymers self-assembly allows fabrication of ordered mesostructures with characteristic lengths in the range of 2–50 nm.

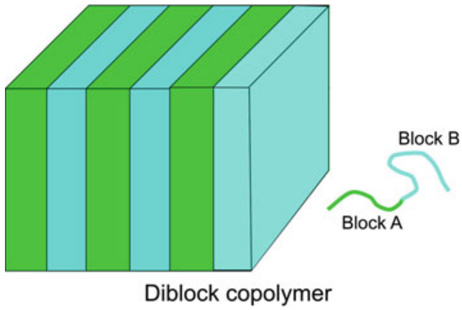


Fig. 2.5 Schematic illustration of a diblock polymer

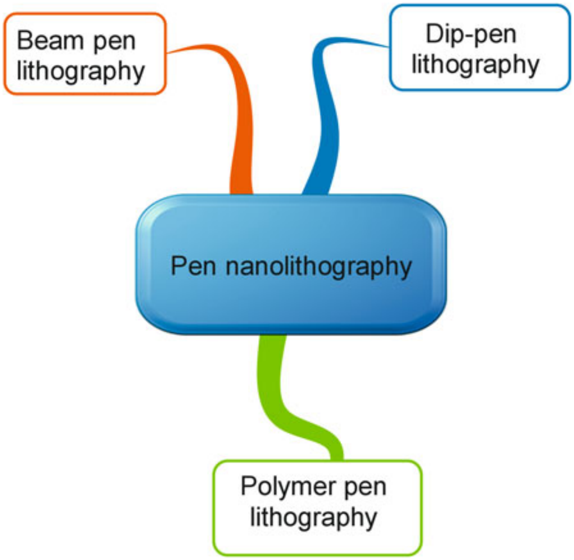


Fig. 2.6 Different pen nanolithography techniques

An illustration of the type of structure (diblock polymer) which can be obtained is shown in Fig. 2.5.

2.1.4 Pen Nanolithography

There are three main types of pen nanolithography (Fig. 2.6).

Dip-pen nanolithography uses the tip of an atomic force microscope (AFM) coated with a chemical or biological compound to pattern the surface of a substrate with accuracy below 100 nm. The tip of the cantilever of the AFM acts as a "pen," the chemical or biological compound as an "ink," and the surface of the substrate as a "paper." One-dimensional and two-dimensional arrays of cantilevers increase the speed of patterning. For example, two-dimensional arrays of 55,000 tips can make 88 million dots in 5 min. Today, dip-pen arrays with more than a million tips have been made. Different inks can be deposited in the patterning process.

Dip-pen nanolithography allows manipulating individually single biological structures like viruses or cells. The aim in the near future is to develop high-resolution dip-pen nanolithography of high throughput with the ability of multiplexed deposition on a substrate.

Polymer pen lithography combines the principles of dip-pen nanolithography and contact printing to pattern large areas (larger than several square centimeters). An array of inked elastomeric tips is used to print features with dimensions between about 90 nm up to 10 μm. The interesting thing is that it is not necessary to reink again the tip after each printing.

Beam-pen lithography uses a polymer pen array coated with a thin layer of gold. UV light entering the polymer tip in the backside of the pen is channeled through a nanometer-size aperture. This method allows pushing the lateral resolution of features that are produced to below the diffraction limit. For example, using 400 nm wavelength, it has been possible to make 100 nm features. The advantage of this method is a high throughput.

2.2 On-Wire Lithography

Several powerful methods exist to make zero-dimensional systems (e.g., nanoparticles and nanodots). Many studies are today devoted to one-dimensional systems (e.g., nanowires and nanorods). The diameter, length, and composition of these one-dimensional systems can be controlled on demand. On-wire lithography is a novel method allowing synthesis of segmented structures and introducing changes by post-chemical treatment; for example gaps in one-dimensional systems. Segmented structures with disks or gaps can be synthesized with disks having different properties than the initial material of the nanowire and gaps can be filled, by subsequent chemical treatment, with organic or biological molecules, so giving the system new functionalities.

Usually, nanowires and nanorods are synthesized by several methods such as vapor–liquid–solid growth and specific nanolithography techniques. However, there is a demand to make more complex objects, based on one-dimensional systems, providing new functions. This requires being able to make segments of different chemical compositions, to coat them with specific metals or molecules to dope them chemically, and so on.

The principle of on-wire lithography is the following (see Fig. 2.7). Multilayered nanowires are made in a porous alumina template (which is a thick disk with cylindrical holes) by electrodeposition. Different plating solutions are used so that segments of different metals can be made. The length of the segments is controlled by the amount of electrical charge delivered during electrodeposition. After dissolving the template, nanowires are released and put onto the substrate. A thin layer of silica or metal can be deposited by plasma-enhanced chemical vapor deposition. Afterward, the substrate is immersed in ethanol and sonicated, which releases the nanowires.

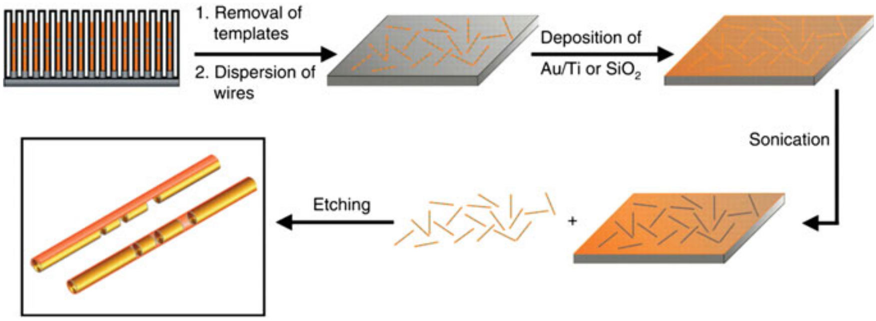


Fig. 2.7 Principle of on-wire lithography. Science, 2005. Courtesy of C.A Mirkin

Some of the segments can be removed by wet-etching, for example, for creating gaps in the nanowire.

Several applications of the objects produced in this way are photonic devices, plasmon guides, electrical devices, and chemical and biological sensors. Based on the synthesis of nanowires by electrochemical deposition within a template and wet chemical etching, the advantage of the on-wire lithography technique is that it can be easily controlled and implemented. It has a high throughput and does not require expensive equipment. Nanowires with gaps as small as 2.5 nm can be obtained for example.

2.2.1 Nanoimprint Lithography

Nanoimprint lithography is a low-cost process with high throughput and moderately high resolution allowing production of nanometer scale patterns. It is able to make 25 nm feature size over large areas. It can also be used on nonflat surfaces. Several applications of nanoimprinting are possible such as nanowires, silicon nanodots, or nanophotodetectors. The principle of thermal nanoimprinting is shown in Fig. 2.8. In the first step, a mold (stamp (1)) with nanostructures is pressed into a thin film of a resist cast on a substrate (2). This step is made easier by heating the resist above the so-called glass transition temperature, i.e., the temperature above which the resist becomes thermoplastic (it behaves like a viscous liquid, the viscosity decreasing as the temperature increases). An image of the mold is impressed onto the resist (3). In the second step, this image is made more precise using an anisotropic etching process to remove the residual resist present in the compressed area. Silicon oxide or silicon can be used as mold materials and the pattern is made by *e*-beam lithography, for instance. The resist can be PMMA (poly-methyl-methacrylate) which has a glass transition temperature at about 105 °C. This technique is based on the thermoplastic behavior of the resist and is sometimes referred as thermoplastic nanoimprint. There is another close technique known as photo nanoimprint lithography where a curable liquid resist is used. This is a polymer material with chemical additives which becomes hard under irradiation (curing), for example using

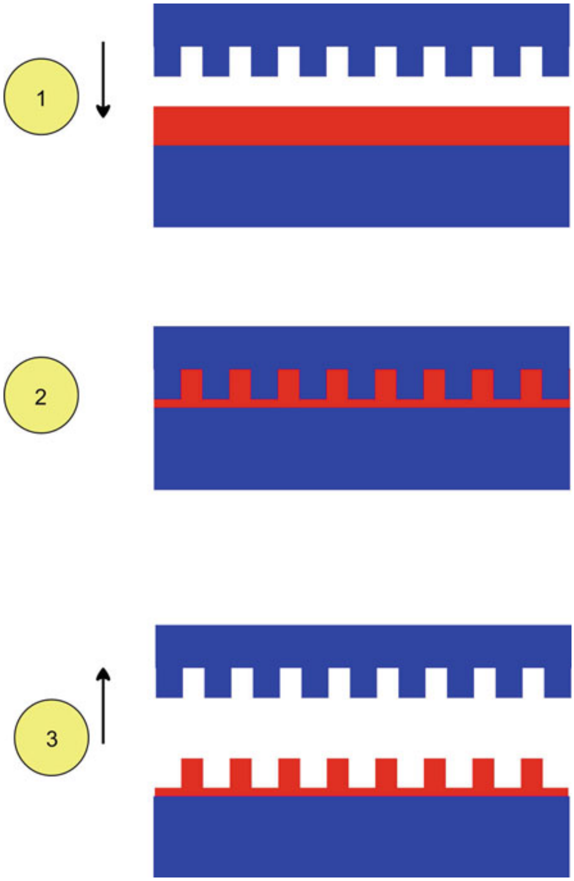


Fig. 2.8 Principle of thermal nanoimprint lithography

UV light. This occurs because there is cross-linking between the polymers chains of the curable liquid under irradiation. In this process, the mold is pressed onto the substrate where a thin layer of curable liquid is deposited. The resist is cured with UV light which necessitates that the mold is made out of a material transparent to the wavelength used.

2.3 Nanochemistry

It is possible to make nanoscale building blocks using synthetic chemistry. This is the essence of nanochemistry. These blocks can have different size, shape, structure, composition, functionality, etc. More complex architectures can be built from these blocks to get new functions and properties. To make nanostructures from single molecules or molecular units, they have to be assembled in more complex structures by means of specific interactions. Supramolecular chemistry is the way to do that.

The research in this area was pushed in particular by Cram et al., who were awarded the chemistry Nobel Prize in 1987 for their contribution to this subject. Supramolecular chemistry is the area of chemistry where chemical systems are made from single molecules, chemical subunits, or components, using weak forces like intermolecular forces, ionic or hydrogen bonds, or metal–ligand interactions. Covalent bonding can also be used, provided it does not affect the structure of the elementary units used. Self-assembly is the driving force to create complex structures from elementary elements. It can be spontaneous or directed self-assembly using templates. When self-assembly of molecules and materials are directed by templates, additives are used that can be involved in co-assembly or they can guide the assembly during a lithographic process.

The process of self-assembly can be reproduced at several scales leading to hierarchical systems with different building rules at different length scales. From the elementary component (molecules or other subunits), the different steps generate more and more complex structures of different sizes. Biological structures are used to build hierarchical structures at different length scales and this is also now being achieved for artificial materials. New properties can appear, unknown at the single component level because collective properties come into play. Organic chemistry is interesting to produce elementary components of a structure because a large variety of molecules with different shapes and functionalities can be synthesized.

2.4 Langmuir–Blodgett Films

Langmuir–Blodgett films are made of one or more monolayers of an organic material deposited onto the surface of water. The principle of fabrication is schematically shown in Fig. 2.9. The monolayer is made by putting the organic molecules onto the water surface in such a way that they are not closely packed. A sliding barrier is used to make a closely packed layer. The process is followed by measuring the surface pressure. The organic molecules which are used have generally a hydrophilic head (a polar group) and a hydrophobic tail. They are often a fatty acid. A substrate, dipped into the water, is moved up and a monolayer deposits onto its surface. The process is monitored by checking the surface pressure and moving the sliding barrier.

One or more monolayers can be deposited in this way onto the substrate. Figure 2.10 shows an example of several monolayers fabricated by the Langmuir–Blodgett technique on a hydrophilic substrate. The construction is done head-to-head and tail-to-tail.

The Langmuir–Blodgett technique is interesting for preparing highly organized thin films. One can have a homogeneous deposition of a thin film over large surfaces, typically several cm^2, with precise control. Multilayers from two to hundreds of monolayers can be fabricated. The choice of the substrate and the nature of the molecules makes the method very flexible. For example in Fig. 2.11, where a hydrophilic substrate is used, we have a tail–head construction. Using a hydrophilic substrate it is possible to produce tail-to-head or tail-to-tail structures (Fig. 2.10).

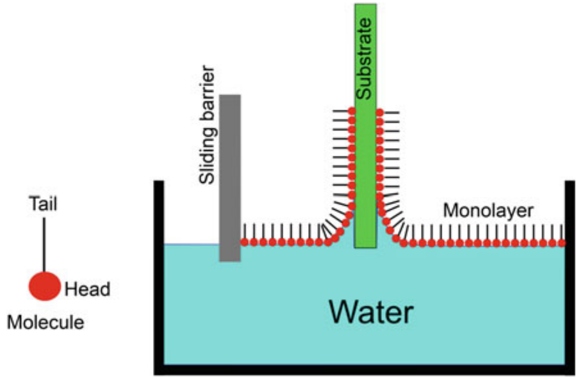


Fig. 2.9 Principle of the preparation of Langmuir–Blodgett films

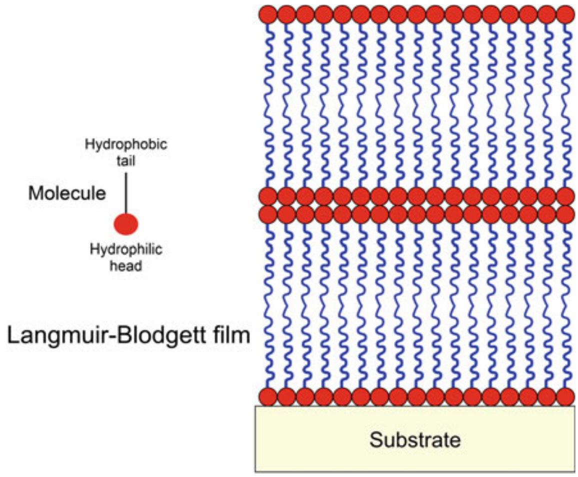


Fig. 2.10 Schematic drawing of multilayers obtained with the Langmuir–Blodgett technique on a specific substrate

With a hydrophobic substrate one can make head-to-tail deposition with the tail located onto the substrate.

2.5 Self-assembled Monolayers

The self-assembled monolayer (SAM) technique encompasses methods in which amphiphilic molecules, i.e., with a hydrophilic head and a hydrophobic tail self-assemble onto the surface of a two-dimensional metal or semiconductor, or on the curved surface of nanoparticles. Self-assembly takes place because there is chemisorption of the hydrophilic head of the molecules onto the substrate surface. After some time, ranging from minutes to hours, a semicrystalline or crystalline structure is formed on the surface of the substrate. This process was first developed with a long chain of alkanethiolates that could assemble on gold surfaces. A schematic representation of a self-assembled monolayer is shown in Fig. 2.12. The head is

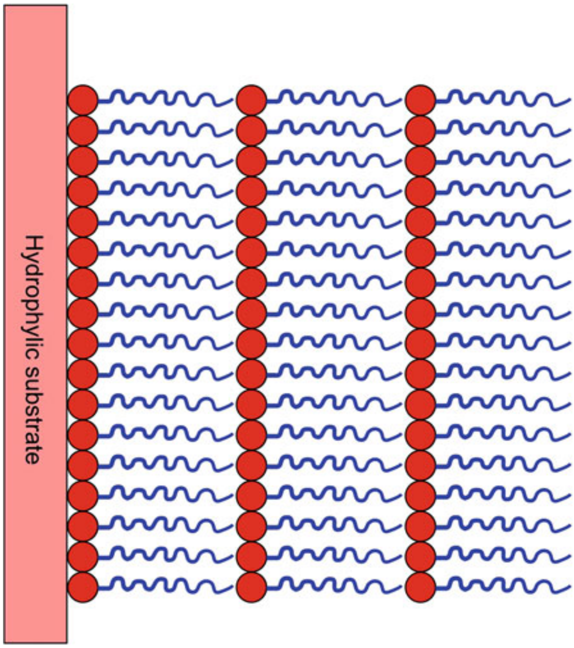


Fig. 2.11 Schematic drawing of a tail-to-head structure of three monolayers made by the Langmuir-Blodgett method on a hydrophilic surface

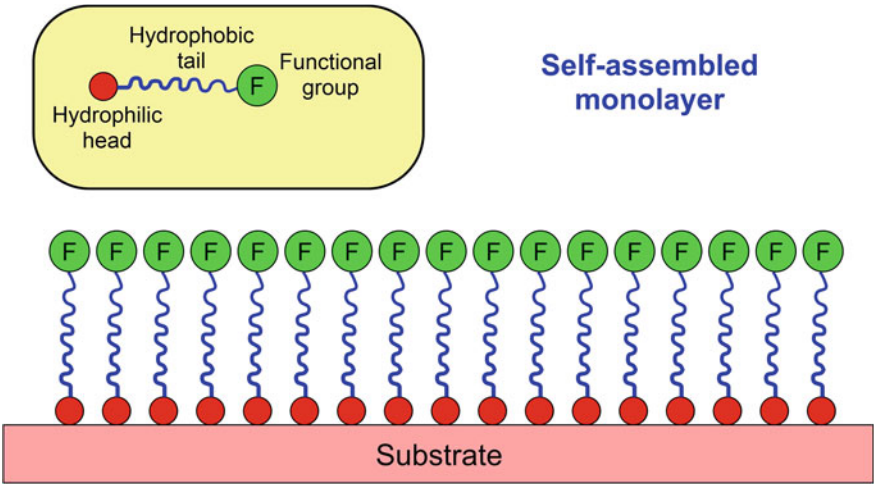


Fig. 2.12 Representation of a self-assembled monolayer

hydrophilic and is connected to an alkyl chain that can eventually be functionalized to tailor the interfacial properties of the SAM.

2.6 Conclusion

There are basically two approaches to manufacture nano-objects:

- The *top-down* approach where nano-objects are built starting from macroscopic objects using different tools and techniques to remove or add material. Lithography techniques are now sophisticated enough to work at the nanoscale and are extensively used to do that. Adding material can be done by various techniques such as evaporation or chemical vapor deposition. Using a scanning tunneling microscope to build nano-objects starting from elementary building blocks can eventually be classified in this category.
- The *bottom-up* approach starts from molecules which are synthesized on demand and self-assembled to form the nano-object. The building blocks, which can be molecules, can be functionalized and their geometry controlled.

Hybrid approaches combining the top-down and bottom-up approach offer more possibilities and flexibility.

Chapter 3
Quantum and Mesoscopic Physics

This chapter is a brief overview of the physics governing processes at the nanoscale. We are used to the macroscopic world and have developed an understanding, based on what is usually called “classical physics”, of the behavior of the objects that we see with our eyes. However, classical physics is not able to explain certain phenomena occurring at the atomic or molecular level or below. Compared to macroscopic systems, quantum effects can become important and certain classical physical effects, which are negligible for macroscopic objects, can become prominent. We present here some new aspects showing how nano-objects behave compared to what is expected by extrapolating our knowledge on macroscopic systems. Further items will be introduced in the subsequent chapters when needed.

At the macroscopic level classical physics applies: we have, on one hand, *classical mechanics* describing the motion of everyday life objects, the motion of planets or the trajectory followed by a car moving on a road,…; and, on the other hand, *wave theory* describing for example the propagation of electromagnetic waves (for example for radio and TV) or the scattering of charged particles, or the propagation of sound. Particles carry energy and mass while waves carry energy only.

At the atomic or molecular level many of the classical effects we are used to with macroscopic objects are not present or visible and new effects, called “quantum effects,” appear. Quantum mechanics is the proper theory to describe these microscopic systems. Quantum mechanics applies at any scale but, for macroscopic objects, classical theories give a perfect description and there is usually no need to use quantum mechanics. For this reason, and for practical purposes, a phenomenon is said to be quantum if it cannot be interpreted within the frame of a classical theory.

3.1 Quantum Mechanics

In classical physics, we deal with *particles* corresponding to an energy density localized in space, and *waves* corresponding on the contrary to delocalized energy. The dynamics of a particle is described by classical mechanics and the position and

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_3, © Atlantis Press and the authors 2014

velocities of the particles are continuous variables. For example, a car can take all speed values between zero and its maximum speed. Partial differential equations with boundary conditions are used to describe waves and not all energies are now possible when they are confined (plucking a guitar string generates only one frequency and its harmonics, not a white noise or multiple frequencies). If they are not confined, all frequencies are possible (electromagnetic waves propagating in free space, for example). In the following we shall use *corpuscle* to indicate a classical particle and keep the word *particle* for an object at the microscopic level. The reason for this choice will be clear in a moment.

3.1.1 Postulates of Quantum Mechanics

Any theory is based on postulates and the validity of the theory depends upon the agreement obtained with experiment. Classical mechanics, which determines the dynamical evolution of macroscopic objects, like the motion of planets or the trajectory of a stone falling on the ground, is *deterministic* (Fig. 3.1). This means that if we know the initial conditions (the initial position and velocity vector of the object) and the field of forces it experiences (the gravitational or an electromagnetic force, for example) it is possible to calculate the position and the velocity at a later time. The object follows a *trajectory* which can be calculated. The position and the velocity at any time characterize completely the state of a corpuscle.

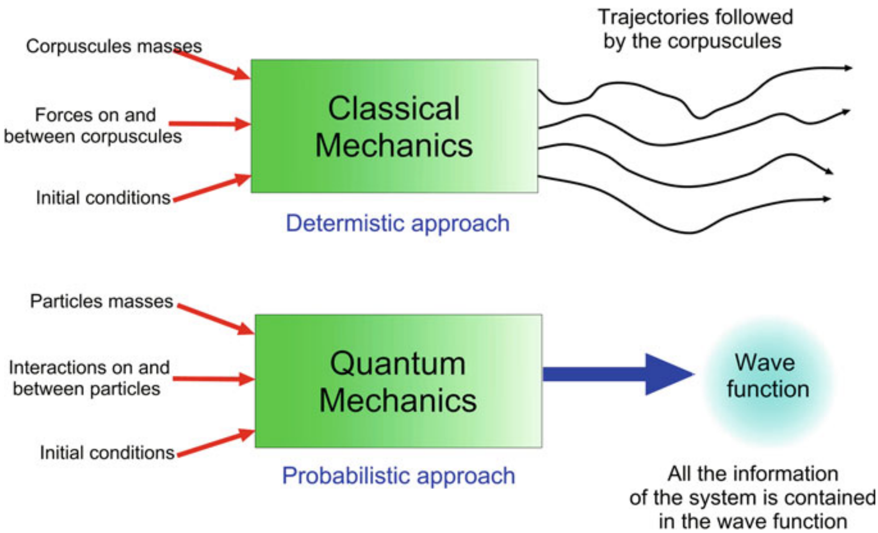


Fig. 3.1 Comparison between classical and quantum mechanics

In quantum mechanics, the notion of trajectory breaks down and is replaced by a *wave function*. The important point is that the wave function contains all information on the system. This is the first postulate of quantum mechanics. Physical quantities are represented by mathematical functions in classical physics. In quantum mechanics they are represented by another kind of mathematical object: *hermitian operators* which are a subset of *operators*. For each measurable physical quantity (called an *observable*) is associated a hermitian operator.

In classical physics, a corpuscle remains a corpuscle and a wave behaves always as a wave. This is not the case at the microscopic level where, depending upon the physical conditions, a particle can behave either like a particle or like a wave. This is called the *Wave-particle duality principle* (Fig. 3.2). It depends upon the conditions. A particle that behaves like a corpuscle at the macroscopic level may behave like a wave at the microscopic level and vice versa.

There are several examples where a wave at the macroscopic level behaves like a particle at the microscopic level. This happens for example in the photoelectric or Compton effects, both of which reveal the corpuscular nature of light. Light, which is classically described as an electromagnetic wave, consists actually of photons which are elementary particles (quanta of light). In the photoelectric process, photons impinging a metal surface can emit electrons if their energy is large enough. In the

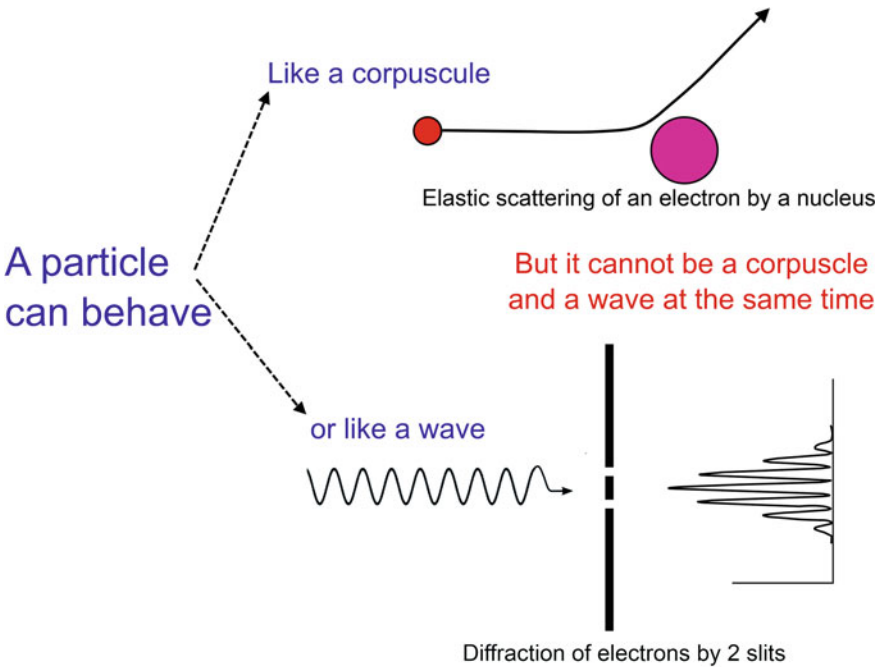


Fig. 3.2 Wave-particle duality: an electron can behave like a corpuscle or like a wave but it cannot be both of them at the same time

Compton effect, an energetic photon undergoes a collision with an electron and is scattered, like a corpuscle, at an angle which can be calculated. On the other hand, neutrons or electrons, which are corpuscles, can be diffracted by the atoms of a crystal if they have the appropriate kinetic energy. In this case these corpuscles behave like waves. Many applications using these phenomena exist in the macroscopic world: for example, photovoltaic panels are based on the photoelectric effect, the Compton effect occurs in detectors used to detect the gamma rays emitted in medical imaging measurements, diffraction of particles can be used to determine the structure of materials, etc.

A wave can be associated to each particle. The corresponding wavelength is called the *de Broglie wavelength*. A frequency is associated with this wavelength just as a radio broadcast is characterized by an emission frequency corresponding to an emission wavelength. It is important to note that a particle can, depending on the conditions, behave like a corpuscle or like a wave but it cannot behave simultaneously like both of them at the same time. Contrarily to classical mechanics, where it is possible to make a measurement without notably perturbing the system (measuring the speed of a car with radar hopefully does not modify the trajectory of the car), this is not the case for quantum systems where measurements generally perturb substantially the state of a system.

The second postulate of quantum mechanics makes the connection between the system and the observer: it defines the observables, i.e., the physical quantities that can be measured. This postulate states that a *hermitian operator* is associated to each observable and that the result of a measurement is always an eigenvalue of this operator. A set of special wave functions (known as eigenfunctions) will always return the same value (an eigenvalue) of the observable.

The third postulate assumes that in quantum mechanics the wave function obeys a partial differential equation known as the *Schrödinger equation*. There is a time-independent Schrödinger equation that allows calculating the properties (energy levels, for example) of a stationary system and a time-dependent Schrödinger equation that allows calculating the time evolution of the wave function of a system in a fully deterministic way.

The fourth postulate indicates how it is possible to build the hermitian operators associated with a physical observable from their expression in terms of classical variables.

3.1.2 Measurement

A measurement generally makes a strong perturbation of a quantum system except if it is already in a quantum state that is an eigenvalue of the observable. Indeed, before the measurement we have some probability to obtain an eigenvalue of the operator but, after the measurement, we are sure of the result (a subsequent similar measurement would lead to the same result) which means that the wave function has been changed by the measurement: after measurement it is the eigenvector of the operator associated to the measured eigenvalue.

Wave function

A wave function is complex (it has a real and an imaginary part). However, we know that any measurements performed on a system in our world always gives real numbers. This is why the operators describing an observable are hermitic. Indeed, these operators have real eigenvalues and the result of any measurement on the system is an eigenvalue of the operator associated to the observable. If we consider a particle, the wave function, $\Psi(x, y, z, t)$, is the *probability amplitude* for finding the particle at a given point in space and at a given time. The probability of finding the particle at point (x, y, z) and at time t is the square of the modulus of the wave function Ψ or of the product $\Psi\Psi^*$, where $\Psi^*$is the complex conjugate of Ψ:

$$Probability \propto |\Psi|^2 = \Psi\Psi^*$$

Since the probability of finding the particle somewhere in space is 1, the wave function should be normalized: the sum of the probability over all space should be equal to 1.

3.1.3 Quantization

The most striking feature of the quantum world is the fact that some observables have discontinuous values. In classical mechanics, the kinetic energy of a corpuscle confined within a harmonic oscillator (a classical spring is an example of harmonic oscillator) or confined within a cubic box can have any value starting from zero to the maximum value we can give to it. This means that energy values are continuous. In quantum mechanics this is no longer true. The energy can only take fixed values as shown in Fig. 3.3 for a harmonic oscillator.

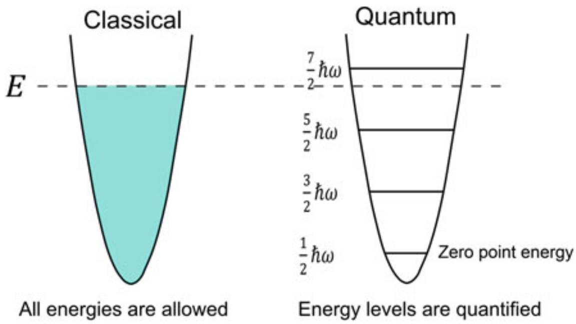


Fig. 3.3 Harmonic oscillator potential. Given an energy E, all the energies from the bottom of the well up to E are allowed in classical physics. At the microscopic level discrete values are allowed only

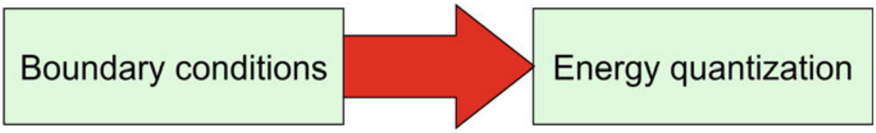


Fig. 3.4 Spatial boundary conditions lead to energy quantization (discrete energy levels)

This comes from the fact that the Schrödinger equation is a partial differential equation that has to be solved with boundary conditions. As a result all energies are, in most cases, not allowed and discrete values only are possible (Fig. 3.4). This is exactly what happens at the macroscopic level with a guitar that can only produce sounds of discrete frequencies. This reflects once more the wave character of particles.

3.1.4 Uncertainty Principle

The Heisenberg uncertainty principle states that, contrary to classical mechanics, it is not possible to measure *simultaneously*, as precisely as we want, two physical quantities like the position and the momentum (or speed) of a particle. If Δx and Δp_x are for example the uncertainty in the position x and in the momentum p_x along the x direction, we have:

$$\Delta x \times \Delta p_x \geq \hbar$$

where $\hbar$ is the Planck constant $\hbar$ divided by 2π ($\hbar = \frac{h}{2\pi}$). In other words, either the position or the momentum of a particle can be measured as accurately as we want, but not both. The more precisely one variable is known, the less precise the measurement of the other is. Position and momentum are fundamentally incompatible observables. This uncertainty relationship applies at the macroscopic level also, but we are never aware of it because the accuracy of the measurements is never sufficiently high to expose the quantum uncertainties. There are similar identities along the y and z axes. However, it is always possible to simultaneously measure x and p_y for example.

A similar uncertainty relationship exists between time and energy which can be written as:

$$\Delta E \times \Delta t \geq \hbar$$

This means basically that if a system has a finite lifetime it is not possible to determine its energy with an infinite accuracy. In this case the quantum state has a width (the energy is not precisely defined). This width can be large if the system has a very short lifetime. For example an elementary particle existing for 10^{-23} s has an energy uncertainty of about 70 MeV (this is equivalent to the energy necessary to create more than 60 electron–positron pairs). It also means that if we are to observe a system during a time Δt, energy is conserved with an accuracy of ΔE only.

Measurement and mathematical operators

The reason it is not possible to measure simultaneously some physical quantities comes from the fact that observables are represented by hermitian operators. The result of the measurement is an eigenvalue of these operators to which is associated an eigenvector. Consequently, two observables can be measured at the same time if the two corresponding operators have a common set of eigenvectors. This occurs only if the two operators commute,[a] which is not always the case. For example, the operators associated with position and momentum along the same axis do not commute. This is why we have the uncertainty relationship above.

[a] If two operators **A** and **B** are non-commuting, it means that $\mathbf{AB} \neq \mathbf{BA}$. Applying **AB** on a wave function does not give the same result as if we apply **BA**.

Classically a corpuscle can be motionless. At the microscopic level a particle cannot have zero kinetic energy if it is confined in a finite region of space Δx. Indeed, the Heisenberg uncertainty relation $\Delta x \times \Delta p_x \geq \hbar$ gives the lowest uncertainty on Δp_x. Since the largest uncertainty in the position of the particle Δx corresponds to the region of space where the particle is confined, the corresponding value of Δp_x is finite meaning that the particle moves even in the lowest energy state. The corresponding energy is called the *zero point energy*. A quantum object can never stay at rest if it is confined in a space.

3.1.5 Spin

A degree of freedom of a particle is an internal degree of freedom if it does not depend on its spatial position. This is the case for *spin,* which is an internal degree of freedom with no classical equivalent. It has the properties of an angular momentum and follows the rules of angular momenta in quantum physics. Electrons or protons, for example have a spin $S = s\hbar = \frac{1}{2}\hbar$. It is said that their spin is $s = \frac{1}{2}$. It is like a vector but its projections on an axis are quantized. The value of the projection of this vector on an axis can take only two values: $-\frac{1}{2}\hbar$ and $+\frac{1}{2}\hbar$. Spintronics (spin transport electronics) is a new technology exploiting the spin of the electron and its associated magnetic momentum. Spintronics allows an efficient treatment of information at low energy cost.

3.1.6 Quantum Numbers

The wave function of a system defines completely its properties. In the case of a discrete energy spectrum (energy levels), the wave function often depends on discrete numbers that are indices of the wave function of the system. These numbers are called quantum numbers and are equivalent to describing a quantum state. A system with N degrees of freedom is described by N quantum numbers.

Quantum numbers of a harmonic oscillator

The wave function of the ground state and excited states of a one-dimensional harmonic oscillator (quantum spring) is proportional to Hermite functions, which are basically the product of a Gaussian times a polynomial. They can be obtained by solving the Schrödinger equation of a particle of mass m in a harmonic potential $V(x) = \frac{1}{2}kx^2$ where x is the position coordinate and k *a constant characteristic of the oscillator. The Hermite functions can be classified according to an index* n which is an integer number: $n = 0, 1, 2 \ldots$ The value $n = 0$ corresponds to the ground state wave function, $n = 1$ to the first excited state, etc. The energy levels of the harmonic oscillator are given by $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$ *where* ω is the angular frequency of the oscillator $\omega = \sqrt{\frac{k}{m}}$. The index n is the quantum number of the oscillator. It is equivalent to describe a state of this system by its wave function or to say that it is in state n. As we can see, using the quantum number is more convenient.

In quantum mechanics, we need to have a complete set of hermitian operators representing the observables that commute two-by-two (otherwise it is not possible to measure simultaneously the observables). The number of operators necessary to make a complete set of observables is equal to the number of degrees of freedom of the system.

Quantum numbers of a hydrogen atom

The electron of the hydrogen atom has three degrees of freedom in space and two additional internal degrees of freedom associated with the spin of the electron. A quantum state is then determined by five quantum numbers: three for ordinary space $(n,\ l,\ m)$[a] and 2 for the spin of the particle (sm_s).[b] In order to completely determine a particle at rest, we need to know its three coordinates because this system has three degrees of freedom.

[a] n is called the *principal quantum number* (it corresponds to the shell number of the hydrogen atom). $n = 1, 2, 3 \ldots$ l is the orbital or *azimuthal quantum number* and is related to the orbital angular momentum of the electron. $l = 0, 1, 2 \ldots n - 1$. Finally, m is *magnetic quantum number*. It corresponds to the projection of the angular momentum along the z axis. $m = -l,\ -l + 1, \ldots, l - 1, l$.

[b] s is the spin quantum number ($s = \frac{1}{2}$) and $m_s = -\frac{1}{2}, +\frac{1}{2}$, the projection of the spin along the z axis.

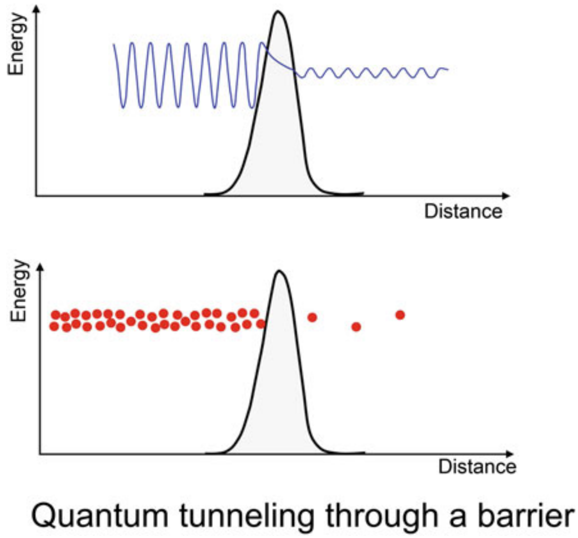


Fig. 3.5 Schematic illustration of quantum tunneling. On top the wave function decays exponentially inside the barrier and has lower amplitude beyond the potential barrier

3.1.7 Quantum Tunneling

If a classical particle is on one side of a potential barrier and has a kinetic energy lower than the top of the barrier it cannot go to the other side. At the microscopic level this is no longer true and a particle has some probability to escape even if its kinetic energy is smaller than the top of the potential barrier. This phenomenon, called *quantum tunneling*, does not exist for a classical corpuscle (Fig. 3.5). The escape probability depends on the properties of the particle, on the difference between the height of the barrier and the energy of the particle, and on the thickness of the barrier. This probability increases, for example, if the width of the barrier decreases.

We know that classical waves can also penetrate also "forbidden" regions. A so-called *evanescent wave* is for example observed for electromagnetic waves in the microwave region or in optics and acoustics. An evanescent wave is a standing wave with an intensity decaying, in the forbidden region, exponentially with the distance to the boundary where it has been formed. Since a particle can behave like a wave, it can also go into the forbidden region and eventually escape to another allowed region if the conditions are fulfilled. A *scanning tunneling microscope* is based on the tunneling of electron waves.

3.1.8 Bosons and Fermions

All elementary particles found in nature have a spin. This has an important consequence on the way many of these particles interact with each other. Most macroscopic

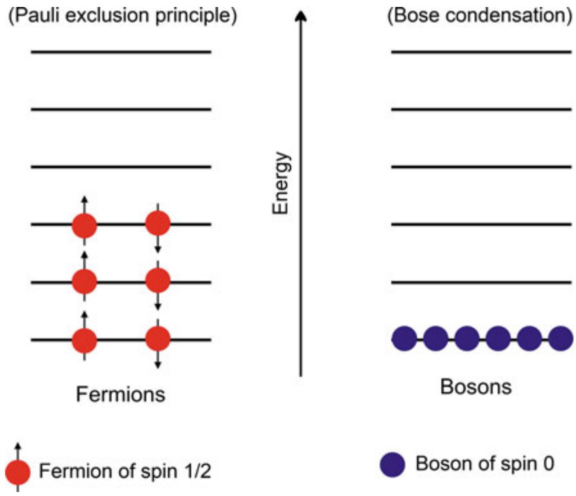


Fig. 3.6 Fermions cannot be in the same quantum state. In the case of spin $\frac{1}{2}$ particles, two projections are allowed corresponding to different quantum states. This means that we can put two particles of opposite spin projection on the same energy level. On the contrary there can be several bosons on the same energy level (here the ground state)

objects are discernible. For example, we can color differently two identical billiard balls to discern them. At the microscopic level all particles of the same nature are indiscernible. Particles can be classified into two families: those having an integer spin which are called *bosons*; and those having a spin which is a half-integer number called *fermions*. The important fact is that two fermions cannot be in the same quantum state while bosons can be (Fig. 3.6). It is said that fermions obey *Fermi-Dirac statistics* while bosons obey *Bose-Einstein statistics*. The fact that fermions cannot be in the same quantum state is called the *Pauli exclusion principle*. Electrons or nucleons (protons or neutrons) are fermions. Their spin is equal to $\frac{1}{2}$: we cannot put two electrons or nucleons in the same quantum state. Photons are bosons and their spin is 1: we can put as many as photons in a cavity as we want.

Property of fermions and bosons wave functions

The basic principle governing the behavior of fermions and bosons with respect to each other comes from the fact that the wave function of several identical fermions is completely antisymmetric with respect to the exchange of any two fermions, while the wave function of several identical bosons is completely symmetric. Mathematically, a completely antisymmetric function is a determinant and we know that it is zero if two columns or rows are identical.

3.2 Mesoscopic Physics

"Mesoscopic Physics" is a relatively new branch of physics dedicated to the world between the macroscopic and the microscopic world. "Meso" is Greek and means "in between." Macroscopic and mesoscopic objects have in common that they both contain a large number of particles. While a macroscopic object obeys the laws of classical mechanics and can be described by the properties of the material from which it is made, when scaled down to the mesoscopic level this is no longer true. As we decrease the dimension of a system, changes in the behavior of the system can occur, so some effects which were negligible can become prominent. Indeed, surface, adhesive, and friction effects become significant. At low dimensions, the surface becomes more and more important compared to the volume. For example, a lump of aluminum is difficult to burn, but when ground into a powder of fine particles—with a much larger global surface area—it burns easily and may even explode due to the much larger surface in contact with oxygen molecules.

To obtain a feeling for the evolution of physical quantities as we scale down the dimension of a system, we shall suppose that it is characterized by a "length" L. As the size of a system decreases, the surface becomes more and more important compared to the volume. Indeed, the surface varies with L^2 whereas the volume varies with L^3. Therefore the volume/surface ratio scales with L, so that the volume properties dominate for large L and the surface for small L. Surface effects are dominating the physics at low dimensions. The example below illustrates this point.

Reducing the size of objects enhances surface effects

The surface of a cube with a side of 1 cm has an area of 6 cm^2. If this cube is cut into nanocubes with a side of 1 nm, there will be 10^{21} nanocubes with an area of 6×10^{-14} cm^2 each. This will represent a global area of 6,000 m^2, even though the total overall volume of material is the same as our original cube.

At the nanoscale, the gravitational force (responsible for the weight of objects, for example) becomes negligible compared to the adhesive forces between two surfaces. This is due to the fact that adhesive forces vary with L^2 while gravitational forces vary with L^3. The main adhesive forces between two surfaces separated by a distance $\approx$ 2–10 nm comes from the van der Waals forces. Pinch forces, which correspond to

Fig. 3.7 At the nanoscale, fluids behave more like honey than water

adhesive and friction phenomena, are also more and more important at low dimensions compared to gravitational forces. In that case, resonating nanoscale objects are also characterized by larger frequencies compared to macroscopic objects.

If we now consider fluids, viscous forces are more important. This explains in particular why a micro- or nanoparticle standing in calm air remains motionless. For macroscopic fluids, we know that when the speed of a fluid increases, turbulence appears and there is a transition from laminar to turbulent flow. Turbulence is important to mix fluids of different nature. At the micro- or nanoscale level turbulence cannot be reached anymore and, compared to the macroscopic scale, a fluid behaves more like honey than like water (Fig. 3.7). This makes it difficult to mix different fluids by standard methods.

3.3 Conclusion

Modern technology operates more and more at a scale where quantum effects are important and significant. Through our everyday life interaction with macroscopic objects, we have built our intuition for the physics of everyday life. At the micro- or nanoscale, new concepts, which were not visible at our macroscopic scale in classical physics, become important and our intuition may often be misleading. This does not mean that the physical laws are different, but that some effects, negligible at the macroscopic scale, become prominent at the nanoscale. Quantum effects can become significant leading to a profound change in the technologies by imposing substantial restrictions or new possibilities. Downscaling systems can give rise to novel opportunities useful for everyday life applications and we shall present some of them in the rest of the book.

Part I
Exploring and Working in the Nanoworld

Conclusion

Nowadays, scientists are able to observe atoms, manipulate them on a surface and build nano-objects from different materials and building blocks. The mesoscopic domain to which these nano-objects belong has to deal with both classical and quantum effects. Some variables describing mesoscopic systems will have a classical behavior, others are purely quantum like. However, several can have a semiclassical behavior because the quantum numbers involved have large values. Experimental results can help to model the behavior of the systems since it is always easier to cope with semiclassical approximations rather than with a full quantum problems.

There is an evolution from a pure classical behavior to a quantum behavior as the size of the system decreases. This is expressed in Fig. I.1 which shows also that manufacturing can be made either by a top-down or a bottom-up approach.

Part I has been mostly devoted to nanotechnology practice and just a few quantum concepts have been addressed. It was shown that we can see, move, and manufacture nano-objects. However, practice and theory are closely related and need each other to make progress. Theory helps to understand the phenomena governing manufacturing and the functionality of nano-objects. It allows us to model the phenomena of nano-objects which are involved with the final goal of being able to model and simulate the whole system. Both experiment and theory are therefore needed in nanotechnology (Fig. I.2) and progress in a self-consistent way.

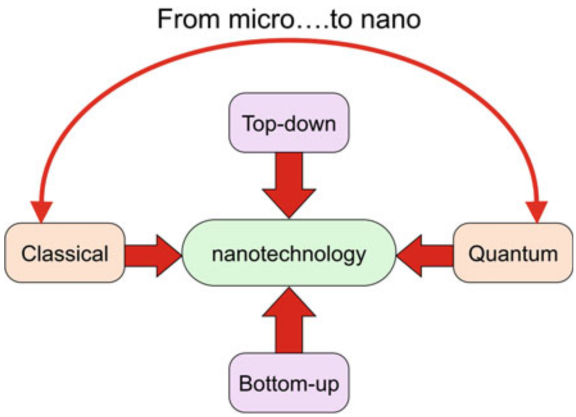


Fig. I.1 Nano-objects can be made by a top-down or bottom-up manufacturing. As the size of the nano-object decreases, there is a shift from a classical system to a quantum system

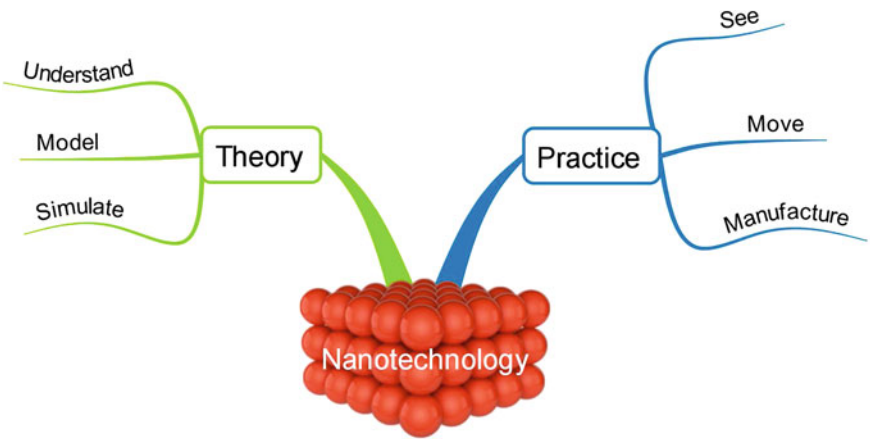


Fig. I.2 Interplay between theory and experiment of nano-objects in nanotechnology progress

Part II
Nanomaterials

Introduction

Nanomaterials is a term used to describe a broad and disparate range of materials containing characteristic features with dimensions below 100 nm. These features can be organized in random or well-ordered patterns. In general, both the properties of the individual nanoscale features and their organization will contribute to the properties of nanomaterial. Confusingly, a nanomaterial can be a macroscopic size component containing many nano-objects but it can also be an individual object investigated as a material at the nanoscale. A nanomaterial is often characterized by a dimension linked either to the dimension of the salient nano features making up the material or to their organization. When an interesting property of a material stems from the organization or pattern at the nanoscale it is often referred to as a *nanostructure* or a *nanostructured material*.

It should be mentioned that nanoscience, nanotechnology, and the concept of nanomaterials is not new; examples are ultra-thin films, wires, clusters, aggregates, catalysts, and the grain sizes in metals and ceramics. For comparison, the largest lateral size of human blood cells is about 6,000 nm; the approximate size of the common human herpes virus is 100 nm. Stained glass windows, made already as early as 500 AD, were more luminous and durable than dyes could produce at that time. This was just because nanoparticles were embedded in the glass.

Macroscopic materials can be built from nano-objects. One advantage of developing nanomaterials is that it is possible to perform the same function or provide the same service using—in most of the cases—much less raw material. Because of that, nanomaterials lie along the path of sustainable development because they minimize the amount of raw materials used.

Besides this important aspect, nanomaterials exhibit new features compared to macroscopic materials because of an increase of surface phenomena compared to bulk phenomena. Furthermore, quantum phenomena can come into play with volume reduction at the nanoscale. This concerns optical, magnetic, electrical, and

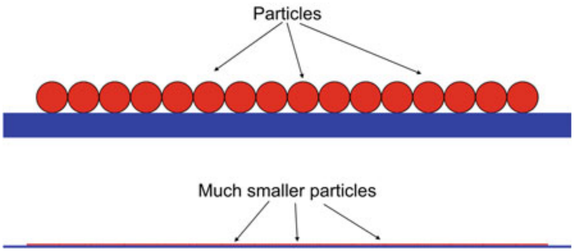


Fig. II.1 Particles (in *red*) are coated onto the surface of a material (*blue*). Smaller particles provide a much better coverage than large particles although here we are far from the real difference existing between micro and nanoparticles

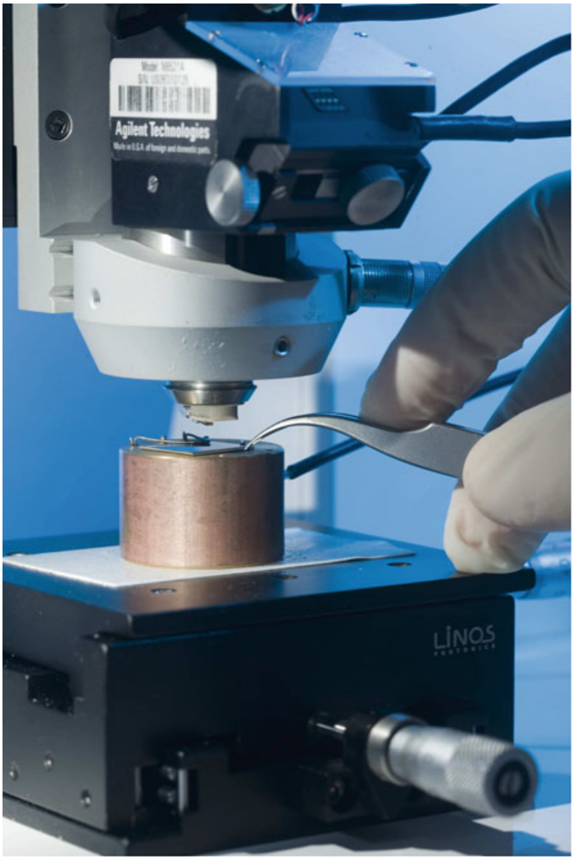


Fig. II.2 Characterization is the backbone of material studies. Figure II.2 shows an atomic force microscope, a simple and multipurpose tool, enabling the exploration of the surface of materials with high resolution. Clef CEA n°59. Image courtesy of CEA/Saclay (France) mechanical properties which can be different from those seen for macroscopic systems.

Coating a surface with nanoparticles rather than with microscopic particles is more efficient in terms of the amount of material used and of the actual surface area of the coating. This is schematically shown in Fig. II.1 using microballs and nanoballs. A monolayer of microballs contains more material than a monolayer of nanoballs. Furthermore, the surface really in contact is also smaller for the microballs. Another advantage of using a nanocoating is that it can be almost transparent to incident and reflected light.

Most of the materials we use in daily life look homogeneous to us. However, looking closely at them shows that they are inhomogeneous at the nanoscale. They are made of small structures: grains, fibers, aggregates, etc. They also contain impurities and defects which have a direct influence on their physical properties (mechanical, electronic, electrical, thermal, and so on).

A good understanding of nanomaterials relies on good characterization tools. There are now many characterization methods from simple to sophisticated. Some of them use large facilities such as synchrotron radiation or neutron scattering. Figure II.2 shows a simple and easy to use atomic force microscope currently used in laboratories working in nanotechnology.

Chapter 4
Nanomaterials: Doing More with Less

Nanomaterials are interesting in many respects. Some have been used (or developed) over a considerable time and have been manufactured by chance without any understanding of the microscopic structure of matter. This is, for example, the case of the "Lycurgus cup", a glass cup with a mythological scene made probably in Rome around the fourth century AD. It is a vessel known as a cage-cup, which was made by blowing or casting a thick glass blank. The glass was then cut and ground away leaving a decorative cage at the surface. The cup is made with a dichroic glass probably synthesized by accident. A change of color of the cup is observed when it is illuminated from inside: the opaque green cup becomes glowing translucent red. This phenomenon is caused by gold and silver nanoparticles, which were formed during the fabrication of glass. The technique was further developed during the medieval age to make stained glass windows. The so-called "Ruby glass" is still used today in order to make cadmium free intensely red glass.

Nanomaterials and nature

Nanomaterials can be found everywhere in nature and have been a part of the environment since our planet was created about 4.5 billion years ago. Fullerenes or graphene, which are of nanosize, have even been found in space while they have been synthesized by man only recently. Wood is one of the most common natural nanomaterials. It has a hierarchical scale structure. At the largest scale, wood contains soft fibers with a diameter of about 20–30 μm and a length typically between 2 and 5 mm. At an intermediate hierarchical scale, nanofibers are present with a diameter less than 100 nm and a length greater than 1 μm. The smallest scale contains crystallites with a width less than 5 nm and a length less than 300 nm. It turns out that mechanical properties improve as the size of the structure decreases. For example, the elasticity is multiplied by almost 12 and the strength by 100 as one goes from softwood structure to wood nanocrystals.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_4, © Atlantis Press and the authors 2014

Nanocellulosic materials are also found in nature. These can be collagen fibrils originating from animal sources; nanofibers originating from wood, plants, crops or bacteria; crystals or whiskers deriving from wood, plants, and crops. Cellulose nanocrystals or whiskers can be isolated by mechanical and chemical processes for subsequent use in polymer nanocomposite materials. Nature has developed several ways to build macroscopic systems from nanobricks, like seashell or bones, for example. The synthesis is carried out using nanocrystals at moderate temperature and pressure. The biomineralization process involves calcium carbonate or phosphate. Biomimetic strategies are now frequently used.

4.1 Top-Down and Bottom-Up Approaches

The synthesis of nanomaterials is key to the future success of this new technology and in principle, the approaches to the synthesis of nanomaterials can be divided into two main classes: Top-down approaches and bottom-up approaches.

4.1.1 Top-Down Approaches

In top-down approaches, a bulk material is restructured (i.e., partially dismantled, machined, processed, or deposited) to form nanomaterials (Fig. 4.1). The aggressive scaling of electronic integrated circuits in recent years can be considered the greatest success of this paradigm. For top-down methods, the challenges increase as devices size is reduced and as the desired component designs become larger and more complex. Also, the top-down assembly of nanocomponents over large areas is difficult and expensive.

4.1.2 Bottom-Up Approach

In bottom-up approaches, nanomaterials are assembled from basic building blocks, such as molecules or nanoclusters (Fig. 4.2). The basic building blocks, in general, are nanoscale objects with suitable properties that can be grown from elemental precursors. The concept of the bottom-up paradigm is that the complexity of nanoscale components should reside in their self-assembled internal structure, requiring as little intervention as possible in their fabrication from the macroscopic world.

A typical example of bottom-up processing is shown in Fig. 4.3 for nanocomposite magnets from individual high-magnetization and high-coercivity nanoparticles. The assembling critically depends on availability of anisotropic (single crystal) hard magnetic nanoparticles. Anisotropic nanoparticles produced via surfactant-assisted high energy ball milling satisfy the major requirements for this application.

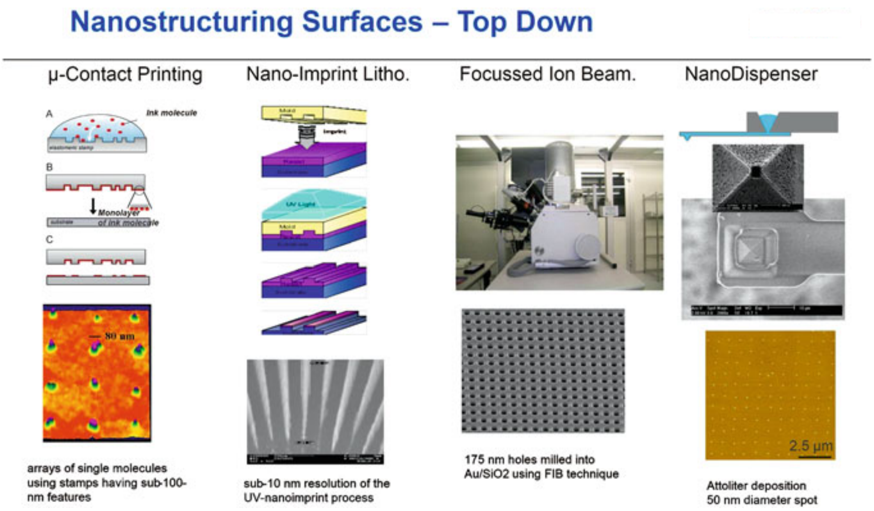


Fig. 4.1 Top-down nanosynthesis methods. Image courtesy of CSEM—International Conference on Mechatronics and Automation (ICMA), Beijing, China, August 2011

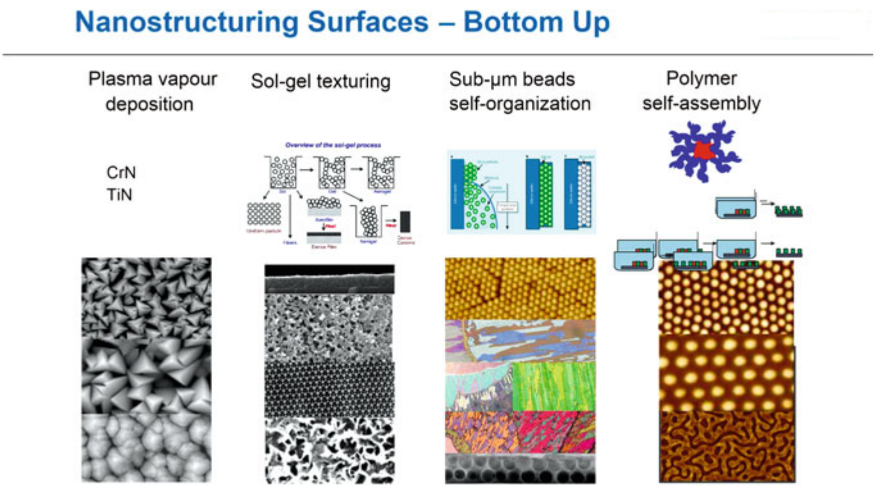


Fig. 4.2 Bottom-up methods for nanosynthesis. Image courtesy of CSEM—International Conference on Mechatronics and Automation (ICMA), Beijing (China), August 2011

4.1.3 Two Approaches with the Same Goal

The practical applications of the two nanosynthesis approaches are shown in Fig. 4.4.

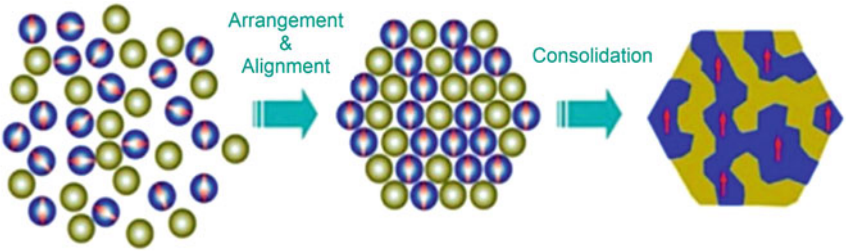
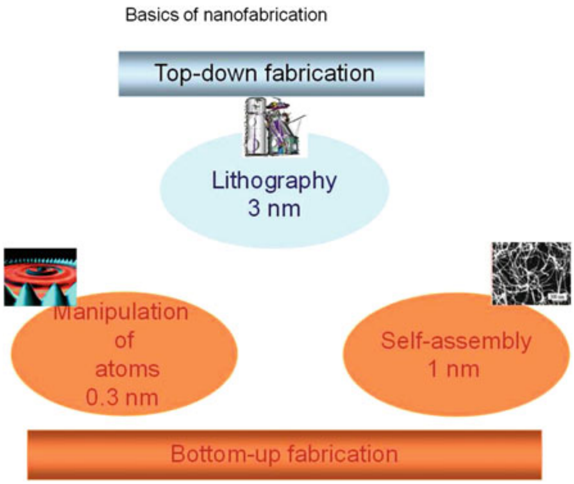


Fig. 4.3 Bottom-up fabrication of nanocomposite magnets. Image courtesy of P. Perlo Torino e-district, IFEVS—GENNESYS Barcelona conference 2010

Fig. 4.4 Schematic position of top-down and bottom-up fabrication mechanisms for nanoelectronics Image courtesy of IMEC (Belgium)



4.1.4 The Nanobulk Stage (10–15 years)

Where are we heading in terms of nanomaterial synthesis? Two stages will be followed as nanotechnology develops: the *"nanobulk"* stage and the *"nanoworld"* stage. They are conceptually different and reflect the two major paradigms of nanofabrication.

In the nanobulk stage, which has already begun and that is expected to further develop for 10–15 years, the benefits of nanomaterials will be exploited at the macroscale. In this stage, a nanomaterial is classified by its action at the human scale with novel properties determined by its nanoscopic internal structure.

To clarify this, let us review a few realistic examples of bulk nanomaterials:

1. Cosmetics containing nanoparticles are found on the market today;
2. In healthcare, nanoparticle suspensions or solutions can be injected into living tissues to help diagnostics or drug delivery;

3. Energy: large-scale nanostructured materials can enhance every type of surface- or interface-based chemical reaction, such as are important in energy generation, conversion, and storage;
4. Automotive/infrastructure: composite materials containing nano-objects with extraordinary mechanical properties can result in outstanding performance enabling for instance the application of novel coatings with unprecedented resistances.

From the implementation point of view, it is clear that the most important figure of merit for the above-mentioned applications is yield. If nanomaterials are to be implemented in macroscale applications, cost-effective mass production is essential. Important parameters will come into play such as uniformity, purity, toxicology, and stability. Today, applied research will try to target these requirements, with the aim of using relatively cheap and environment-friendly synthesis facilities.

However, solving specific issues and unveiling performance-limiting factors will call for a deep understanding of the chemical and physical processes involved in the fabrication. This is where basic research and characterization techniques come in. Even if the ultimate aim is producing trillions of nominally equivalent nanocomponents, the focus is put on the study of the synthesis of an *individual* nanocomponent, to understand how it is formed and how we can better control the process. What can occur during synthesis must be understood, including why two components may be nominally equivalent but not fully equivalent.

4.1.5 The Nanoworld Stage (15–40 years)

This paradigm no longer considers nanocomponents as all nominally equivalent, but aims to take advantage of the natural or induced diversity between nanoblocks. Different nanounits fabricated by the same technique may diversify to have different functions. Treating nanocomponents no longer as a mass but as individuals is obviously more challenging. It implies that the synthesis should have a very precise and independent degree of control over the structure of every single nano-object and/or the location where it is assembled or grown.

Technologically, the nanoworld stage is similar to the nanobulk one. However, basic and applied research now merge. The fabrication will no longer target mass production nor cheap strategies. The goal is to fabricate an "intelligent" nanoworld, without necessarily the driver of low cost. Precision will be more important than yield. Therefore, the facilities that only played a characterization and fundamental role for the nanobulk could become the only possible way toward applied synthesis with nanoscale deterministic control. A good example is 3D lithography that uses high-brilliance synchrotron light to guide the process during manufacturing.

The development framework for the nanobulk stage can be summarized by Fig. 4.5 which represents the traditional mode of innovation.

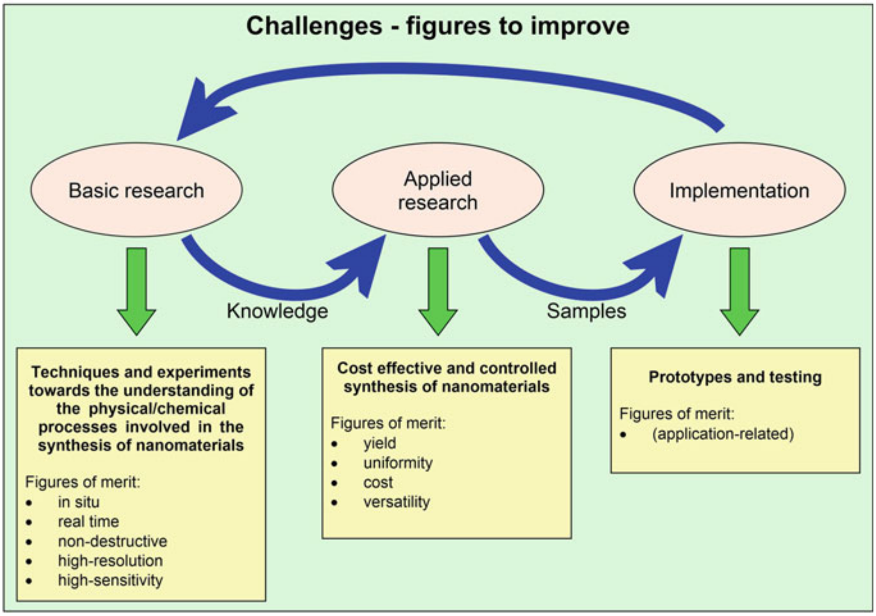
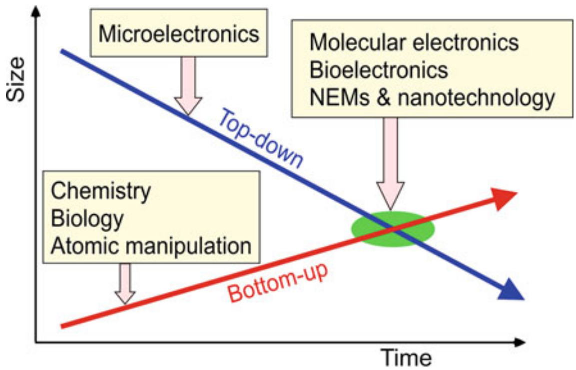


Fig. 4.5 Roadmap for improvements of nanotechnology

Fig. 4.6 Convergence from Top-down and Bottom-up approaches in the case of nanoelectronics



Top-down strategies already exist today and will continue to play an important role despite their intrinsic limitations. Bottom-up methods will drive the nanobulk stage and ultimately take over certain aspects of top-down processing via intelligent self-assembly. The history of nanosynthesis methods for electronic materials is shown in Fig. 4.6 as a function of a time showing a crossing point around 2010.

4.2 Nanostructuration

Nanomaterials are important because they can be used in many domains giving strategic assets to those who use and develop them. This point is, for example, pointed out by Eiji Kobayashi, from Panasonic, who says: "*Those who control materials control technology*." Scientists are now able to create a wide variety of building blocks that they assemble to make nanostructured materials. Using nanoscale building blocks allows us to have high surface areas, many interfaces and, in the case of nanostructures, size confinement (Fig. 4.7).

The nanostructuration of materials may lead to several changes of the properties of materials:

- A global change of the properties can be obtained. This is, for example, observed by including nanoparticles in a polymer material. Because there is a huge interface area between the nanoparticles and the polymer, an interaction between the two components takes place which modifies the properties of the bulk material. This happens for tires where carbon black is used to improve their properties, particularly their durability. This is also the case in cements. Concrete is a building material extensively used around the world. It is a low-cost and easy-to-manufacture material with good structural properties. However, it has a low resistance to tensile forces and is porous. A considerable improvement of its properties is obtained by adding silica smoke containing silica nanoparticles. Concrete with silica smoke is significantly less porous and less permeable to water, which is, for example, valuable when this material is in contact with sea water.
- Nanoparticles can also be used to introduce specific optical, magnetic, and catalytic properties. In many cases, it is the characteristics of the nanoparticles which are important and not the interaction with the inert matrix housing them, but interfaces between nanoparticles and host matrix or support can play an essential role, especially when charge transfer is involved: role of triple lines (or points) in nanocatalysts, role of surface states in luminescence.

Figures 4.8 and 4.9 show examples of the nanostructuration of platinum. In Fig. 4.8, the nanostructuration is done in the form of nanoparticles. The length of the horizontal figure is about 800 nm.

In Fig. 4.9, the nanostructuration of platinum is produced in the form of porous nanotubes, which could be used in catalysis. The green arrow indicates the oriented porous catalytic nanostructure. The length of the horizontal figure corresponds to about 7 μm.

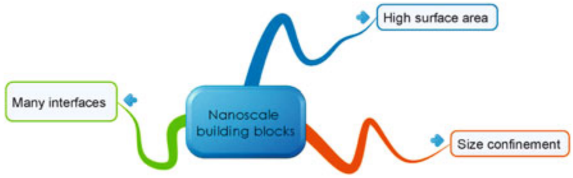


Fig. 4.7 Properties of nanoscale building blocks which will have tremendous consequences for nanostructured materials

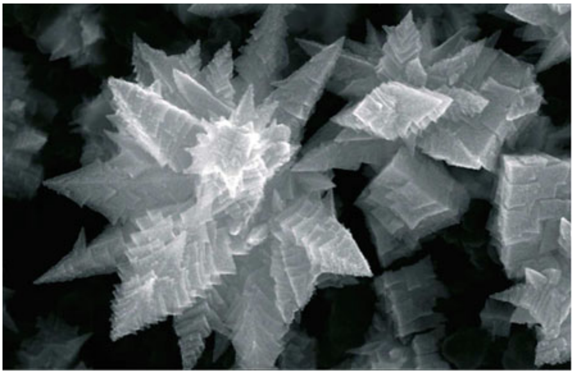


Fig. 4.8 Nanostructuration of platinum in the form of nanoparticles. Clef CEA n°59. Image courtesy of CEA/LETI (France). The results have been obtained by the CEA in the framework of a Challenge innovation program

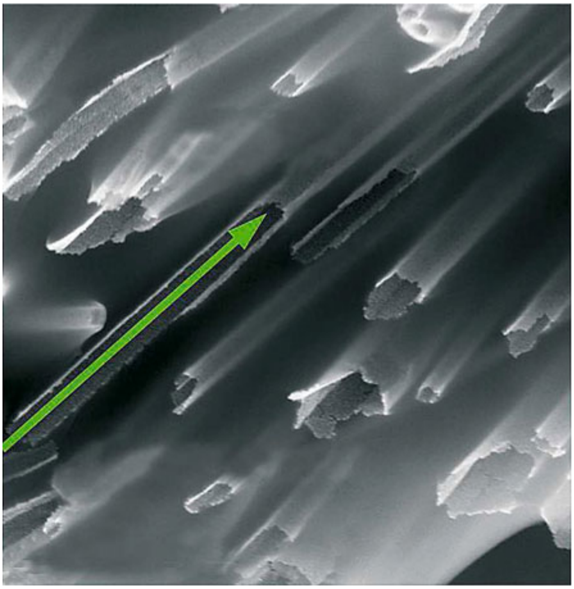


Fig. 4.9 Nanostructuration of platinum in the form of porous nanotubes. Clef CEA n°59. Image courtesy of CEA/LETI (France)

4.3 Classifying Nanostructured Materials

There are several ways to classify nanomaterials. This depends very much on the applications and philosophy, which are adopted. We shall just present here two extreme classifications, which can be found in the literature.

In the first one, the focus is done on the macroscopic dimensions of the material. Nanomaterials are then defined as materials containing structures having at least one dimension less than about 100 nm. According to this definition, a thin film (with a thickness less than 100 nm) is considered as a nanomaterial (Fig. 4.10) since one of the dimensions is nanometric. Thin films have been used for a long time, before there was any interest in "nanotechnology." If two dimensions are "nano," we have

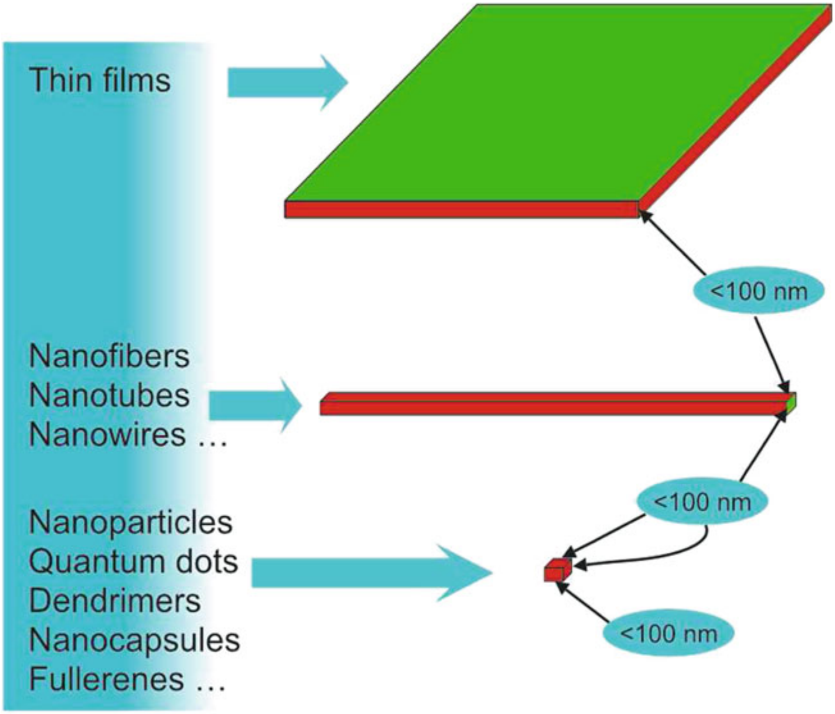


Fig. 4.10 Classification where 1D, 2D, and 3D objects have one, two, or three dimensions in the nanometer range

nanofibers, nanowires, etc., and if all three dimensions are "nano" we have quantum dots.

In this classification, there is no reference to the structure of the material.

Another classification, which might be more relevant as far as the nanostructure of a material is concerned, is to consider the dimensionality of the nanoscale component with which the material is made. A nanostructure is said to have one dimension, for example, if it has a length larger than 100 nm in one direction only. According to this definition, a nanoparticle is considered to have zero dimension (it has no dimension with a length larger than 100 nm). A wire or a fiber is a one-dimensional object and a thin film a two-dimensional nanostructure. To summarize, 0D nanomaterials contain spheres or clusters which are considered as point-like particles. One-dimensional nanomaterials contain nanofibers, wires, rods, etc., 2D use films, plates, multilayers, or networks. Three-dimensional nanomaterials are nanophase materials consisting of equiaxed nanometer-sized grains. This is shown schematically in Fig. 4.11.

Bulk nanomaterials are larger objects made from structures having well-identified domains with an average size less than 100 nm, for instance, the grain size in ceramics. For comparison, the diameter of a human hair is about 100,000 nm and the size of a single particle of smoke is around 1,000 nm.

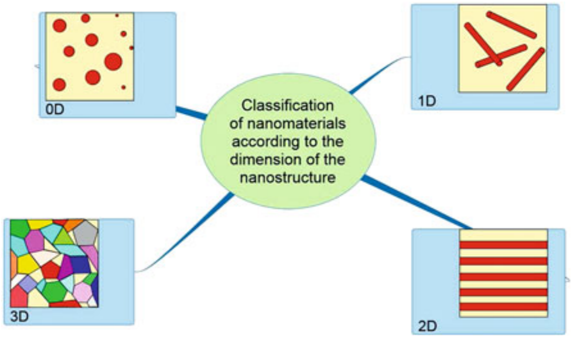


Fig. 4.11 Classification of materials according to the dimensionality of the nanostructures. 0D, 1D, 2D, and 3D nanostructured materials are sketched in this figure. In the 2D illustration, we have 2D layers embedded in the bulk and in the 3D crystallites or grains

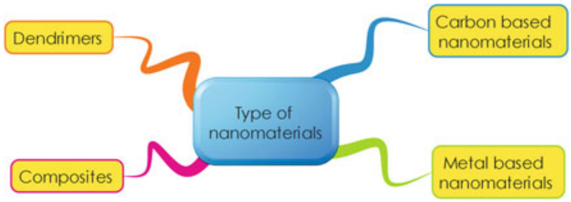


Fig. 4.12 Different types of nanomaterials according to their composition (see text)

It is also possible to classify nanomaterials in families reflecting their composition. This gives, as a possibility, the classification shown in Fig. 4.12. It is possible to distinguish the four types of nanomaterials as shown in Fig. 4.12.

Carbon-based nanomaterials are composed mostly of carbon. They play such an important role in applications as well as in the historical development of the nanotechnology domain that the next chapter will be completely devoted to them. This classification includes fullerenes, carbon nanotubes, graphene, and the like.

Metal-based nanomaterials are materials made of metallic nanoparticles like gold, silver, metal oxides, etc. For example, titanium dioxide (TiO_2) nanoparticles are extensively used in applications such as paint, sunscreen, and toothpaste.

Dendrimers are nanosized polymers built from branched units. They can be functionalized at the surface and can hide molecules in their cavities. A direct application of dendrimers is for drug delivery.

Composite nanomaterials contain a mixture of simple nanoparticles or compounds such as nanosized clays within a bulk material. The nanoparticles give better physical, mechanical, and/or chemical properties to the initial bulk material.

4.4 Nanostructured Materials

Nanostructured materials are materials with structures in the nanoscale range (1–100 nm). The properties of the nanostructured materials depend on the size and nature of their microstructure. If the characteristic length scale of the microstructure is comparable to the lengths associated with fundamental physical phenomena, large changes in the properties of the material compared to a nonnanostructured material can be observed. The whole structure—like for many materials—can be in or out of thermodynamic equilibrium. Using crystallites of nanometer size of elements like gold or sodium chloride, for instance, can produce a great variety of nanostructuration depending on the crystallographic orientation, the chemical composition of the mixture and the possibility to have nonequilibrium structures, which provides certain property advantages.

Nanoparticles are of course often used as building blocks to make nanostructured materials. They can be of various natures: fullerenes, nanotubes, nanocrystallites, nanofibers, etc. If the simplest building blocks of nanostructured nanomaterials are nanoparticles, more complicated elementary structures can be used as well, as in nanocomposites, for example.

Nanointermediates are the building blocks of nanostructured materials. Nanoparticles are the simplest objects we may think of from which to build nanomaterials. However, it is not always easy to align nanoparticles according to a given template by self-assembly. There are only few examples (mainly sulfides or selenides) combining with success soft templates, self-alignment of nanoparticles by dipolar interactions and oriented attachment resulting in 1D structures or hierarchical structures. Hard nanotemplates can be designed using different techniques such as electron lithography, for example, or anodization as for alumina membranes. Soft nanotemplates (such as mesophases and micellar systems) may also be used in the synthesis of nanoparticles with controlled size and shape, or mesoporous materials.

Films with a thickness less than 100 nm, supramolecular assemblies, dispersions of nanoparticles, etc., are nanointermediates currently used to improve different technologies such as solar cells, batteries, catalysts, and drug delivery systems.

Example of a nanostructured film

An illustration is shown in Fig. 4.13. The picture shows a transverse section observed with a transmission electron microscope of a nanostructured FeHf(NO) film. The horizontal length of Fig. 4.13 is about 750 nm. Ferromagnetic grains of a size between 5 and 10 nm are dispersed inside a high-resistivity amorphous matrix. The resulting nanostructured film has both high resistivity and high saturation magnetization value. These properties, obtained at the CEA, are interesting because they allow integrating this material in circuits close to inductive components, while minimizing parasitic capacities at high frequency operation (up to more than 2 GHz).

Nanostructured materials can be ordered into different families shown in Fig. 4.14. Fullerenes and carbon nanotubes will be treated in the next chapter.

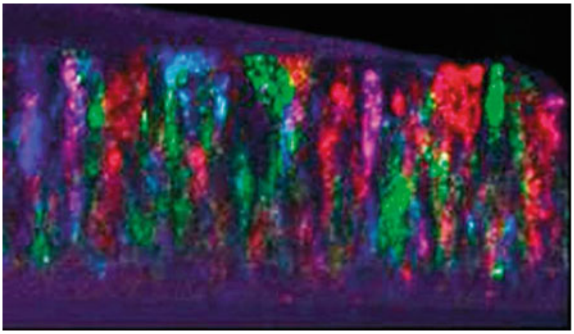


Fig. 4.13 Transverse view of a thin film of FeHf(N,O) nanostructured material. The ferromagnetic grains have a size between 5 and 10 nm, finely dispersed across a high-resistivity amorphous matrix. This gives the material a high permeability and a high resistivity. From clef CEA n°59. Image courtesy of CEA/LETI (France)

Fig. 4.14 Families of nanostructured materials

4.4.1 Nanocrystalline Materials

Nanocrystalline materials include metals or metal oxides like ceramics nanoparticles as building blocks. The building blocks are nanometer-sized crystallites. Nanocrystalline materials are inhomogeneous structures at the nanoscale. They differ from microstructurally homogeneous structures like gels. The atomic structure, the crystallographic orientation, and the chemical composition can be chosen to provide required macroscopic properties. Furthermore, a strategy can be used to assemble the building blocks, for example concerning the interface arrangement between the building blocks (such as the grain boundaries). The way the heterogeneous structure looks is an important issue regarding many of the properties of the nanostructured materials. Taking materials with the same chemical composition but of different structures, it turns out that nanostructured nanomaterials having a lot of grain boundaries at the nanoscale have their properties strongly modified compared to a single crystal structure or an amorphous structure-like glass.

A high density of grain boundaries, obtained during processing or by careful engineering, changes some of the properties of the bulk material, making it more valuable for many applications. The changes depend upon the size of the nanostructures and could for example lead to increased ductility of the material or a lower melting point. Because of the small dimensions involved at the interfaces, quantum effects can appear. Metal nanocrystalline materials are often used in heterogeneous catalysis.

4.4.2 Dendrimers

A dendrimer is a macromolecule made up of monomers, which assemble into a tree structure around a central core. It is a highly branched 3D structure offering a large surface functionality and versatility. Dendrimer comes from the Greek word "dendra" meaning a tree. Dendrimers are used in nanoparticle synthesis or they can encapsulate nanoparticles.

Dendrimers can be synthesized either by a divergent method or by a convergent method. In the divergent method, which is mostly used, the dendrimer grows outward from a multifunctional core molecule. In the first step, the core molecule reacts with a monomer molecule containing one reactive group and two dormant groups leading to a first-generation dendrimer. After activating the dormant group of the first step dendrimer, the monomer reacts again and a second-generation dendrimer is obtained. The process is repeated until the desired size is obtained and, at each step, a new layer is added. The divergent method allows the preparation of large quantities of dendrimers.

Dendrimer chemistry was introduced in 1978 by F. Vögtle and collaborators. The first family of dendrimers was synthesized in 1985 by D.A. Tomalia. The macromolecule has a spherical structure. Modern synthesis methods allow a precise control over the molecular design of the dendrimer. It is possible to tailor the size, the shape, the surface and interior chemical functionalization, the flexibility, and the topology of the dendrimer. Grafting new chemical functions onto the surface of the dendrimer is also possible.

In the simple divergent synthesis method schematically shown in Fig. 4.15, there is only one type of terminal group located at the surface of the dendrimer. However, more complex dendrimer structures can be synthesized. For example, different chemical bonding can be made at some generation steps in a divergent synthesis method, creating layer-block dendrimers (Fig. 4.16).

In the convergent method, the dendrimer is constructed by steps, starting from the end groups and progressing inward. When the branches are large enough, they are attached to the multifunctional core molecule.

Dendrimers can be used as nanocarriers in medical applications such as drug delivery, diagnostics, and tumor therapy. Their structure and synthesis can be tailored to fulfill specific applications.

Most synthesized dendrimers have a single function at their surface and they are generated with similar sequences. However, there also exist other kinds of dendrimers, called layer-blocks, where the chemical sequences between two generations can be different. These are mainly synthesized by the divergent method (left segment of Fig. 4.16). Using the convergent method, two types of complex dendrimer structures can be obtained. If part of the surface of the dendrimer has a different chemical function than the other, the dendrimer is called surface-block (central segment of Fig. 4.16). If some volume parts, starting from the core, are different, these are called segment-block dendrimers (right part of Fig. 4.16).

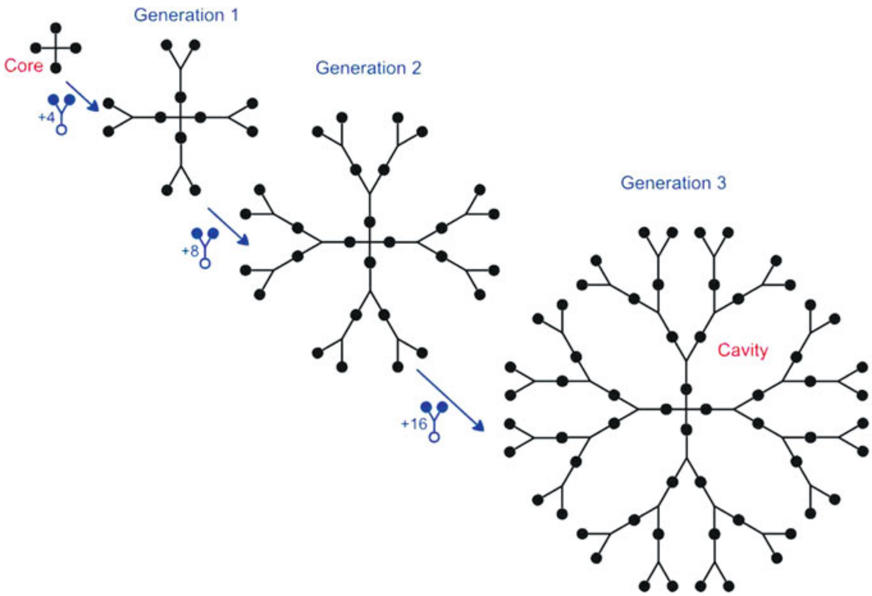


Fig. 4.15 Schematic synthesis of a dendrimer by the divergent method

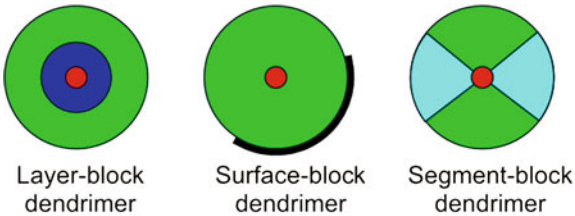


Fig. 4.16 There can be sophisticated architectures of dendrimers (see text). Blue and green colors correspond to two different generations in the building up of the dendrimer

4.4.3 Metal Organic Frameworks

Hybrid materials are interesting because they can have both the good physical properties of ceramics and the advantage of organic molecules in terms of reactivity and functionalization. There is great interest in hybrid materials containing silicon atoms in organic polymers such as polyhedral silsesquioxanes. The name of these structures comes from the fact that each silicon atom is bound to one and a half oxygen atoms. The global chemical formula reads $RSiO_{3/2}$, where R is either hydrogen or a hydrocarbon group. They can have a cage structure (from cubic or hexagonal to dodecagonal prisms) allowing placement of small molecules to be put inside.

These hybrid materials turn out to be interesting in electronics (low dielectric constant films) or photonics (light-emitting diodes).

They are also interesting as a support for catalysts for both homogeneous and heterogeneous systems. Chromium or vanadium metals can be used in catalysts. Silsesquioxanes can also be used in pH-sensors.

Silsesquioxanes can be functionalized to produce antimicrobial coatings. For example, quaternary ammonium salts can be used to make functionalized polyhedral oligomeric silsesquioxanes. Quaternary ammonium salts have the ability to kill bacteria and fungi while being harmless to humans and animals.

4.4.4 Nanocomposites

A nanocomposite is a material composed of several phases where at least one of the phases has one, two, or three dimensions less than 100 nm. It can also be made of nanostructures occurring in repeating units. Nanoparticles are often combined with bulk materials because they improve their properties.

Thanks to the presence of nanostructures in the bulk, the material may become stronger, have a higher ductility, be lighter, etc. The final properties depend on the process of manufacturing, of the nature of the nanostructure, and its arrangement within the bulk material. As mentioned earlier, carbon black nanoparticles are used in the rubber of tires. Besides the effect of making black-colored tires, this substance improves the strength and tensile properties, the tear and abrasion resistance and increases the hardness of the tire. The improvement from the reinforcement increases with the concentration of carbon black nanoparticles up to a certain point until it decreases. Many mechanisms are involved in this reinforcement but they are basically due to the interaction between the grains of black carbon and the rubber material. Another example is aluminum alloys were even parts-per-million (ppm) concentration of nanoimpurities drastically changes the properties of the initial material by increasing their strength and corrosion resistance.

Nanocomposite materials can be multilayer structures. There are several ways to make multilayers: by gas phase deposition, or from self-assembly of monolayers. In some cases, spinodal decomposition can be used to obtain multilayered structures in the bulk of mixed oxides ($TiO_2 - SnO_2$, for example). Magnetic multilayered materials used in storage media are an example of multilayer nanocomposites.

Polymer-clay nanocomposites also have successful applications today. They can improve significantly the properties of an initial polymer at low cost. For example, they are less flammable while maintaining good mechanical properties. This is not the case when flame-retardant additives to polymers are traditionally incorporated.

The size of the nanostructures incorporated into the nanocomposite may provide specific applications. For example, nanostructure sizes less than 5 nm are interesting for catalytic applications. Hard magnetic materials have nanostructures typically less than 20 nm. If the size of the nanostructures is less than 50 nm, nanocomposites show refractive index changes while if the size is less than 100 nm mechanical strengthening or superparamagnetism can be observed.

One can classify nanocomposites as organic, inorganic, or inorganic/organic. Inorganic/organic composites can be made by sol-gel techniques, by adding nanoparticles.

One can also classify nanocomposites as ceramic-matrix, metal-matrix, or polymer-matrix nanocomposites. Ceramic-matrix nanocomposites are materials where the ceramic (oxides, nitrides, silicides, etc.) is the main component. The second component can be a metal. These nanomaterials have improved optical, electrical, magnetic, and/or corrosion-resistance properties compared to traditional materials.

Metal-matrix nanocomposites are reinforced similarly to traditional metal-matrix composites using, for example, carbon nanotubes. Another application is the manufacture of superthermite (called also nanothermite) materials, which are highly energetic materials containing an oxidizer and a reducing agent. The explosive reaction proceeds much faster than in the case of thermite materials manufactured with microparticles. This kind of material has military applications as explosives or propellants and in pyrotechnics.

Chapter 5
New Forms of Carbon and New Opportunities

Carbon is an important chemical element found in simple and complex molecules of the living and nonliving world. Living systems are based on carbon and extremely complex structures can be found in nature. Organic chemistry, which is the chemistry of carbon, is a domain in its own right playing an important role in many fields. Until 1985, only three allotropes (forms) of carbon were known: amorphous carbon with no crystalline structure, graphite, and diamond. Since then, the situation has changed with recent discoveries showing the existence of other allotropes of carbon which were already existing in nature but remained unknown to scientists. They opened up a whole world of potential applications in the nanotechnology domain with some of them already available today.

5.1 New Forms of Carbon

Forms of carbon different from graphite and diamond were existing in nature and produced by humans long before they have been scientifically recognized. However, their identification and the study of their properties have opened a huge number of applications. We are at the beginning of exciting developments.

5.1.1 Buckyballs

Vaporization of graphite and condensation of its vapor in an atmosphere containing an inert gas produces clusters of different size. This was discovered in 1985 by F. Curl, H. Kroto, and R. Smalley assisted by their students. They were awarded the 1996 Nobel Prize in Chemistry for this discovery. Actually, such structures were predicted and observed by other scientists before, but not with such accuracy. Clusters made of 60 or 70 carbon atoms turned out to be unexpectedly stable. Each carbon atom is

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,

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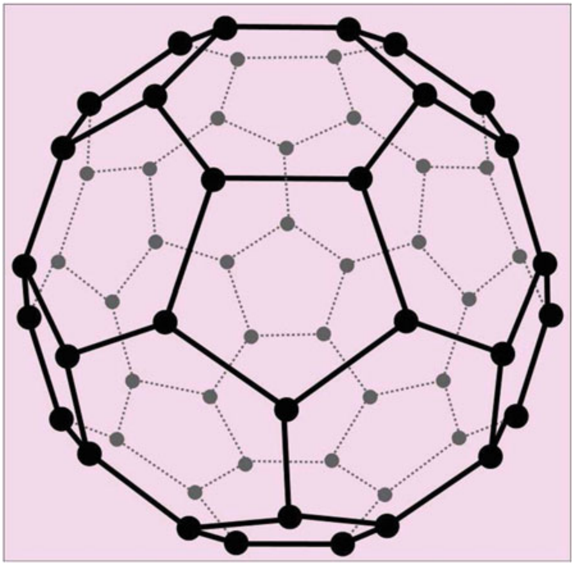


Fig. 5.1 Schematic representation of a C_{60} molecule. It is formed of 20 hexagons and 12 pentagons. Pentagons have no common edge

bounded to three neighboring carbon atoms by covalent bonds. C_{60} and C_{70} are new forms of carbon belonging to a larger family of carbon molecules called *fullerenes*. A fullerene is a molecule, containing only carbon atoms, having a hollow shape (sphere, ellipsoid, tube). This form of carbon was predicted in 1970 by E. Osawa. C_{60} was produced in sizeable quantities about 5 years after its discovery, by W. Kratschmer and D. Huffman, allowing detailed study of this new allotrope.

The C_{60} molecule looks like a soccer ball with 20 hexagons and 12 pentagons. It can be enclosed in a sphere of about 1 nm size. A carbon atom is located at the vertices of each polygon, and the chemical bonds between carbon atoms are directed along the edge of the polygons. Figure 5.1 shows a schematic representation of the C_{60} molecule. Note that in C_{60} there are no two pentagons with a common edge. Since this shape resembles the geodesic domes designed by the architect Buckminster Fuller for the 1967 Montreal world exhibition, it has been called *buckminsterfullerene*. Sometimes it is just called: a *buckyball*.

A fullerene is stable if the pentagons have no common edge. The general structure of a C_n fullerene is made of $(n-20)/2$ hexagons and 12 pentagons. The C_{60} molecule is the smallest molecule of this family. Other fullerenes have an even number of carbon atoms. For example, C_{70}, C_{76}, C_{78}, C_{82}, and C_{84} belong to this family as well. From spectroscopy and Euler's theorem C_{60} was found to have 32 faces.[1] Heavier fullerenes still have 12 pentagons but more than 20 hexagons.

[1] Around 1750, the mathematician Leonhard Euler published an important theorem about simple polyhedrons. This theorem, originated by Descartes in 1639, was rediscovered by Euler and published in 1758. It was proven by Legendre in 1794. In a polyhedron, the faces are polygonal. Applied to a C_{60}, it tells that there should be 12 pentagons and 20 hexagons.

An important chemical property of C_n fullerenes is that they can be tailored to fulfill a given application. Derivatives of C_n fullerenes with specific chemical groups functionalizing the C_n molecule can confer to the derivatives new properties such as making them hydrophilic (water-loving), more lipophilic (fat-loving) than the initial C_n molecule, or amphiphilic (both water-loving and fat-loving). Electronic and optical properties can also be changed.

5.1.2 Nanotubes

In the early 1990s, S. Iijima, looking carefully at the soot produced in a machine dedicated to C_{60} production, discovered new carbon structures: *nanotubes*. Although there were previous experimental indications of the existence of nanotubes, it was really only in the 1990s that scientists realized their important implications as far as applications are concerned. Indeed, 1952, carbon nanofilaments exhibiting an inner cavity had been observed with a transmission electron microscope. Furthermore, more than a century ago carbon nanofilaments, which were probably carbon nanotubes, were prepared by thermal cracking of hydrocarbons enhanced by a catalyst.

Carbon nanotubes are graphitic structures similar to tiny tubules of graphite. The cylindrical tubes are a few nanometers wide and have a length ranging from below a micrometer to several millimeters. The diameter of a carbon nanotube is about 10,000 times smaller than that of a human hair. Nanotubes belong to two main families which can be obtained from one or more sheets of graphene[2]:

1. A single-walled carbon nanotube is a graphene sheet wound on itself in a cylindrical manner, eventually closed at the end by a hemisphere (see Figs. 5.2 and 5.3). As mentioned above, graphene is a form of carbon whose structure is a one-atom thick sheet. Single-walled carbon nanotubes are often produced in tight bundles.

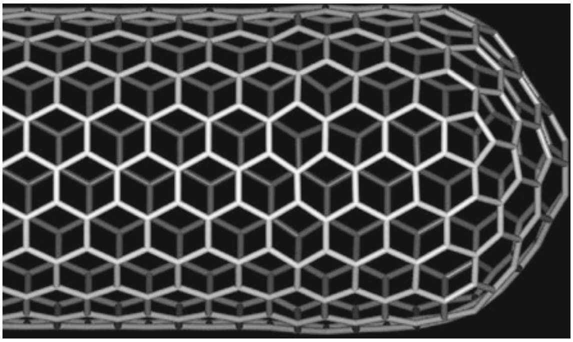


Fig. 5.2 Schematic picture of a closed single-wall carbon nanotube. Image courtesy of CEA/LETI (France)

[2] Graphene is a form of carbon consisting of a one-atom thick planar sheet of carbon atoms densely packed in a honeycomb crystal lattice. Details will be given in Sect. 5.1.3.

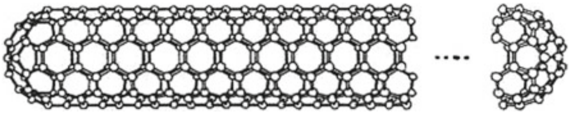


Fig. 5.3 Schematic drawing of a carbon nanotube obtained by rolling up a graphene sheet, closed at the two ends by half of a fullerene. Image courtesy of CEA/LETI (France)

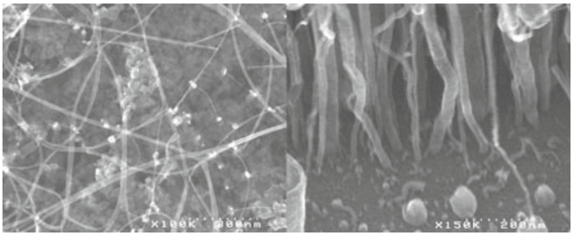


Fig. 5.4 Scanning electron microscope images of carbon nanotubes on a silicon substrate grown in a reactor at the CEA. The dotted line on each image shows the scale. Image courtesy of CEA/LETI (France)

2. Multiwalled carbon nanotubes consist of several concentric tubes of graphene. One may imagine two ways to build multiwalled carbon nanotubes. The first one is like a Russian doll where sheets are arranged in concentric cylinders, the other is like a parchment where a sheet is rolled as we roll a sheet of paper. The distance between two sheets is of the order of 0.34–0.36 nm, close to the distance separating two layers of carbon atoms in graphite. The diameters of multiwalled carbon nanotubes range between a few nanometers up to hundreds of nanometers, while their lengths range from hundreds of nanometers to tens of micrometers.

The ends (tips) of nanotubes can be open or closed. Because of the empty space inside nanotubes, they have a high storage capacity for some atoms or molecules. Other more complicated shapes also exist but we will not go into detail here.

There are many ways to produce nanotubes in bulk quantities. It can be done at high temperature using an electric arc, by laser ablation, or by using a solar beam. These high-temperature energy sources are used to sublime a graphitic rod placed in an inert atmosphere. There are also processes working at medium temperatures like catalytic chemical vapor deposition where nanotubes are produced from the pyrolysis of hydrocarbons. Figure 5.4 shows such a production.

Nanotubes can be considered as one-dimensional objects with a diameter in the nanometer range and lengths reaching several micrometers. They have outstanding mechanical properties. Their high tensile modulus makes them as stiff as diamond and their high strength makes them one of the strongest materials for fibers. The mechanical elastic modulus is about 1 TPa which is about 5 times that of steel. At room temperature, the thermal conductivity is 3,000 W/mK which is eight times larger than that of cooper and similar to the thermal conductivity of diamond.

Because their length is much larger than their diameter, carbon nanotubes can bend easily. These properties allow them to be used in combat jackets or in some extreme sports materials. It is necessary to refine carbon nanotubes because their mechanical properties vary according to their structure (single-walled, double-walled, or multiwalled).

Rolling up nanotubes

The way to build a nanotube from a sheet of graphene is not unique. A carbon nanotube is made by curling a graphene sheet in the same way as we can do with a sheet of paper. There are infinite ways of folding a graphene sheet into a nanotube resulting in a great number of carbon nanotube structures of different helicities. Because of this, carbon nanotubes can be classified in three main types: zigzag, armchair, and chiral , depending upon the way they are rolled up. Figure 5.5 gives a schematic view of this. The sheet can be rolled along one of its symmetry axes. In this case, one obtains either a zigzag or an armchair nanotube. In the other case, a chiral nanotube is obtained. The structure of a nanotube can be characterized by a vector whose components are (n, m) *in the frame of reference with the origin at (0, 0). The unit vectors (*$\mathbf{a}$ and $\mathbf{b}$*) are shown in brown in Fig. 5.5. The vector corresponding to* (n, m) *is just given by (*$n\mathbf{a} + m\mathbf{b}$*). Some points in the graphene plane are explicitly shown. A carbon tube characterized by* (n, m) *means that the sheet is rolled in such a way that the atom labeled (0, 0) is superimposed with the atom located at* (n, m)*. In the example of a zigzag structure shown in Fig. 5.5, the atoms located at (0, 0) and (7, 0) are superimposed. Actually, we have always (*$n$sl , 0) for a zigzag nanotube *and* $n = m$ *for an armchair nanotube. If we look along the symmetry axis of a nanotube, we see the arrangement shown in Fig. 5.6 for the zigzag and armchair configurations.*

The structure of a nanotube has a great influence on its electrical properties. If we characterize a nanotube by the indices (n, m) defined above, it turns out that if $n = m$ (armchair nanotube) the nanotube behaves like a metal. Other configurations are semiconducting with a bandgap inversely proportional to the radius of the nanotube. If *nm* is a multiple of 3, the nanotube is semiconducting but with a very small bandgap. There are, however, exceptions to this rule for nanotubes with a very small radius due to curvature effects and, for example, some nanotubes expected to be semiconducting can be metallic. Metallic nanotubes can, in theory, carry 1,000 times more current than copper. The presence of defects on the body of the nanotube can modify its electronic structure and some regions can have different electronic properties (semiconducting or metallic). This can be interesting because a single nanotube can work as a three-point junction. Furthermore, a component, such as a transistor, can possibly be made using a single nanotube.

5.1.3 Graphene

Graphene was first isolated by A. Geim and collaborators in 2004. Together with K. Novoselov, they were awarded the Nobel Prize 2010 for this discovery. Graphene is a two-dimensional honeycomb lattice and can be considered as an infinite two-dimensional aromatic molecule. Indeed, like benzene, which is a hexagonal

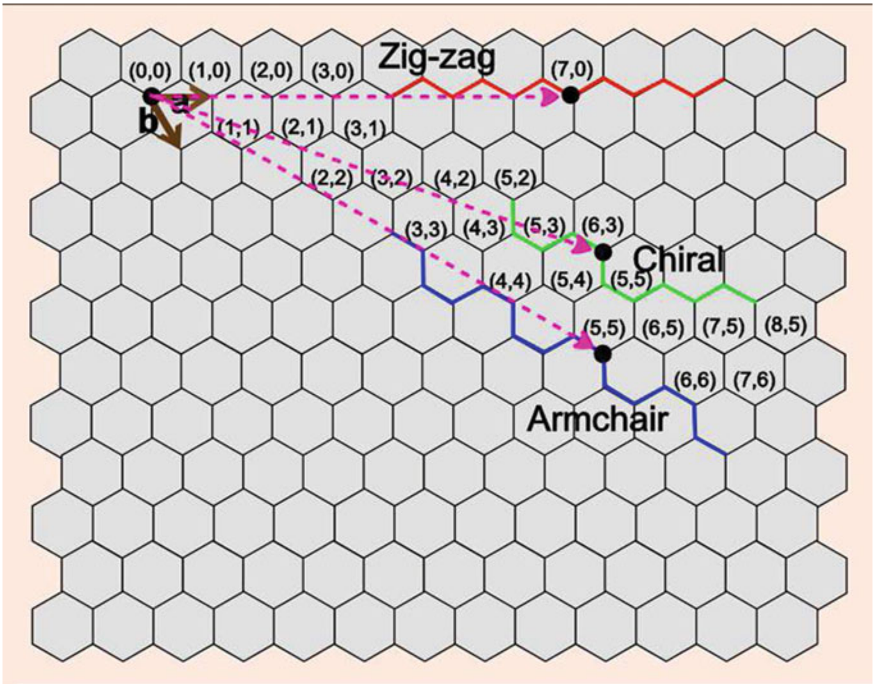


Fig. 5.5 Graphene plane from which a single-walled nanotube is formed by rolling up the sheet according to instructions given above

molecule where electrons are delocalized within the hexagonal cycle, graphene has delocalized electrons over the plane. The almost infinite nature of the two-dimensional plane gives special properties to these electrons which behave as if they have no mass. Electrons are not governed by the Schrödinger equation but by the Dirac equation because relativistic effects are important. This is so because the speed of electrons is only 300 times less than the speed of light in the vacuum. Because of the Pauli principle, electrons can travel large distances without being scattered. These new properties make graphene an interesting material for electronic applications.

Graphite, a well-known form of carbon, consists of a stack of graphene sheets with an interplanar spacing of 0.335 nm. The length of the carbon–carbon bond in graphene is about 0.14 nm.

Initially, graphene was obtained by mechanical rubbing off a layer of graphite, a process which cannot be easily scaled up for applications. However, great progress has been accomplished and roll-to-roll graphene can now be produced. Graphene can be obtained from SiC which is heated up to 1300 °C in vacuum. At this temperature, Si atoms evaporate and the carbon atoms that are left reorganize in graphene foils.

Although graphene has been discovered very recently, it is produced, without being aware of it, by many people using a pencil. Writing with a pencil "lead"

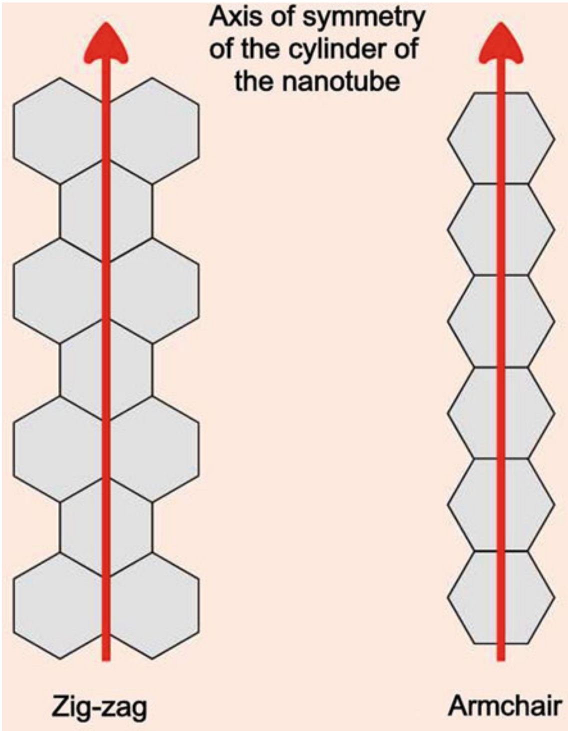


Fig. 5.6 Difference between zigzag and armchair forms of carbon nanotubes as seen by looking along the symmetry axis of the nanotube

separates the graphite of the pencil and is likely to create small graphene flakes on the sheet of paper.

5.2 Applications

Many applications of the new forms of carbon discovered recently are, possible today and many more will be available in the future.

5.2.1 Buckyballs

Fullerenes are interesting because they open the possibility for production of sophisticated engineered molecules for products tailored to specific applications. There are basically three types of engineering as summarized in Fig. 5.7.

In exohedral fullerenes, atoms, molecules, or complexes can be grafted outside the buckyball. Applications like hydrogen storage are possible. Endohedral fullerenes

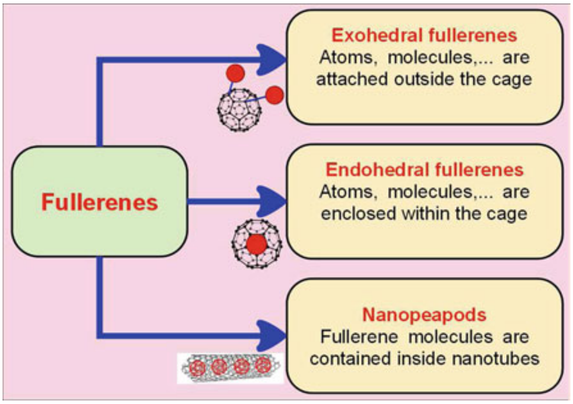


Fig. 5.7 Different types of engineering of fullerene molecules

have atoms, ions, or molecules enclosed within their inner volume; for example, transition metals can be put inside ("metallofullerenes") alone or together with nitrogen (trimetal nitride fullerene). This technology opens the way to magnetic applications. Nanopeapods are single-walled carbon nanotubes encapsulating buckyballs. The possible modulation of the electronic bandgap will make it possible for the design of new molecular electronic devices.

Derivatives of C_n buckyballs can confer to the initial C_n molecule specific properties needed in applications. As mentioned above, a derivative can be more soluble in water; others are designed to have the ability to dissolve fats, oils, etc. An example of a derivative is the [n]PCBM (Phenyl C_n Butyric Acid Methyl Ester) which is commercially available and used to develop organic solar cells. Organic field-effect transistors see their performances increased if they use, for the n-type semiconducting part, derivatives of fullerenes (C_{60}, C_{70} or C_{84}, for instance).

Fullerenes are strong antioxidants with the ability to quickly react and neutralize free radicals, which can cause damage or death to cells of living systems. They can also prevent oxidation and radical processes in several domains such as metal corrosion, plastics deterioration, or food spoilage. Research is also carried out in pharmaceutical industry to develop drugs against neurodegenerative diseases resulting from radical damage.

Fullerenes are also added to polymer structures to create new copolymers with specific mechanical properties. They can also be used in composite materials, especially as polymer additives to improve performances.

Many other potential applications of fullerenes exist related to the domains of catalysis, water purification, membranes, fuel cells, hydrogen storage, etc.

5.2.2 Carbon Nanotubes

Carbon nanotubes have great potential for applications in many fields: energy storage, composite nanomaterials, nanoelectronics, sensors, actuators, etc. Some of these will be addressed in subsequent chapters. It is a rapidly emerging field even though most of the current applications use bulk nanotubes consisting of unorganized pieces of nanotubes. Many developments are still at the laboratory scale but encouraging results have been obtained. Some current and potential application domains for nanotubes are displayed in Fig. 5.8 but many others are possible as well.

Carbon nanotubes have specific structural, mechanical, and electronic properties, interesting for many applications. Carbon nanotubes can often be considered as one-dimensional objects because their diameter is in the range of nanometers while their length is in the range of micrometers. This property makes it possible to generate huge electric fields at the tip of the nanotube. This can be exploited to make electron field emitters or gas breakdown sensors.

Single-walled nanotubes can be used as chemical or mechanical sensors. Their atomic structure can be formed by controlled wrapping of a stripe of single layer of graphite sheet (graphene). The direction of wrapping determines the properties of the nanotube which can have metallic or semiconducting properties. The carbon nanotube can be used as a nanowire connecting two metallic electrodes. Since the electronic properties of the nanowire strongly depend on its atomic structure, any

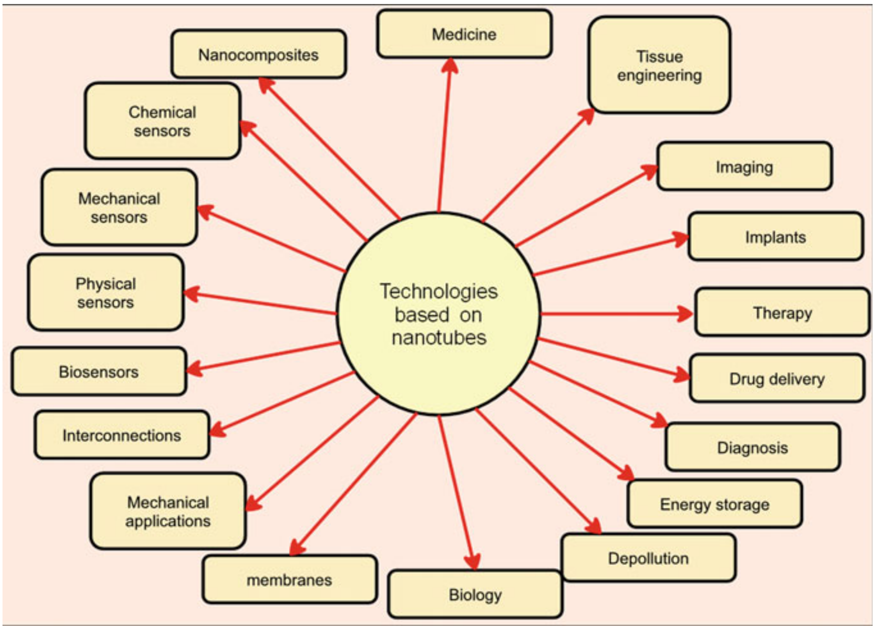


Fig. 5.8 Some actual and potential applications of carbon nanotubes

Fig. 5.9 Aligned carbon nanotubes after growth on a silicon wafer of 300 mm. This shows the output of the prototype reactor. Image courtesy of CEA/LETI (France)

mechanical deformation or chemical doping of the nanowire induces strong changes in the conductance. These changes can be detected and measured. The nice thing is the high sensitivity of this device with respect to mechanical or chemical perturbations. For example, the electrical conductance increases when exposed to NO_2 while it decreases when exposed to NH_3. A threshold detection of 20 ppm of NO_2 and 1 % of NH_3 have been reported by scientists. However, it has also a disadvantage as slightly different nanotubes give vastly different responses.

It is possible to manufacture self-supporting membranes of aligned nanotubes which will be subsequently used in various applications. They are produced by lift-off from a silicon wafer. Figure 5.9 shows the output of an experimental reactor: aligned carbon nanotubes have been produced on a 300 mm silicon wafer. Figure 5.10 shows the membrane of carbon nanotubes when silicon has been removed.

Carbon nanotubes are produced efficiently by the so-called vapor growth technique, where a gaseous source of carbon, such as methane, is decomposed in the presence of a growth promoter. The challenge is to produce carbon nanotubes

Fig. 5.10 Self-supporting carbon nanotube membrane obtained after removing the silicon wafer. It has a diameter of 300 mm and is obtained from the output shown in the Fig. 5.9. Image courtesy of CEA/LETI (France)

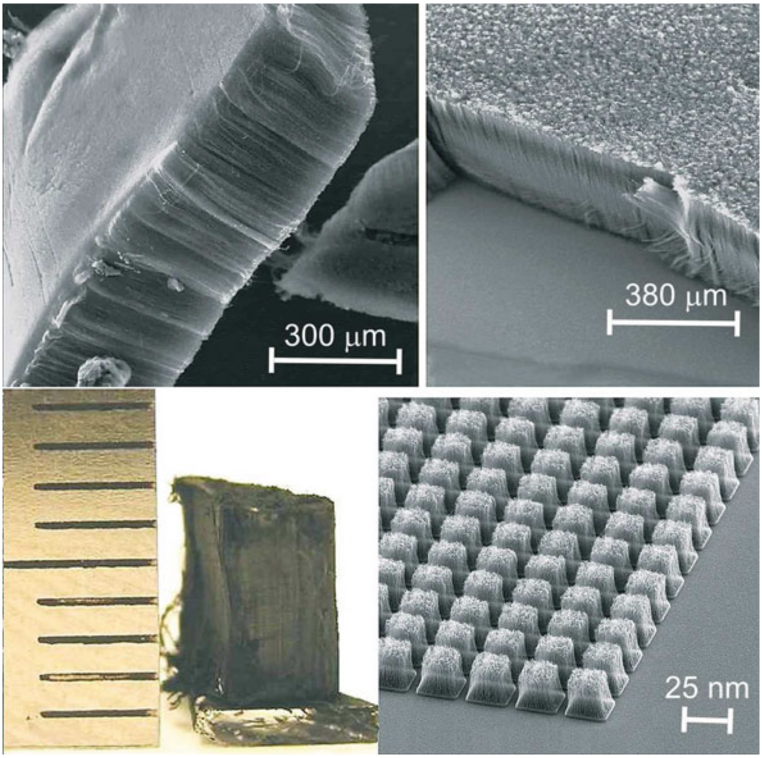


Fig. 5.11 Carbon nanotube forests. *Top left* a monolayer forest. *Top right* a multilayer forest. *Bottom left* forest of ultralong (>5 mm) nanotubes. *Bottom right* a forest featuring controlled localized growth. Image courtesy of CEA/LETI (France)

with preplanned physical properties by controlling the number of walls of the nanotubes, their diameter, defects, chirality, etc., in order to produce specific electrical properties.

Figure 5.11 shows an example of a carbon nanotube forest obtained in the CEA laboratories. Nanotubes have grown perpendicular to the substrate like trees in a forest. These structures can be used to make high-performance electrical wires. They can also be used as pores of a membrane dedicated to water filtration. Another application of nanotubes is as emission tips in portable X-ray generators.

The nanometer size of carbon nanotubes allows them potentially to interact at the cellular or molecular level. They can be functionalized to increase their biocompatibility, for example. This flexibility allows development of biomedical applications such as cellular imaging, chemical or biological sensing, drug delivery, and tissue engineering. Nanobiosensors allow rapid and real-time tests which are sometimes an advantage compared to more accurate but slower traditional techniques. Demonstrations at the laboratory level have been performed in several cases. Glucose biosensors of high sensitivity, high selectivity, and low detection limit based on amperometric methods, using a carbon nanotube electrode modified with platinum nanoparticles, have been developed and cholesterol in blood can be monitored with carbon nanotube modified biosensors.

Searching out and destroying cancer cells

Functional carbon nanotubes have been developed in US laboratories to detect and destroy an aggressive form of breast cancer. Studies have been performed so far with almost 100 % success on laboratory cell cultures. Experiments on animals have commenced and there is great hope that this method could be applied to humans in the future. HER2 is a protein expressed by a gene belonging to a family that regulates the growth and proliferation of human cells. It turns out that in about 20–30 % of breast cancers there is an overproduction of HER2 due to gene mutation. These breast cancers, which are called HER2-positive, grow faster and are more aggressive than other types of breast cancers. They are less responsive to chemotherapy or hormone treatment. About 40,000 women are diagnosed each year in the United Sates with this form of breast cancer. US scientists have attached to short carbon nanotubes an anti-HER2 antibody. The antibody was derived from chicken and not from humans. The reason for this choice is that the antibody produced in this way reacts strongly with the protein expressed on tumor cells and ignores normal cells. Detection and destruction is performed using a near-infrared laser. At 785 nm the laser light reflects strongly from nanotubes and can be detected using Raman spectroscopy. After detection of the nanotubes, a 808 nm light beam obtained by increasing the wavelength of the laser is strongly absorbed by the nanotubes. The power of the laser light is such that the carbon nanotubes are incinerated and the cancer cell to which the nanotube is attached is destroyed at the same time. Similar way of treating cancer is used with metal gold nanoparticles and optical tweezers.

5.2.3 Graphene

Graphene is a single atomic layer with many potential applications thanks to its remarkable electrical and mechanical properties (Fig. 5.12). It is now possible to produce large areas of graphene and it has been shown, on prototype displays, that it can be used as transparent conducting electrodes. This is particularly interesting since these electrodes are today made with indium tin oxide and indium is a metal that will become scarce and expensive in the future.

As far as electronics is concerned, graphene has the advantage, compared to carbon nanotubes, of being planar and is potentially a good substrate for integrated electronics. It can carry high currents, and has an excellent thermal conductivity and good mechanical strength. In earlier methods, graphene was exfoliated from graphite and deposited on SiO_2. Attempts to use graphene in field transistors have not been successful because graphene is a zero bandgap semiconductor; However, by doping graphene, it is possible to open the gap by doping and this is a field in progress. There are presently basically three routes for graphene doping: hetero atom doping, chemical doping, or electrostatic field tuning. This may open in the future possible applications in circuits beyond conventional CMOS technology.

The properties of graphene are well suited for high-frequency analog applications such as wireless communications, radar, imaging, etc. For example, cutoff frequencies of about 100 GHz have been obtained by IBM with radio frequency (RF) graphene transistors. This is 2.5 times better than with conventional transistors using Si-CMOS technology. In a near future, it will probably be possible to produce cheaper graphene foils thanks to simpler technologies. In this case, they will become

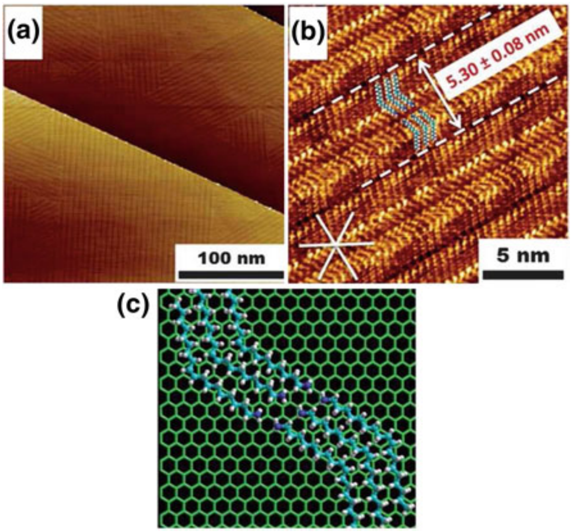


Fig. 5.12 Experiment to tune the electronic properties of graphene. Image courtesy of IMEC (Belgium)

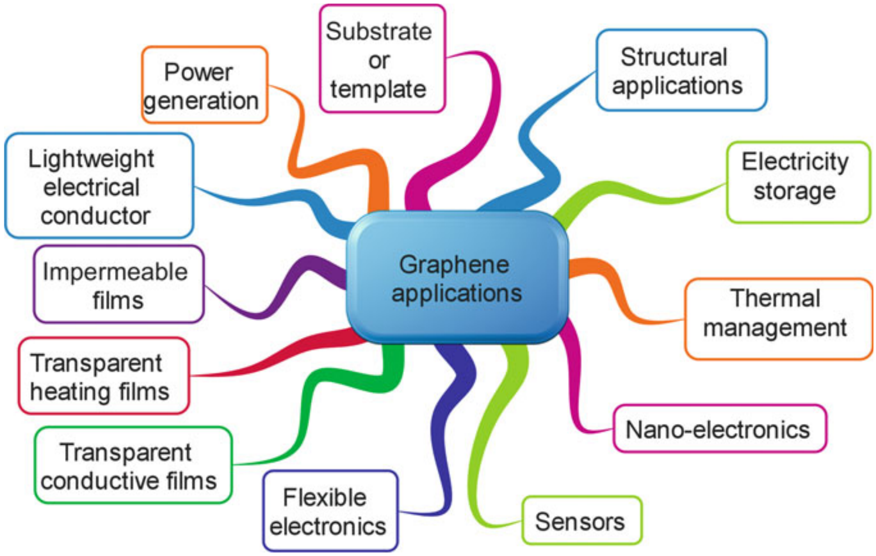


Fig. 5.13 Some domain of application of graphene, among others, as shown. Inspired from a 2011 presentation of R. S. Ruoff, http://bucky-central.me.utexas.edu

more competitive than the III-V semiconductor technologies used today in these applications.

Graphene, thanks to its exceptional transport properties of charge carriers and to its strong optical absorption, is also interesting in optoelectronics for photodetection and perhaps, in the future, as a THz radiation emitter.

It is important to improve graphene manufacturing. Growth techniques where the thickness, defects, and impurities can be controlled, are still needed before commercial applications are available, but it should be noted that it is a very new domain that is developing rapidly. Many applications in various domains can be envisioned. Some of them are shown in Fig. 5.13.

Chapter 6
Nanoengineering for Material Technology

Structural, Functional, and Biomaterials

In this chapter, we return to nanomaterials and focus attention on different applications. Materials are at the heart of all industrial endeavor, and even in those sectors where nanoengineering has been a goal for many decades, new processing and characterization methods will provide advancements that will lead to new applications and products. Figure 6.1 shows one example of applications in the aerospace industry.

One of the key areas for nanotechnological advance is in the optimization of the properties of materials through engineering at the nanoscale. Because of the ubiquity of materials throughout engineering, nanotechnologies that seek to enhance material properties truly span all industrial and commercial sectors, encompassing a market of several billion euros per year. They may be developed and selected for their high strength, their self-healing properties, biocompatibility, or the ability to provide a suite of properties not available in a conventional material. For example, the size, constitution, and shape of dissolved nanoparticles made from noble metals and metal oxides determine the color of the solution (Fig. 6.2).

Nanomaterials can be classified into different types depending on where in their structure and properties the benefits of the nanoscale are employed:

- materials and devices with reduced dimensionality such as nanometer-sized particles, thin wires, and microelectromechanical systems;
- materials and/or devices in which the nanostructured region is limited to a tailored localized surface region of a bulk material;
- bulk solids with a nanometre-scaled structure throughout.

Figure 6.3 gives an overview of nanomaterials which, as far as applications are concerned, can be roughly be classified into structural materials, functional materials, and biomaterials.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_6,

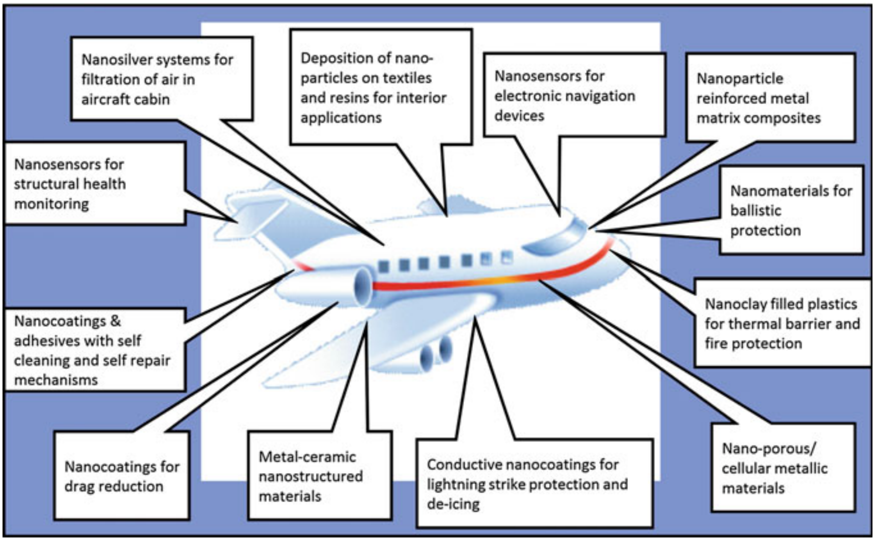


Fig. 6.1 Applications of nanotechnology in the aircraft sector. Image courtesy of IoN, UK

Fig. 6.2 Dissolved nanoparticles from noble metals show different colors depending on the size. Image courtesy of IMEC

6.1 Structural Nanomaterials

Nowadays the majority of structural materials have reached a high degree of scientific and technical maturity. For worthwhile future developments of structural materials so that they surpass conventional technologies in performance and cost, it is necessary to be able to predict and exploit the materials properties of complex nanoscale structures; control microstructural refinement during processing at the nanoscale; and understand and control damage accumulation and failure mechanisms in nanostructured materials.

Nanomaterials exhibit properties that differ extensively from those of conventional materials. They can utilize ultrafine grain sizes to achieve very high strength, or have a unique nanostructure that "self-heals" damage caused in service. Figure 6.4 gives an overview of the different classes of structural nanomaterials.

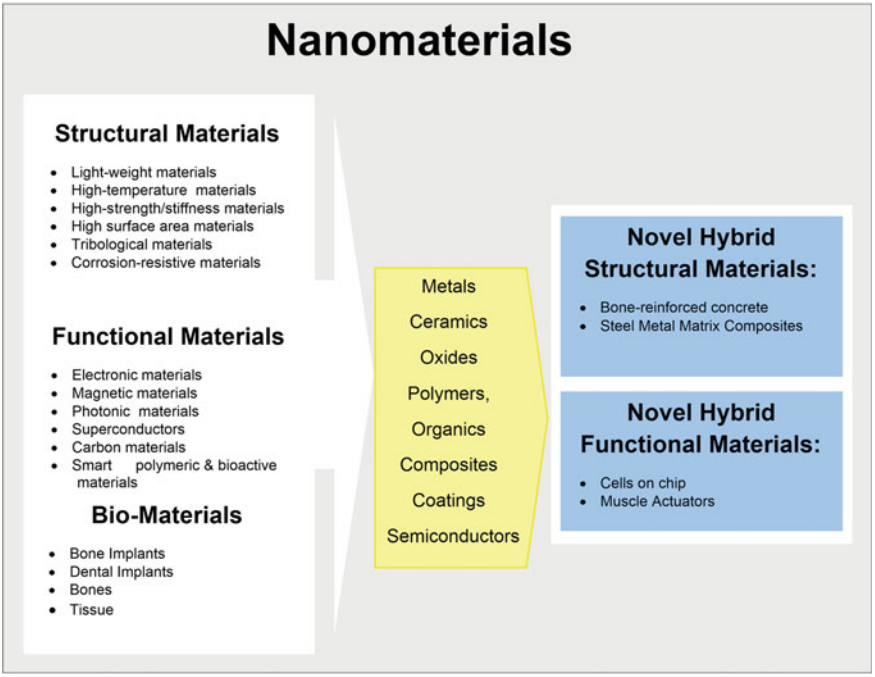


Fig. 6.3 Overview of nanomaterials

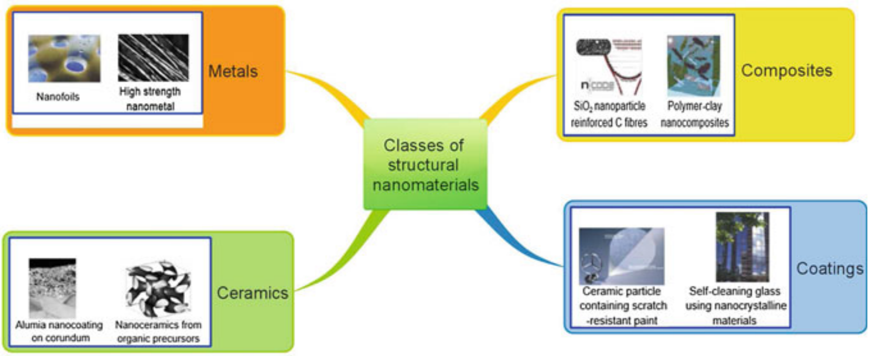


Fig. 6.4 Overview of structural nanomaterials: metals, ceramics, polymers, composites. Inspired from GENNESYS white paper, http://www.mpi-stuttgart-mpg.de, H. Dosch and M.H. Van de Voorde (2009)

6.1.1 Metallic Materials

Many conventional metal alloys are already dependent on what is essentially a nanoscale structure: the village blacksmith in the seventeenth century was engineering his iron at the nanoscale, but with craft skills rather than technical know-how. Metals based on nanostructuring can offer a range of advantages: a promising candidate material for future nuclear fission and fusion applications is oxide dispersion strengthened (ODS) steel where a nanoscale dispersion of oxide particles provides resistance to high-temperature deformation and irradiation embrittlement.

Nanoscale phases incorporated in bulk materials can exhibit remarkable properties, such as enhanced magnetism, mechanical strength, high-temperature tolerance or ultralight weight. Applications exploiting nanoscale precipitates include structural components for high strength, magnets in motors and transformers, filters, and wires. A finer microstructure gives metals with improved strength and toughness. The goal is to make the individual metal crystallites smaller than carbon nanotubes about tenth of a billionth of a meter in size. Material like this is now used for Channel Tunnel railway rails. The main challenge is to enable the production of bulk quantities on an industrial scale.

Steel with a tensile strength of 2500 MPa, more than twice that of conventional high strength grades, has been developed by creating a fine structure of a phase called bainite. Slender plates of ferrite are formed inside the material, just 20–40 nm thick giving rise to the extraordinary properties.

Nanocorrosion/erosion protection of metallic materials can be realized via a sol-gel technique: by spraying and subsequent thermal curing in a furnace. A dense and very durable layer is established with a thickness of about 5 microns (μm), as compared to several 100 μm for conventional protective layers. The property of the thin layers leading to a good adhesion to the metal and the surface is water repellent (hydrophobic).

6.1.2 Ceramic Materials

There is a great scope for tailoring of the properties of ceramics through nanoscale engineering. Ceramics can be produced with zero defects to allow full benefit to be obtained from their very high strengths and temperature resistance. Processing control is extremely important, and whilst nano-enabled ceramic processing may not have the goal of producing a final "nanomaterial," but there is a critical nanodependent stage in achieving the desired result.

One approach toward designing tougher ceramics is the intelligent use of nanostructural interfaces, such as employed by nature in sea shells. The shells of some molluscs, like those of clams or snails, cannot easily be cracked. Mother-of-pearl (or nacre) is an extremely fracture resistant material even though it is composed from aragonite, a calcium compound, which is itself extremely brittle. The trick lies in

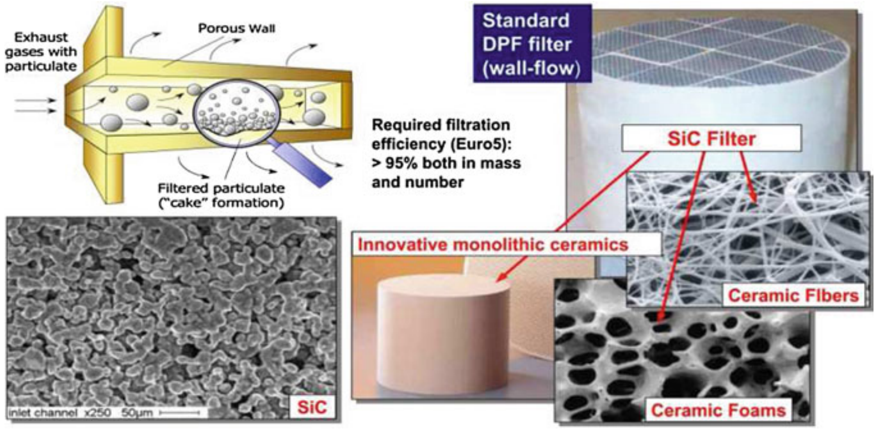


Fig. 6.5 Nanoceramics in diesel filters for exhaust gases. Image courtesy of P. Perlo Torino e-district, IFEVS—GENNESYS Barcelona conference 2010

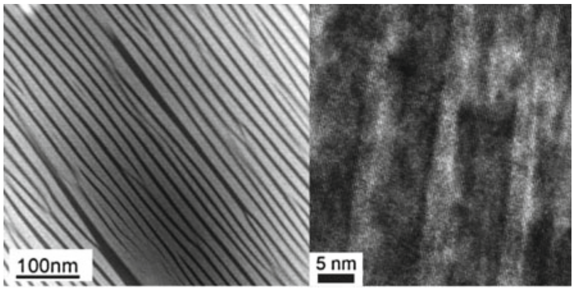


Fig. 6.6 Multilayered Ti-rich/Sn-rich oxides with coherent interfaces parallel rutile (001) planes. Image courtesy to Ecole des Mines, Paris

the special structure of the shell with micrometer-sized aragonite platelets assembled like bricks. These bricks are connected by a nanomortar from helical, highly elastic proteins. Just 3 % by weight of this protein filler increases the toughness of an abalone shell by a factor of 3,000 as compared to a pure limestone crystal.

Another example of a nanoceramic component is the diesel particle filter in the catalytic conversion of exhaust gases; see Fig. 6.5.

During cooling, some solid solutions may lead spontaneously to bulk dense nanostructured ceramics, either by nucleation or by spinodal decomposition. A well-known system is $Ti_xSn_{(1-x)}O_2$ with compositions around $x = 0.5$: after spinodal decomposition, dense ceramics exhibit large domains with alternate Ti-rich/Sn-rich oxide nanolayers with coherent interphases (Fig. 6.6). This nanostructuration lowers the thermal conductivity by phonon scattering at the interfaces, which could be interesting for new thermoelectric materials.

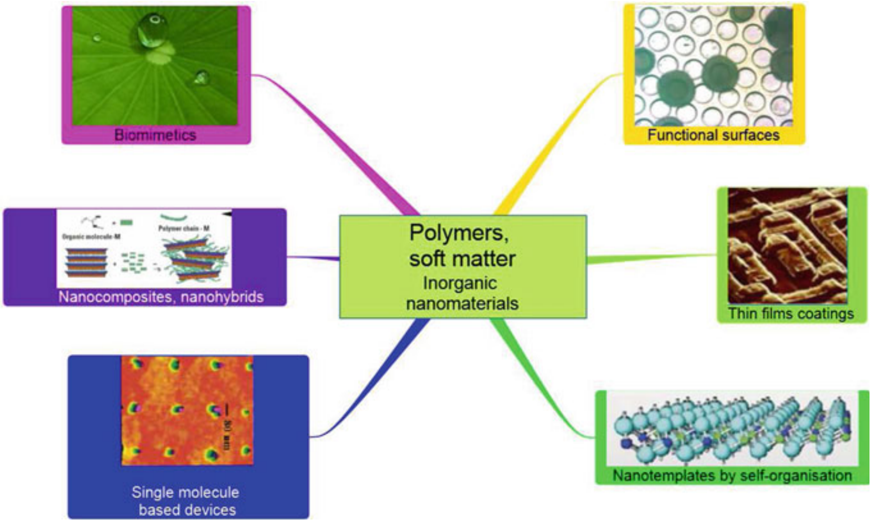


Fig. 6.7 Use of polymers in the design of nanomaterials

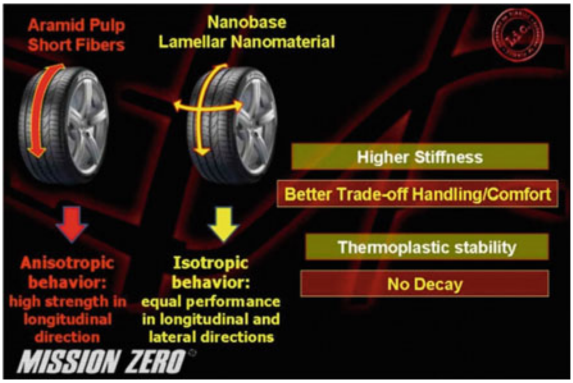


Fig. 6.8 L. Giannini–Pirelli Tyre S.p.A.—Nanorubber-tyres for automobile application—Pirelli experience—ANFIA Torino April 2010. Image courtesy of P. Perlo, Torino e-district, IFEVS—GENNESYS, Barcelona conference, 2010

6.1.3 Polymers

Moving on to polymers (Fig. 6.7) all synthetic polymers and biopolymers are by their nature nanostructured materials, giving rise, depending on their chemical chain microstructure and their processing, to an amazing variety of properties and applications. Structural control at the nanoscale level is the key to inducing the desired properties for polymers for applications ranging from bulk structural materials to biomedical, electronic, photonic, display, and biomimetic materials.

Moreover, the addition of nanoparticles to materials may electrically modify the viscosity of liquids, or change the properties and behavior of tires: see Fig. 6.8.

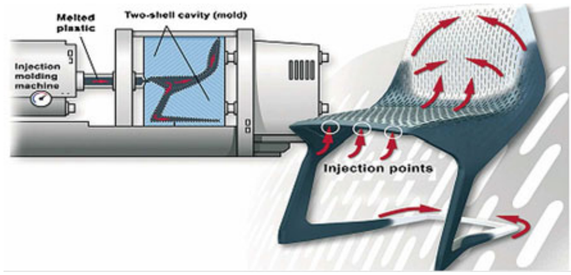


Fig. 6.9 How nanostructures change the flow properties. Image courtesy of BASF Ludwigshafen

The effect of nanoparticles can strongly influence the flow behavior in polymers chemical engineering; the manufacturing of a chair is represented in Fig. 6.9. The MYTO chair is produced from “Ultradur High Speed” an easy-flowing plastic that fills the mould completely, solidifies on cooling and is then removed from the mould.

The innovation lies in the selective nanostructuring of polymer liquids. The challenge is to develop specific mixing processes so that a nanometer-sized structure can be obtained. The viscosity of the plastic melt—as well as the flow temperature—is then drastically reduced and consequently the flow properties of the plastic profoundly modified which enables many new applications.

6.1.4 Nanostructured Hybrid Organic–Inorganic Materials

Nanostructured hybrid organic/inorganic materials play an important role for a variety of applications including catalysis, selective separation and purification, chemical and biological sensing, and optical communications. This family of materials includes dispersions of inorganic nanoparticles in polymer matrices, porous metal organic framework materials (MOFs), and the inclusion of organic macromolecules into mesoporous oxides such as silicas. MOFs are in most cases crystalline solids with one-, two-, or three-dimensional porous networks with pore dimensions from 1 to 5 nm. The materials show high thermal stability (up to 500 °C) and have potential applications as adsorbents, molecular sieves, and catalysts.

6.1.5 Engineering with Nanostructural Materials

Engineering with nanomaterials is still in its infancy compared with the revolutionary developments already made in nanoelectronics. The focus has been on improving existing materials by simply adding nanoparticles or substances, or to extend the microstructure to submicron and nanostructures.

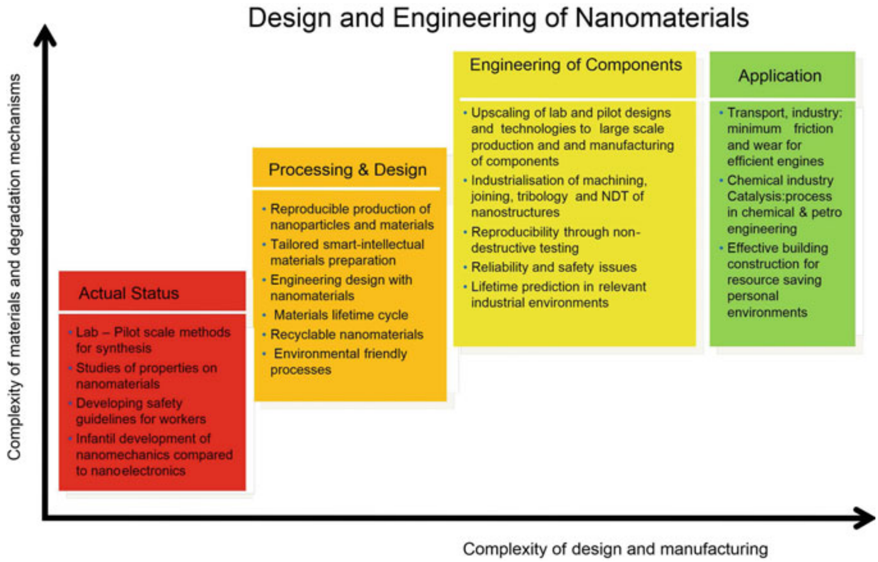


Fig. 6.10 Principles in designs with structural nanomaterials

Nanomaterials in mechanical applications are mainly limited to applications coming from nanoelectronics or photonics technologies such as sensors in cars, and coatings in self-cleaning windows. Properties of nanomaterials as well as relevant measuring equipment and methodologies are developed. Limited work has been done in the fields of nanomachining, joining, nondestructive testing (NDT) or designing with nanomaterials: including reliability studies and lifetime predictions. The next decade will certainly bring revolutionary developments in structural design and manufacture with nanomaterials and nanotechnologies in machine constructions, engine designs, and applications in aeronautics, automotive, building construction, petroleum, and chemical engineering (Fig. 6.10).

6.2 Functional Nanomaterials

Functional materials (Fig. 6.11) have additional performance characteristics beyond or apart from any structural capability. This can cover a wide range of functions such as catalysis, absorption, chemical sensing, and electrochemical behavior. An important subset of functional materials is the so-called "smart" materials: materials that can adapt or respond to their environment.

Moving into the nanometer regime offers exciting opportunities far beyond simple scaling of size, because new phenomena occur at the nanoscale that are not present in conventional bulk materials. Nanotubes, nanorods, and nanowires are exciting

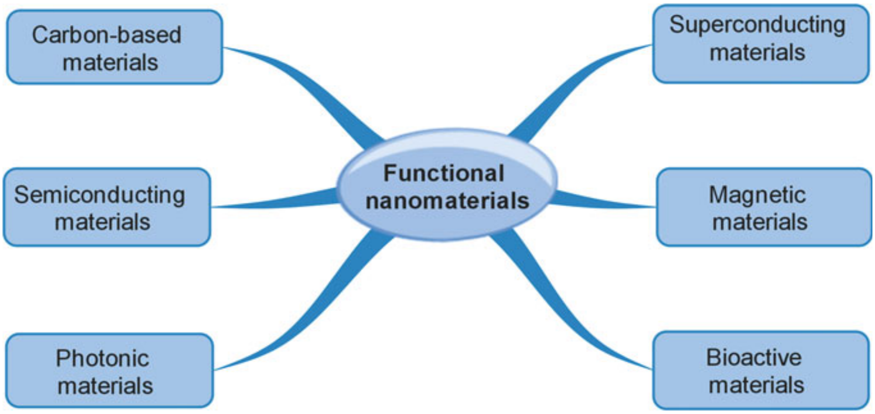


Fig. 6.11 Overview of functional nanomaterials

additions to the range of functional nanomaterials, for applications as diverse as sensors, actuators, transistors for molecular computers, flat display devices, hydrogen storage for fuel cells, photovoltaic cells, and water purification.

A novel discovery is that the behavior of polymer chains in confined space is completely different from bulk behavior: hence a completely new field of research has emerged to probe the nanostructures of synthetic polymers and biopolymers under confinement in nanolayers, nanodroplets, nanotubes, nanoporous systems, and microfluidic systems. This will lead to the development of protective coatings, reactive coatings, adhesives, membranes mimicking biological systems, and catalytic systems.

It is expected that long-term developments will focus on materials that can fulfill several functions, *multifunctional materials*. For example, a material with sensing properties that will also be able to adjust its properties: perhaps a smart drug-release patch that will alter the drug dose depending on a sensing of the chemical environment of the skin.

6.2.1 Hybrid Organic–Inorganic Nanomaterials

Hybridized organic/inorganic nanomaterials and plastic electronic materials could give rise to new electronic and photonic devices that will form the basis of next generation technologies and components such as printed electronics, transistors, energy generation devices, and photovoltaic. The majority of these concepts require novel process development to enable cost-effective manufacture. These materials and the processes suffer from measurement issues which are very different and much more challenging than for conventional electronics.

6.2.2 Nanostructured Composites

A nanocomposite material is a solid multiphase material where at least one phase has dimensions of less than 100 nm. Nanocomposites can exhibit properties superior to conventional composites, such as higher strength, stiffness, electrical conductivity, thermal, and chemical resistance. They can have unique properties like tuneable biodegradability, using nanofillers from agro-industrial waste to sea-grasses. Potential and prototype products include polymer heat exchangers, turbine components, self-cleaning industrial furnaces, biomolecular drug delivery materials, and materials for tissue engineering and gene-based medicines.

In most cases a nanoscale filler material such as clay, carbon black, carbon nanotubes or nanohorns, silicon carbide, or graphene is embedded in a matrix material to form the composite. The matrix materials could be a polymer, ceramic, metal or biological material. Nanocomposites offer particular advantages in efficient use of the second phase: the filler greatly enhances the properties of the materials. This is especially true for nanoparticles, as using smaller particles greatly increases the surface area, which has advantages in applications where interfaces impact on the desired properties.

The intercalation of a polymer into silicate interlayers increases the active surface area of the filler. In addition, polymer chains confined between silicate layers are immobilized, and so intercalation increases the effective volume of the filler.

The automotive industry has begun to take advantage of the properties offered by nanocomposites, such as conductive nanopolymer composites reinforced with carbon nanotubes. Nanocomposites offer the possibility for automotive and aircraft industries to significantly reduce the weight of mechanical and electric components. Carbon nanotubes as fillers of epoxy resins have potential for use in automotive fuel system components and body parts. Nanocomposites can replace steel in some applications, including exterior body panels and suspensions. They can also be engineered to have much higher fire retardant properties than conventional materials, by using nanoscale ceramic fillers, making them attractive for applications in vehicle interiors. Organoclays nanocomposites have potentials for example in automotive applications (see Fig. 6.12).

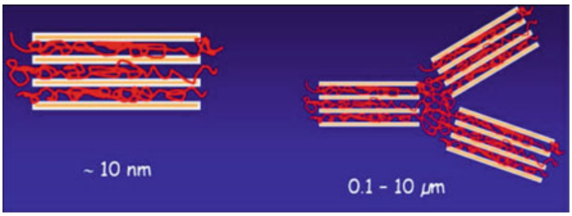


Fig. 6.12 Rubber clay nanocomposite reinforced rubber compounds for tire applications. Image courtesy to L. Giannini–Pirelli Tyre S.p.A. Image courtesy of P. Perlo Torino e-district, IFEVS—GENNESYS Barcelona conference 2010

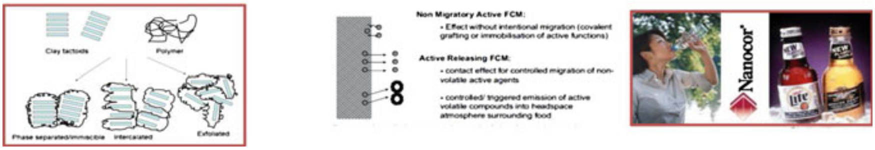


Fig. 6.13 Nanocomposites for improved barrier properties. Image courtesy of IoN

Lithium-ion batteries with long lifetimes, produced at low cost and with high safety during operation would enormously boost the development of hybrid vehicles. Nanocomposite materials offer great opportunities: for example, a flexible ceramic membrane using Al_2O_3/SiO_2 particles increases the battery safety, energy capacity, and durability, and allows roll-to-roll production. Existing batteries rely on anodes made from graphite; a silicon-carbon nanocomposite structure has been demonstrated to have a capacity several times higher than the capacity of graphite but it cannot presently be used due to degradation phenomena. Nonetheless, it opens new opportunities for effective future nanotype batteries.

Magnetic metal-oxide/polymer nanocomposites have great potential in device technologies for high-density memory and magnetic recording applications. Self-assembly of magnetic nanoparticles inside a polymer matrix can result in considerable improvement of the magnetic properties.

The concern for conventional polymer composites is their nonbiodegradability and the consequent threat to the environment. Nanocomposites based on biodegradable polymers are therefore very interesting from the environmental viewpoint. In addition, the nanocomposite material avoids the use of fossil fuel resources.

Nanocomposite materials currently used, or being developed, for the food packaging industry contains a polymer plus a nanoadditive. Mostly nanoclay particulates are used; however, other composites containing nanoparticles, nanotubes, or nanofibers are also being developed. Polymer nanocomposites containing nanoclay particulates are currently leading the food packaging market. However, bio-based nanocomposites (PLA-clay, cellulose nanofibers) and metal (oxide)-polymer composites are also being developed. Nanocomposites found their early application in multilayer PET beer bottles used by Miller Brewing Co (Fig. 6.13).

A significant problem for commercial applications of nanocomposites is the high price for many nanofiller materials. In addition, conventional manufacturing methods are not well suited for nanocomposite materials manufacturing; therefore novel technologies for converting them into engineering components are needed, particularly in achieving a homogeneous dispersion of filler material in the composite.

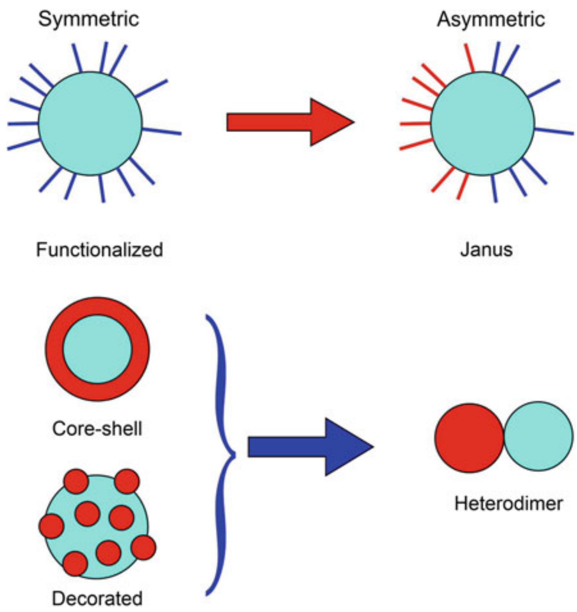


Fig. 6.14 Asymmetric nanoheterostructure model. Image inspired from Mines Paris Tech

6.2.3 Asymmetric Nanoheterostructures

Chemists have recently developed methods to produce asymmetric nanoparticles (Fig. 6.14). A first family is called "Janus" particles, exhibiting two different faces as the roman God, or more precisely two hemispheres with different functionalization. For instance, if one part is functionalized to be hydrophilic and the other one to be hydrophobic, the resulting particle will become a new "nanotool" to stabilize emulsions. Recently, many efforts have been made to synthesize asymmetric objects constituted by two different attached nanoparticles, generally by a controlled nucleation of the second nanoparticle on the first one. Applications of these heterodimers are promising in nanomedicine by coupling different physical properties (magnetic, optical) brought by each part of the dimer.

6.2.4 From Smart to Intelligent Coatings/Surfaces

There are significant advantages in using surface engineering to provide the required functionality or properties in a material or component, without having to engineer the properties of the entire product. The goal is to put the properties where they are most needed, to maximize the cost-effectiveness in obtaining the desired result. Surface engineering is important in products as diverse as armor plating and spectacle lenses.

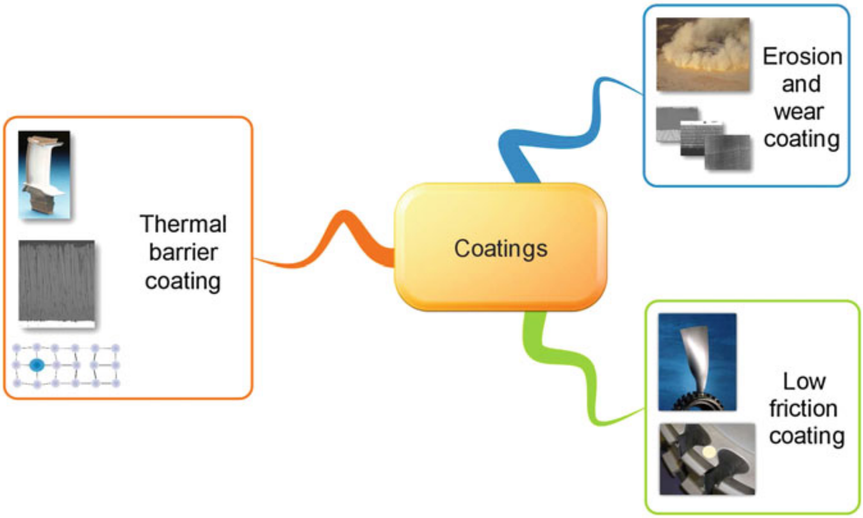


Fig. 6.15 Three types of coating used in the aerospace industry. Nanocoating can improve erosion and wear, act as a thermal barrier, and provide lubrification properties. Courtesy of Rolls Royce Derby

Technology areas of interest for nanocomposites/coatings include: hydrophobic and hydrophilic coatings, anti-smudge and fingerprint coatings, anti-reflective coating, anti-frost/fog/ice coatings, anti-wear and anti-corrosion coatings, anti-fouling coatings for marine applications, and biomimetic coatings for easy cleaning and self-cleaning applications.

Coating is important in the aerospace industry as is shown in Fig. 6.15.

New or advanced coating materials will be developed based on nanocomposites and nanostructured surfaces. Combinations of different layers within a single coating will be used to realize increasingly complex property profiles. For example, combining easy-to-clean properties with scratch resistance and sensing ability. Coated systems are already in use that exploit nanoscale effects and benefit from advances in scientific understanding and fabrication techniques. Advanced coatings can provide self-cleaning surfaces with anti-stain, anti-soil, anti-fingerprint properties, and in engineering components, optimal tribological properties for reduction in friction and heat losses, and corrosion and erosion resistance.

In many mechanical engineering applications, erosive wear mechanisms impact on through-life performance. Current coating systems based on single layers offer some improvement over uncoated surfaces but nanoengineered systems offer the potential to further reduce operating costs with improved durability.

In order to reduce the formation of nitrogen oxides (NO_x) in modern car engines up to 50 % of the exhaust gas is admixed to the air used for combustion, a process known as exhaust gas recirculation. This recirculation is controlled by a valve.

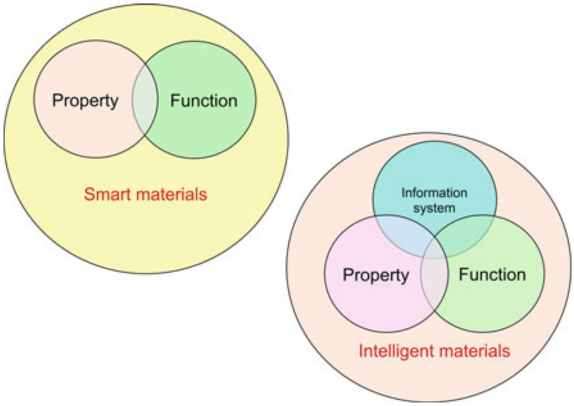


Fig. 6.16 From smart to intelligent materials coatings

One frequent source of failure is accumulation of soot in that valve. Here, a nanoscale and high-temperature resistant nonstick coating solves the problem.

Traditional coatings provide a function, but that function remains constant with time and on exposure to different environments. "Smart" coatings respond to the external environment and stimuli, changing their properties accordingly. Corrosion and erosion resistance can be conferred by "smart" coatings that respond to the external chemical environment and form tailored chemical barrier protection.

Improved damage tolerance can be obtained for a component by ensuring that the surface is able to absorb energy that would otherwise be transmitted to the substrate and lead to failure. Lighting and temperature control in buildings can be achieved by photochromic and thermochromic coatings, reducing the need for air conditioning. Active coatings can repel or break down dirt, removing the need for the traditional cleaning of windows.

Dry Film Lubricants (DFLs) are used to prevent wear on titanium-to-titanium contacts. Current duplex systems, developed in the 1980s offer significant benefits, but nanoengineered systems tailored to the application have the potential to enable an all-in-one solution.

Moving beyond smart coatings, *functional coatings* can provide an active response to changes in the external environment: for example, self-diagnostic coatings provide information on the condition of the component to which they are affixed, removing the need for separate arrays of sensors and giving improved feedback. A classic example is the development of a self-diagnostic thermal barrier coating. Its primary function is thermal protection, but by incorporating thermographic phosphors into the coating, one is able to independently measure bond coat/thermal barrier coating interface temperature, ceramic surface temperature and heat flux in-situ on rotating turbines, providing all the information needed for an engine thermal management system. This is summarized in Fig. 6.16.

The greatest potential advance lies perhaps in combining nanotechnology effects to produce a coating that has both a smart and a functional response, effectively providing three functions from a single nanostructured coating.

Corrosion, commonly called rust, is metal's biggest enemy: corrosion is estimated to cost $1 trillion per year in the USA alone, and hence corrosion protection mechanisms are extremely important. Nanoceramic coatings, very thin and completely even, have been developed for corrosion resistance with efficient application by dipping and spraying. They can be applied quickly at lower temperatures compared to normal coating processes which save energy. These coatings are environmentally-friendly and cheaper than conventional phosphate coating processes. The coatings also offer a good underlayer for excellent paint adherence. These coatings contain no toxic heavy metals or phosphates that have to be disposed, leading to less toxic waste and much less water needed for cleaning production apparatus.

6.2.5 Intelligent Nanomaterials Systems

Intelligent nanomaterials systems are an integration of smart nanostructured coatings and functional surfaces (Fig. 6.17). An example of an intelligent nanomaterials system is a combination of a smart oxidation/corrosion resistant coating coupled with a self-diagnostic barrier coating, co-deposited onto an aero engine component. The smart coating develops a protective film at high temperatures, whilst the diagnostic coating provides information on the strain in this film, as well as information on the temperature experienced, all of which can be used in monitoring the performance and in predicting the lifetime of the component. The biggest challenge is integrating such systems into the manufacture and maintenance systems of, for example, large industrial and aero power plants.

A further extension of this concept is to have self-healing properties. A shell of Al_2O_3 is created around "healing" particles that can fill damaged sites. With this approach, the healing mechanism will become active only when the coating is damaged; Fig. 6.17.

Thermal barrier coatings (TBCs) are used to extend component life in high-temperature systems. Nano engineered systems tailored to the application have the potential to further improve thermal resistance by ceramic alloying.

Nanomaterials and systems based upon them provide future enabling technologies for future coating systems that cross many industrial sectors. In addition to aerospace

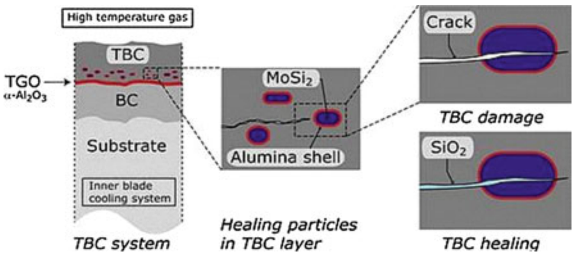


Fig. 6.17 Nanostructured turbine blade coatings that contain healing agents. Image courtesy to W. Sloof Delft

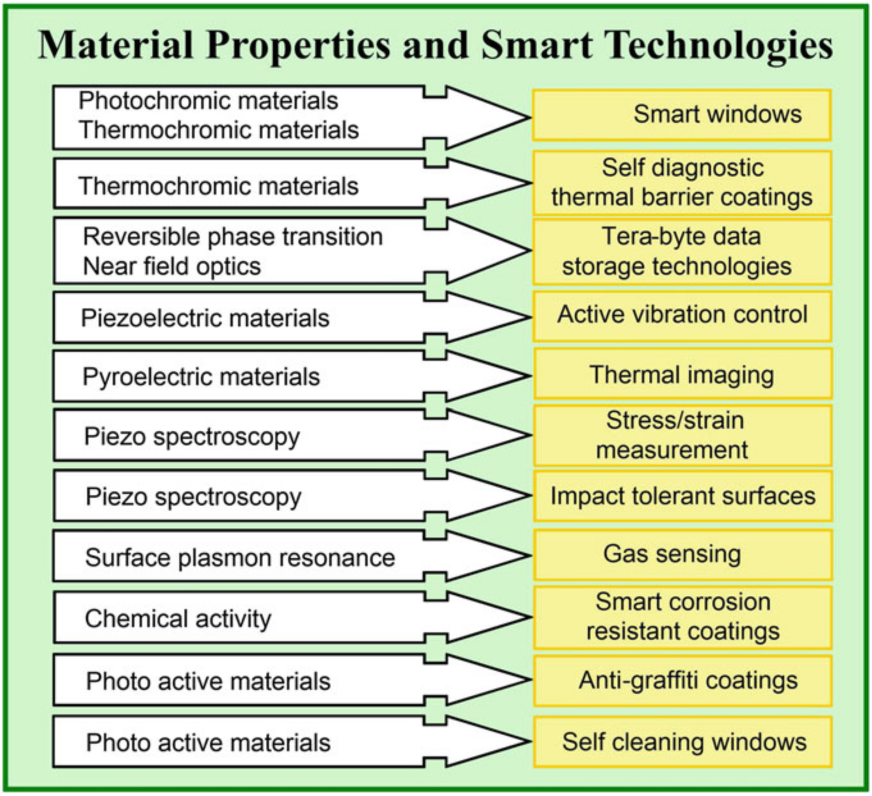


Fig. 6.18 From nanomaterials properties to innovative products

and power generation, these include health care, environmental engineering, food and packaging, sports and leisure, transport, energy, defense, space, agriculture, and the construction industries. Such innovative systems can create high value-added products, permitting us to control our working and manufacturing environment through the use of intelligent systems. Figure 6.18 shows the link between the fundamental materials phenomena that can be exploited and a range of novel applications.

Nanotechnology offers the potential of greatly enhancing the benefit and functionality that can be derived from coating systems, providing revolutionary solutions to problems as diverse as cleaning, corrosion protection, and instrumentation.

6.3 Biomaterials

All materials used by Nature are nanostructured by essence, composed of building blocks such as proteins, filaments, membranes, or mineral particles. Their nanostructures fulfill a variety of functions from energy conversion to chemical synthesis

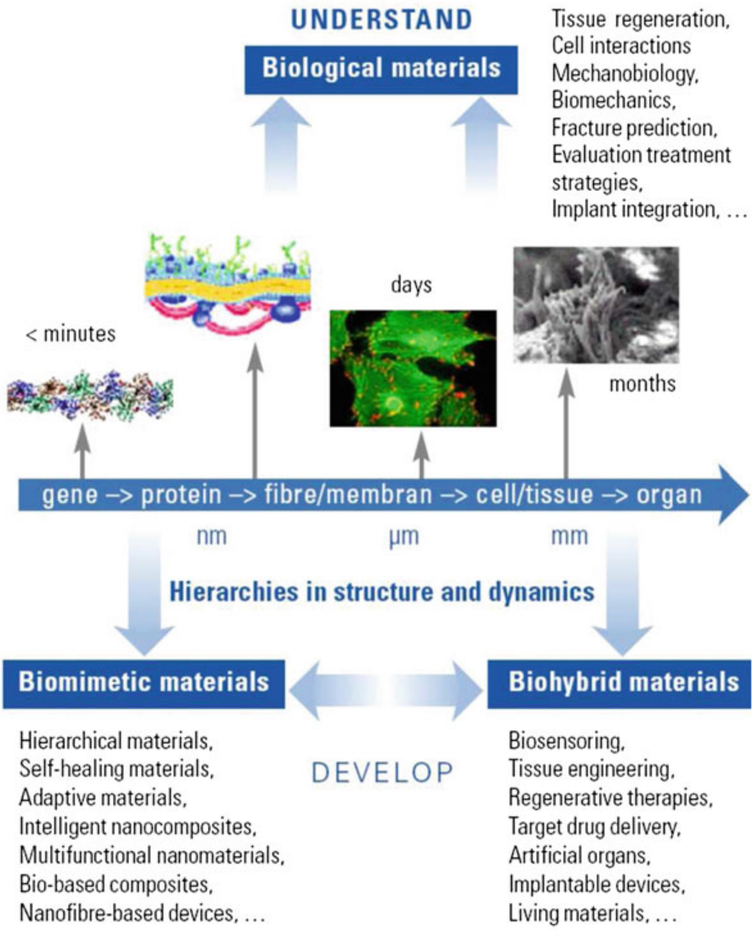


Fig. 6.19 Bio-nanomaterials spectrum. Image courtesy P. Fratzl Max Planck für Kolloidforschung, Potsdam, GENNESYS Conference Barcelona 2010

or mechanical stabilization. Biological materials will have an increasing importance in this century (Fig. 6.19).

Typically, the nanostructures of individual elements are assembled into larger tissues, giving control over the structure and dynamics of materials over many length scales. Mimicking this approach has clear advantages when approaching the design of nanomaterials, particularly for the design of multifunctional and adaptive materials. Exemplar nanobiomaterials are tailored membranes, engineered “viruses,” biosensors and artificial biosynthetic materials designed for biofunctionality and biocompatibility.

Medical and healthcare applications have very high importance: from the provision of optimal nutrition and the provision of clean water, through pain management, improvements in longevity, novel prostheses and body part replacements for maximizing quality of life. Novel pharmaceuticals can be fabricated using nanosynthesis techniques.

Nanomedicine is an emerging area making profit of the mastering of nanoparticle synthesis and functionalization. Nanoparticles can be injected in the body and concentrate specifically in some targeted abnormal cells thanks to *ad hoc* functionalization. They may be used for aid in diagnosis, aiding magnetic resonance techniques and providing better imaging contrast agents. They can also be used for cancer therapy using their behavior under external excitation by magnetic fields, X-ray, or light irradiation for instance: energy conversion into heat able to destroy the targeted cells.

Biomaterials will be addressed in part 4 which is dedicated to health care and we shall not go any further in this chapter.

Part II
Nanomaterials

Conclusion

Recent developments have advanced our capability to rearrange matter at the molecular or atomic level, and to bring problems of material behavior on the nanometer scale into the domain of production engineering. Immediate applications of nanostructures and nanodevices include quantum mechanical and electronic devices, biosurgical instruments, microelectrical sensors, functionally graded materials, and many others with great promise for commercialization. Nanotechnology offers the possibility for local modification of a material, giving localized protection or sensing properties, or some combination of the two, that produce an entirely new functional system.

Across Europe, the materials sector is a major contributor to the economy, in the UK, for example, it represents around 15 % of GDP.[1] The technical and economic impacts of nanomaterials are therefore extremely important for the future industry.

Nanomaterials span metals, ceramics, polymers, and composites. Using nanoscale engineering to improve material properties offers the possibility of novel functional materials (materials developed for magnetic, electronic, sensing, or superconducting properties, for example) as well as structural materials (e.g., for lightweight, high temperature resistance, or high-strength materials). Nanoparticles based on a range of compounds—such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), iron oxide (Fe_3O_4, –Fe_2O_3), zirconia (ZrO_2), zinc oxide (ZnO_2)—can find applications in additives for polymers, for UV protection, in solar cells, pharmaceuticals and medicine, and additives for coatings. Carbon nanotubes can be used as additives for polymer composites to give improved mechanical performance and conductivity. Nanoactivation of metals such as gold, silver, and nickel will

[1] Materials Education and Skills: A Wake-Up Call. Materials UK Education and skills review, MatUK LtD, 2008.

generate new applications for the materials in catalyst applications, optoelectronics, and wound dressing.

Nano-objects have a far larger surface-to-volume ratio than conventional materials. Owing to this larger active surface area or larger interface area, both chemical reactivity and physical interactions can be enhanced. This can lead to higher catalytic activity, stronger interaction with other materials and changes in transport properties. As a consequence it is possible to reduce resource utilization and limit the use of precious or hazardous raw materials when using a nanomaterials.

The behavior of defects is often different in nanoscale objects. Both their creation and propagation can be completely altered in nanoscale objects. In some cases defects may be virtually eliminated giving the nanomaterial high intrinsic strength. This is the case in many nanoparticles and semiconductor nanowires. In other cases the propagation of defects is greatly inhibited which impacts mechanical properties like failure stress.

Building-up nanomaterials with viruses

Using organisms like viruses, that can exist in extreme environments, is a way to build up more complex nano-objects. An American–French team of scientists have for example used viral nanoparticles which can be produced easily in large quantities and are stable in extreme external conditions. The virus used, called SIRV2, is known as having the capacity to infect single-cells organisms living at 80 °C in an acidic medium (pH = 3). The useful property is that these viruses selfassemble with a high accuracy. Before this is done, the viral capsule is opened to modify the virus by functionalization with chemical groups. The modifications can be made on the ends of the virus, to its body, or to both. This operation allows tailoring of the self-assembly process and the property of the synthesized nanomaterial.

In the area of opto—and microelectronics, miniaturization is a strong driver for going to the nanoscale. Decreasing the size of the elements used in electronics (transistors, memory cells, etc.) has allowed leaps in performance and affordability in recent decades. The nanoscale is a natural extension of this evolution. Optical properties can be impacted by shape and size. For many semiconductors quantum effects occur when the material is confined at a small scale; some semiconductor nanoparticles display electronic properties intermediate between those of bulk semiconductors and those of discrete molecules.

Structural materials, still have great scope for development. In many ways, functional nanomaterials are more advanced, as they are based on semiconductor processing and understanding, which requires a relatively small jump into the nanotechnology field. Nanomaterials offer an elegant way to integrate new properties into materials, for example, using semiconductor nanowires or nanoparticles on glass, wood, or paper substrates could add novel active optical properties to these materials.

For structural materials, a greater change in understanding is required. In addition to the challenges in taking the mechanisms of nanomaterials and making them working in practice, there are additional factors that have to be addressed for successful commercialization. The synthesis of nanomaterials must reach production levels of high quality, with the materials being produced in sufficient quantities to meet consumer demand at acceptable cost.

The processing of tailored, multifunctional nanomaterials is a very demanding task. Special fabrication tools will be required, and the development of processing lines will require a research effort to be made alongside the understanding of the basic nanomechanics. New tools for quality control and testing are needed, with the associated interfacing to modern computer control.

Finally, designing with structural nanomaterials is still in its infancy and demands insight into mechanical properties, joining and machining of nanomaterials, nondestructive testing, and studies on lifetime prediction and reliability. These topics are not treated in this book but are of great importance and information can be found in the referenced literature.

The twenty-first century is the century of nanomaterials science and engineering and industries not involved in this new engineering domain may lose their market share. Nanomaterials will give breakthroughs for multiple technologies in the next decades, resulting in new industrial innovations and job creation. It will help in the solution of many socioeconomic problems related to safety and security, the environment, energy supply, and cheap communication. Investment in nanomaterials will allow the economy to remain competitive in a global market.

Part III
Nanotechnology for Information and Communication Technologies

Introduction

Electronics is used to process, transmit, and store information. Its goal is to achieve that function at the cheapest possible costs, as fast as possible, and with the lowest possible energy consumption. Microelectronics, which is a subdomain of electronics, has taken today an overwhelming importance in daily and professional life. It started with the invention of the first integrated circuit, in 1958. This was simultaneously done by Jack Kilby, working at Texas Instruments, and by Robert Noyce and Jean Hoemi at Fairchild. The integrated circuit built by Kirby had just one transistor, one resistor, and one capacitor made on the same crystal with discrete wire interconnections. Noyce and Hoemi's first integrated circuit was made with a planar process and deposited interconnections. However, the first commercially available integrated circuit was developed by Noyce in 1961. Today integrated circuits are manufactured in huge fabrications units and many integrated circuits are produced at the same time on big silicon wafers as shown, for example in Fig. III.1.

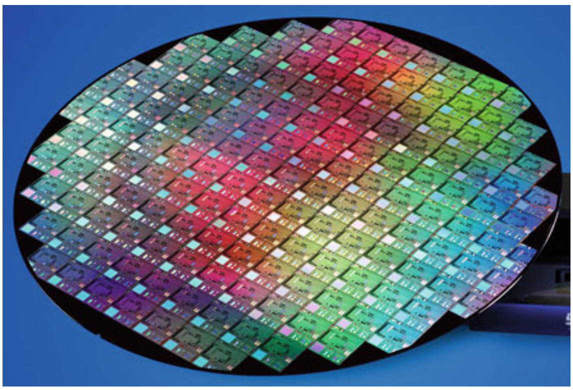


Fig. III.1 300 mm silicon wafer with integrated circuits manufactured on it. Image courtesy of CEA/LETI (France)

Chapter 7
From Microelectronics to Nanoelectronics

Micro and nanoelectronics are mostly based on silicon integrated circuits technology where transistors are present with other components. The cost of a single transistor is now so cheap, due to high-volume manufacturing, that integrated circuits are present almost everywhere in human activities: telecommunications, finance, medical care, education, and throughout daily life. Amazingly, the number of transistors manufactured each year in the world is now larger than the number of rice grains harvested on the Earth.

7.1 Shrinking the Components

If we use the current definition of nano-technology, which consists of being able to operate and manufacture circuits with critical dimensions below 100 nm, today's processors and memory devices can be considered as belonging to the field of nano-technology. Some scientists do not classify micro-electronics below 100 nm as nanoelectronics, and restrict this term to studies where quantum phenomena occur and where mechanisms different from those seen at the macroscopic level are observed. Actually, the transition from the micrometer length scale to the nanometer length scale is continuous and several new phenomena take place at different length scales.

Lithography of microprocessors below 100 nm started to be operational at the industrial level around 2005. For example the Pentium D was manufactured with a process at 90 nm. In 2010–2011, lithographic processes at 45 or 32 nm became usual. Memories follow the same trend. For DRAM (Dynamic Random Access Memory) chips, which are used in computers, manufacturing processes were around the 20 nm range by the end of 2011.

The design features of commercial integrated circuits have accuracy of the order of 20 nm. As a matter of comparison, the diameter of a human hair is equal to about 50–100 μm, that of a blood cell 7 μm and the AIDS virus has a size of 100 nm. These sizes are much larger than the size of a buckyball (1 nm).

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_7,

7.2 Moore's Law

In 1965, Gordon Moore, co-founder of the INTEL Company, noticed that the number of components in integrated circuits had doubled every year between 1958, the date of the invention of the integrated circuit, and 1965. He anticipated that this trend would continue over at least a decade. Actually this exponential increase has been observed during a longer period of time, although the doubling period has now increased from one year to 18–24 months. Figure 7.1 shows the evolution of the number of transistors in some Intel processors at different years. The ordinate is in logarithm scale meaning that a straight line in this plot is indeed an exponential increase.

As we can see, over about 40 years, the number of transistors on a chip doubled every 18–24 months. For example, there were 4,500 transistors in the 8080 microprocessor (which could address 64 kBytes of memory) introduced in 1974. The Intel I7 QuadCore, introduced in 2008, contains 731 million transistors and the 10-Core Xeon available in 2011 has 2.6 billion transistors.

This exponential increase of the information processing power per unit area on the chip is at the same time followed by an exponential decrease of the cost of information processing. However, producing integrated circuits at lower and lower costs requires more and more expensive fabrication plants and huge investments. Typically, the manufacturing plant cost doubles every 3 years or so.

In order to illustrate the strong decrease of the cost of transistors, consider a million of them. Their price was about that of a house in 1973. It has dropped down today much below the price of a single post-it sheet. Because of that, microprocessors are found in many daily life objects such as credit cards, phones, cars, etc.

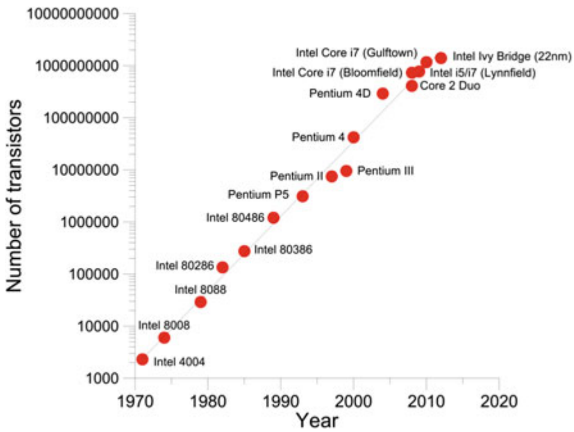


Fig. 7.1 Number of transistors contained in different Intel processors as a function of their year of introduction on the market. The evolution, plotted in log-scale, follows Moore's law

7.3 Smart Systems

The low cost of transistors in microprocessors provides the ability to introduce on-board intelligence in the device for an easier use.

There are several reasons why we need smaller and smaller electronics devices:

- People want to be connected to other people at any time and any place (using smartphones, for example), they want also to listen to their music, watch a video…everywhere. This is possible with portable devices provided they are low-energy consuming.
- People always want easy to use systems. This requires more complex systems to help the user. Part of man complexity is transferred to the electronic system which should be a powerful information treatment device.
- People also need more and more storage capacities since there is much more data to store than before. Videos require a lot more storage than music or books. Typically, more than 100 Gb are needed to keep data of one individual.

The ability, due to fast progress of lithography techniques, to make smaller and smaller components on a silicon wafer, allows to process data information at a speed which is always increasing. High resolution video is now possible and voice treatment can be done in real time as well as image processing. This opens a wide variety of applications which simplify the life of humans and give them the opportunity to spend time on other activities.

From Tubes to Integrated Circuits

The first transistor has been invented in 1947 by J. Bardeen and W.H.Brattain at the Bell laboratories. It was a point-contact transistor. A transistor is a three terminal device where the electric current or the voltage between two of the terminals can be controlled by applying an electric current or voltage to the third terminal. At about the same time W. Shockley imagined a junction transistor which he could build two years later. It was more robust and easier to manufacture than point-contact transistors. At that time, the industry did not pay much attention to this invention but Shockley did and founded the Shockley Semiconductor Company. However, because of his strong personality, eight of the brightest scientists of his Company left it to found Fairchild Semiconductor. Two of them have then founded later the Intel Corporation (B. Noyce and G. Moore). Transistors represent a revolutionary invention which allowed replacing vacuum tubes used before. The triode, invented in 1906 by the American Lee de Forest was the first three-terminal device. It made AM radio possible. However tubes require a large power, take room and have a comparatively short lifetime. The advent of transistors has been really a breakthrough in the electronic domain. The integrated circuit, invented in 1958–1959 by J.Kilby (Texas Instrument) and R.Noyce (Fairchild Camera) was also an important breakthrough by giving the ability to put a large number of components on a single piece of semiconductor.

7.4 Transistors

The first transistor was a bipolar transistor which means that two kinds of charge carriers are involved: electrons and holes. A hole is actually a place in the crystal where an electron is missing. It behaves like a positive charge. A bipolar junction transistor is made of a semiconductor material where regions of the transistor are doped differently with a controlled concentration of impurities.

A semiconductor, like silicon, doped with impurities possessing more electrons than silicon (phosphorus, for example) brings extra electrons in the region and the electric conduction is mostly done there by electrons. We say that we have a *n*-type semiconductor. Doping the semiconductor with impurities having fewer electrons than silicon (boron, for example) leads to a so-called *p*-type semiconductor: the electric conduction is mostly done by holes. A hole is a state where an electron is missing. The propagation of holes goes in opposite direction of that of electrons. This is schematically illustrated for a 1-dimensional lattice in Fig. 7.2.

A *np* arrangement where a *n*-type region and a *p*-type region are close together form a diode which is a device allowing a current to go in one direction only. A bipolar junction transistor is a device of the form *npn* or *pnp* which can be considered as two diodes sharing an anode (or cathode) or two diodes put head to tail. A transistor can be used to amplify or to switch signals.

Soon after the bipolar transistor was introduced appeared another family of transistors: unipolar transistors involving one kind of charge carrier only: electrons or holes. Field-effect transistors belong to this family and especially the so-called MOSFET (Metal Oxyde Semiconductor Field effect Transistor) which is used to amplify and switch electronic signals. This technology is widely used in digital and analog circuits. Compared to a bipolar transistor, a field effect transistor is a faster electronic device with better performances at high frequency.

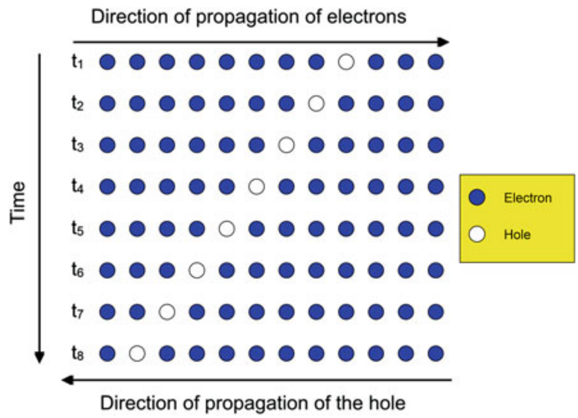


Fig. 7.2 Propagation, for a 1-dimensional lattice of electrons, of a hole (site where an electron is missing). Electrons are *dark circles* and the hole is the *white circle*. Snapshots of the lattice are shown at increasing times $t_1 < t_2 < \cdots < t_8$ as electrons are moving to the *right*. The hole (*empty space*) moves in opposite direction, to the *left*

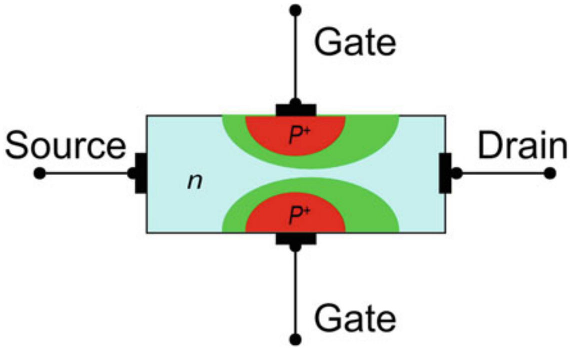


Fig. 7.3 Diagram of a n-channel junction field-effect transistor (FET or JFET). The red areas in the figure correspond to highly p-doped regions. They are for this reason denoted p^+. The body in *light blue* is n-doped. Close to the source and the *drain regions* doping is even higher (n^+) in order to ensure good ohmic contacts. The *green area* corresponds to a *depletion region* (poor in charge carriers). An increasing negative gate-to-source voltage causes the depletion to expand (in an asymmetric way as is sketched in the figure) and the channel through which charge carriers flow from the source to the drain reduces in size. Above a certain bias threshold, the channel is closed (pinch-off of the channel) and no more flow of charge carriers is possible. The transistor can be switch on and off depending on the applied bias. A hydraulic analogy is shown in Fig. 7.4

Principle of a Field-effect Transistor (FET)

Basically two different regions of a piece of p-type silicon are doped n (Fig. 7.3) in a field effect transistor. They are called the *source* and the *drain*, respectively. These two regions are very close from each other and separated by a small region of p-type silicon (the separating length is typically $1\,\mu$m or less) called the *channel*. In the present example the channel is of p-type and the unipolar transistor is named pMOS otherwise it would be a nMOS. In principle, there is no electric current between the source and the drain because they are separated by a region of a different type. It is possible to have a current flow through the channel by applying a voltage on an electrode called the *gate*. The gate is not directly coupled to the $p-$type semiconductor but isolated from it by a thin layer of silicon oxide. The voltage applied on the gate allows controlling the current going from the source to the drain through. It acts like a tap controlling the water flow in a pipe (Fig. 7.4). The device is named field effect transistor because it is the electric field resulting from the voltage applied on the gate which controls the current going from the source to the drain through the channel. The name MOS comes from the fact that the gate, which is a metal, is separated from the channel by an oxide layer.

CMOS (Complementary metal-oxide-semiconductor) is a widely used technology in microprocessors, static RAMs (random access memory), digital logic circuits, image sensors, etc. The word complementary means that CMOS uses complementary p-type and n-type MOSFETs disposed symmetrically to ensure logical

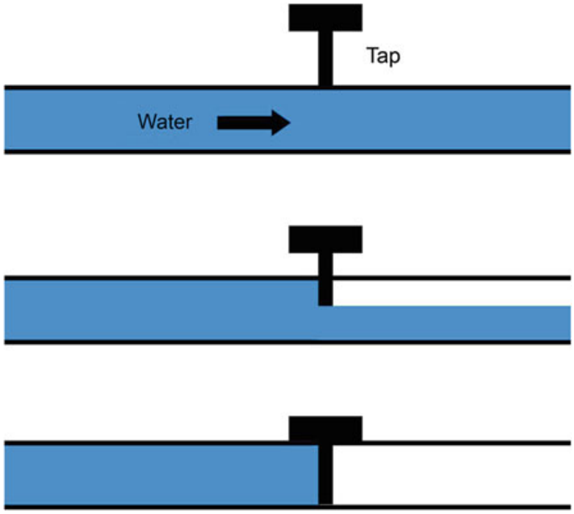


Fig. 7.4 Hydraulic analogy illustrating the operating conditions of a field-effect transistor. The tap plays here the role of the gate. Depending on the bias applied on the gate, the flow can be reduced or suppressed

functions. The main interest of CMOS technology is low power consumption when not switching. Power is just needed for switching operations of the device. A second advantage is to be relatively less sensitive to electronic noise than other technologies.

An Exponential Growth in Computing Capabilities

The first general-purpose electronic computer was the ENIAC (Electronic Numerical Integrator And Computer). It has been in operation in 1946 for the US army. It was, at that time, a thousand faster than electro-mechanical machines but its cost was huge. The later would represent in 2010, corrected for inflation, about \$6 million (\$500,000 in 1946). The entire computer occupied 167 m^2, weighted 27 tons and consumed 150 kW power. There was close to 18,000 vacuum tubes and other component (diodes, relays, resistors, capacitors). Its computing power was very poor, typically 10^8 smaller than a simple PDA (Personal Digital Assistant) sold in years 2000's and was also 10^8 heavier than this PDA. Because of the vacuum tubes, the reliability was very poor (several tubes burned out every day). Consequently, the ENIAC was operational only half of the time.

7.5 Smaller, Faster, Cheaper

The evolution of microelectronics is such that it produces *smaller*, *cheaper* and *faster* electronic devices. This trend has been followed over several decades and still continues. Integrated circuits are made on a silicon wafer by lithographic techniques where many masking levels are necessary during the manufacturing. There has been

Table 7.1 Evolution of the size of silicon wafers in microelectronics

Size (official)	Size	Refer to as	Thickness (μm)	Year of production start-up
1″	25 mm	1″		
2″	51 mm	2″	275	
3″	76 mm	3″	375	
4″	100 mm	4″	525	∼1975
5″	130 mm	5″	625	
150 mm	5.9″	6″	675	∼1980
200 mm	7.9″	8″	725	∼1991
300 mm	11.8″	12″	775	∼2001
450 mm	18″	18″	925	Still under development

Data from Wikipedia and http://www.sumcosi.com

a continuous transition of lithography techniques from features larger than 100 nm to features smaller than 100 nm. Consequently, there is a continuous evolution from microelectronics to the nanoscale domain since we defined its limit to be below 100 nm.

Wafers

A wafer is a high purity (99.9999999 %) circular thin slice of semiconductor material. Applications use mostly silicon crystal wafers although there are other specific applications using other materials such as SiC, GaAs, GaN, for example. Wafers are obtained from an ingot of highly pure single crystal of silicon, manufactured by the Czochralski method. The silicon ingot (weighting about 100 kg) is sliced into disks which are polished carefully to make wafers. The size of silicon wafers has continuously increased over the time while the size of elementary components has decreased. Within the same period, the smallest pattern size, which is the accuracy at which one is able to etch silicon, dropped down from about 6 to 8 μm to about 20 nm. In the early days the diameter of the wafer was equal to 1″ *(25.4 mm) and today sizes of* 11.8″ (300 mm) with a thickness of 775 μm are routinely used in semiconductor fabrication plants (called *fabs*). Table 7.1 recalls the different steps of this evolution. The next generation will use 450 mm wafer size (see Fig. 7.5). It is still under development but is expected to reach an industrial stage soon. *Increasing the size of the wafer allows manufacturing more semiconductor devices at the same time on a single wafer and hence to reduce cost. This is however a great technological challenge in terms of cleanliness or flatness which should be close to perfect. The number of chips which can be produced on a single wafer increases like about the square of its diameter while the cost of the fabs increases less. The evolution of micro and nanoelectronics can be compared to that of a sheet of paper which increases (the size of the wafer) while the size of the letters decreases (Fig. 7.6).*

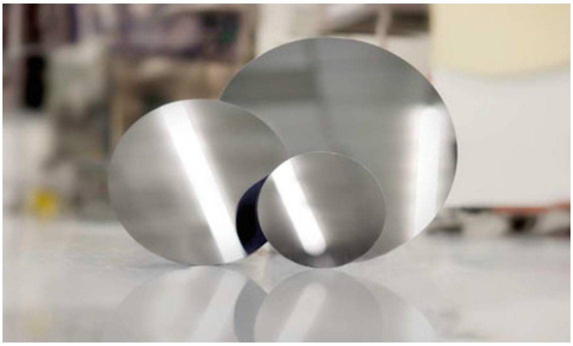


Fig. 7.5 This figure shows a 22, 300, and 450 mm silicon wafer. Image courtesy of IMEC (Belgium)

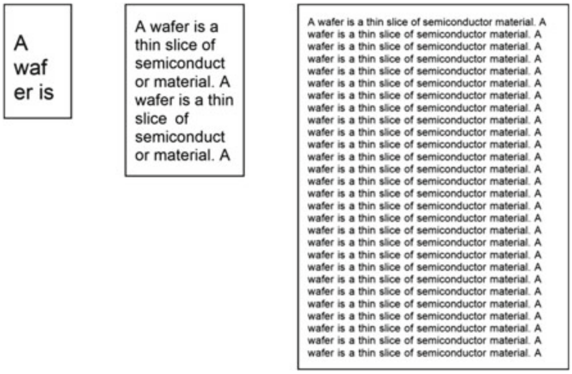


Fig. 7.6 Printing analogy to illustrate the evolution of the size of wafers and progresses of lithography used in microelectronics. The evolution is similar to using *larger and larger sheet of paper* (like greater and greater wafers) and writing *smaller and smaller characters* (decreasing the feature *size* on the wafer by lithography techniques)

In the last decade the size of electronic components has moved from above 100 nm to about 20 nm today and probably less tomorrow. These progresses were possible thanks to an increase of performance in deposition, patterning and characterization. However, in going at such small length scale the thickness of some layers becomes close to 1 nm. For example, the thickness of the oxide layer separating the gate to the channel in a MOSFET has less than 10 atoms. Roughness is also becoming an issue.

Advances in the accuracy of patterning in the microelectronics domains is done by steps or *generations* called *technology nodes*. A 90 nm technology node refers to the size of the transistors in a chip or half of the typical distance (half-pitch) between two identical features in an array of memories. The 1971 technology node was at 10 μm while in 2011 we have a 22 nm technology node. The next generations will be at 16 and 11 nm. Figure 7.7 displays the evolution of semiconductor manufacturing processes for the different generations.

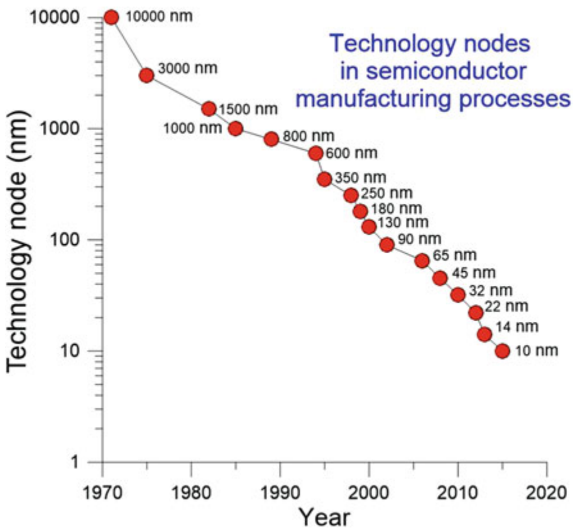


Fig. 7.7 Evolution of the semiconductor manufacturing processes in log scale

7.6 Limiting Issues

Moore's law is expected to break down because it is not possible to infinitely decrease the dimensions of transistors. Even if we could go to individual atom dimensions, it would not be possible to cut them into pieces. However, much before that limit is reached: new phenomena will occur and changes in the physics we are used to will take place such as the appearance of new quantum effects. Furthermore there are also two other limits to reducing the size of elementary electronic components. The first one is energy dissipation. As we shrink the dimensions of components their energy consumption is reduced but their density on the chip increases. The net effect is an increase of the amount of heat to be dissipated. Even if new technologies allow decreasing the size of the elementary components, we may reach a level where it will not be possible to dissipate energy and components will be destroyed. Currently, the heat dissipation per chip area is already one of the limiting factors. Another limit in decreasing the size comes from economics. The investments of the foundry where integrated circuits are manufactured increase strongly and could reach a situation where nobody could afford it.

7.7 Memories

Magnetism is a property of some materials extensively used to store information. Various types of memories have been designed and manufactured to do that. In a magnetic material, binary information can be recorded by locally orienting the magnetization of the material in one of two possible directions. The information density per unit of surface that can be stored continuously increases at an average rate of 45 % per year.

7.7.1 More and More Storage Capacities

The natural evolution of computer memories is to get larger and faster memories. However, in practice, large memories are usually slow and fast memories are small. Most of large memories used today in computers are DRAM (Dynamic Random Access Memory). They are cheap, slow, require low power but need to be refreshed regularly. Fast memories belong to the SRAM (Static Random Access Memory) technology. They require high power, have a much smaller access time (about an order of magnitude smaller than DRAM) but are expensive. They are qualified of static because they keep information as long as power is on. The access time of DRAM and SRAM is the same for all locations of the data. For larger and cheaper data storage, hard drive disk is a good solution which is extensively used in computers. However the access is sequential and therefore slow compared to DRAMs or SRAMs.

Non-volatile Random access memories keep information even if power is off. Flash memories are representative of this category: it is a non-volatile computer memory which can be erased or reprogrammed using electrical signals. They are extensively used to-day in portable devices such as cameras, mp3, etc.

Progress in Hard Disk Drives

The first hard drive was made by IBM in 1956 and called the RAMAC 305. It consisted of 50 24″ magnetic disks. The total storage capacity was equal to 5 million of 7-bit characters which corresponds, translated in our today language to 4.4 Mb. The size of the hard drive disk and its electronic components was about the size of two big refrigerators. In 2006, a current hard drive disk had only two platters of 2.5″ and the density storage reached was 200 Gb/inch^2. The storage density was 2 Mb/inch^{2}only in 1956.

Information has been stored during a long period on continuous magnetic layers. Now, arrays composed of nano-sized dots can be manufactured for information storage. Magnetoresistive materials are used to read and write data on the magnetic materials. Spintronics, which will be presented in the next chapter, allies electronics and magnetism with the great advantage, as far as information storage is concerned, that it requires less power than conventional magnetic storage.

Memory design has greatly improved in the recent years. The packing density has increased and the minimum feature size decreased. The overall performances have increased while reducing power consumption. The main types of memories used in electronics are summarized in Fig. 7.8.

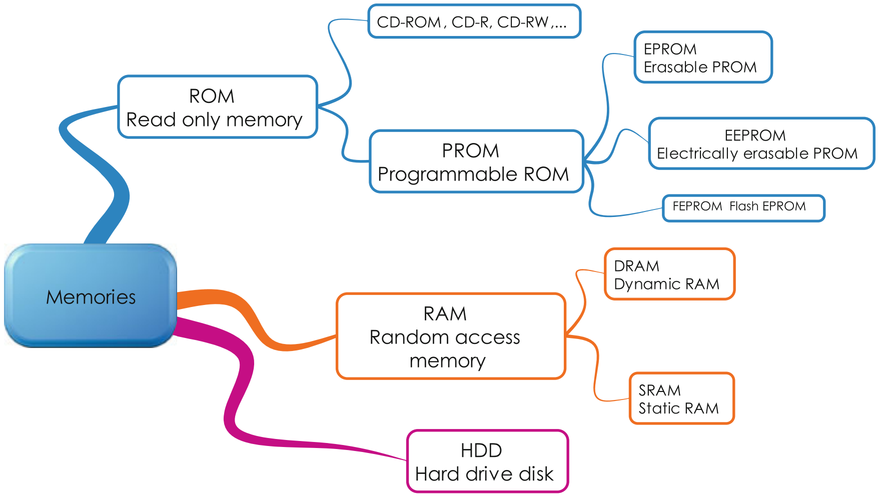


Fig. 7.8 Main types of memories extensively used in computers

RAMs are volatile memory requiring power to keep information. ROMs are on the contrary non-volatile memories and hard drive disks, which can store a great amount of information, are slow.

DRAMs are less expensive than SRAMs but are slower. These memories are mostly used in computers, on a chip next to the processor.

Flash memories, which are EEPROMs (Electrically erasable programmable read-only memories), use cell memories made of two transistors separated by an oxide layer. Flash memories are used in a number of portable devices such as cameras, mp3 or video players, etc.

Hard disk drives contain rotating disks with magnetic surfaces. Huge storage capabilities (over a Tb) are today obtained with hard disks. Almost every computer has one or more hard disks. The capacity of hard drives is exponentially increasing while its cost exponentially decreases. Figure 7.9 shows the evolution of the cost per gigabyte. Over the three last decades, the space per unit cost has, in the average, doubled every 14 months.

One way to increase information density on a magnetic surface, such as a hard drive disk, is to use a perpendicular magnetization with respect to the surface rather than transverse magnetization. Such an improvement has been introduced around 2005 (perpendicular magnetic recording) although it was already proven in 1976. It provides higher storage capacities, an improved reliability and robustness. The basic difference between transverse and perpendicular magnetization storage is illustrated in Fig. 7.10. The storage density is increased by a factor larger than three.

Using discrete areas to store data is interesting in many aspects. For example, the CEA is using a lattice previously patterned in such a way that there are cylindrical dots into the substrate. The size of each dot is about 100 nm of diameter and is

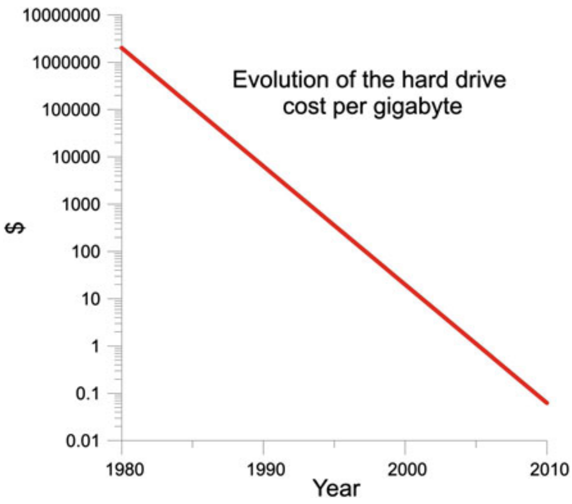


Fig. 7.9 Mean evolution of the hard drive cost per gigabyte over three decades. This curve (in log scale) corresponds to a fit to data performed by Matt Komorowski (www.mkomo.com)

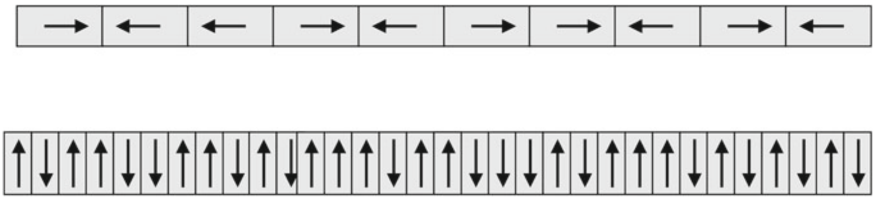


Fig. 7.10 Schematic difference between transverse magnetization (*top*) and perpendicular magnetization (*bottom*). *Arrows* indicate the direction of magnetization

covered with a multilayer of Co and Pt metals. It is in this top part of the dot that information is stored because it is closer to the read and write head of the device. Each dot has an up and down magnetization and the state is readable using a conventional read/write head. Figure 7.11 shows an image of such a media covered by dots. Each dot corresponds to a bit of information. With such dimensions for the dots, a data storage density of 40 Gbit/cm^2 can be obtained. Reducing the size of the dots can increase the storage data density and it is possible to go towards the Tbit/cm^2.

7.7.2 New Memory Technologies

Although dimensions below 100 nm are now reached for the cells in some memories, there are other specific areas of memories where nano-technology can be involved. This concerns new memory technologies. Some of them are displayed in

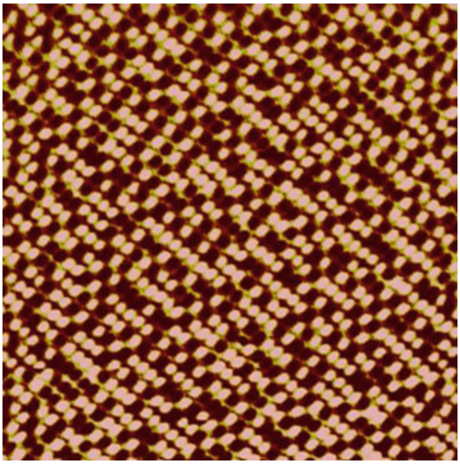


Fig. 7.11 Magnetic force microscopy image of 100–200 nm magnetic domain structures made up of a multilayer of Pt and Co deposited on a pre-etched silicon substrate. Image courtesy of CEA/LETI (France), Clef CEA n°52, 2005

Fig. 7.12 Some new memory development where nanotechnology plays a significant role

Fig. 7.12 taken from the studies made in the Obervatorynano project. Most of these developments are at the laboratory level and their cost is still too high. Memories are based on the fact that there a cells which can have two different states, one playing the role of 1, the other of 0.

MRAM (Magnetoresistive random-access memory) have a high potentiality to have an important future in storage technology. A cell is made of a fixed magnetic layer separated by a thin dielectric tunnel barrier from a free magnetic layer. Such a memory is non-volatile. Each magnetic layer has a polarity which can be parallel or anti-parallel. The resistance of an electric current, used to read the content, is based on the fact that the resistance is lower if the magnetic orientation of the layers is parallel compared to the situation where it is anti-parallel. More recent developments of the

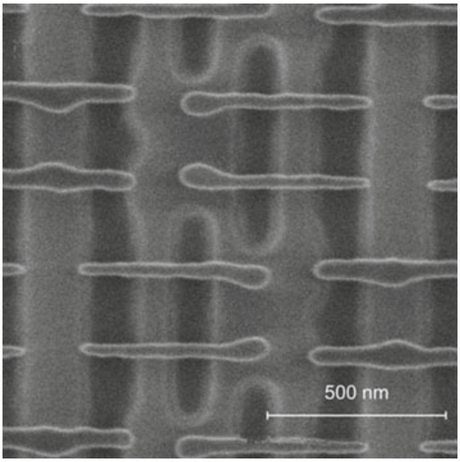


Fig. 7.13 SRAM produced by the Crolles 2 Alliance using the 65 nm technology node on a 0.5 μm^2 surface area. Image courtesy of CEA/LETI (France), Clefs CEA n°52

MRAM technology is the spin-torque MRAM using the electron spin to flip the magnetic field of the layer where information is written.

Programmable metallization cell (PMC) use a thin film electrolyte sandwiched between a layer of inert metal playing the role of one of the electrodes and an electrochemically active electrode. Applying a negative bias to the inert electrode creates a nanowire through the electrolyte and the electrical resistance drops down.

Resistive RAMs use the possibility to change the resistivity of certain dielectric materials by applying a high voltage. High storage densities are expected to be reached and such memories are very fast.

Static random-access memories (SRAM) use MOSFETS transistors to store a bit of information. Generally 6 MOSFETs per bit are needed. Compared to dynamic memories, some static memories can keep information when the power supply is off. An example of such memories is displayed in Fig. 7.13.

Phase-change RAMs use the possibility of change of resistivity of chalcogenide glass as it goes from crystalline to amorphous state. Actually, a chalcogenide alloy GST (germanium, antimony and tellurium) is used. The transition from the crystalline to the amorphous state occurs around 600 °C. Samsung has for example made a PRAM of 8 Gb using a lithographic process at 20 nm. The year before, using 58 nm etching the PRAM size was 1 Gb only. Compared to conventional flash memories, PRAMS are much faster and have also a much greater lifetime.

Racetrack memory is an IBM development where information is stored in magnetic domain walls. Permalloy nanowires are used as magnetic material. Spin polarized currents are able to move the magnetic domain along a permalloy nanowire track allowing to write data which are read using a tunnel junction. Figure 7.14 shows the basic principle of a racetrack memory.

Nanotube-based RAM use suspended nanotubes junctions as memory bits. Applying a voltage pull the nanotube towards the electrode corresponding to a bit one state.

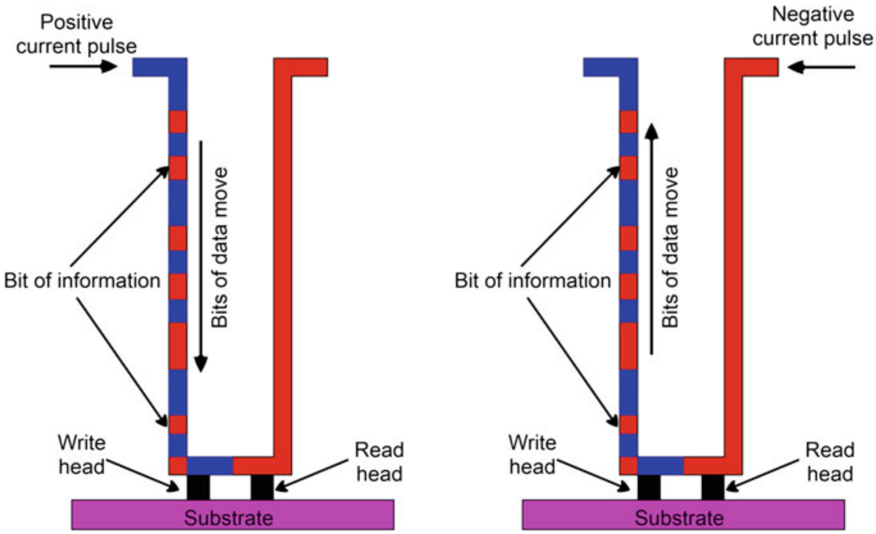


Fig. 7.14 Basic principle of a racetrack memory developed by IBM. Bits of information are stored in a *U-shaped* nanowire as magnetized regions which can be read using the read head or modified using the write head. *U-shaped* nanowires are arranged vertically with respect to the substrate. Applying a spin-polarized current to the nanowire make the magnetic pattern to move like cars on a racetrack. Data can be written and read in less than a nanosecond. Figure inspired from www2.technologyreview.com

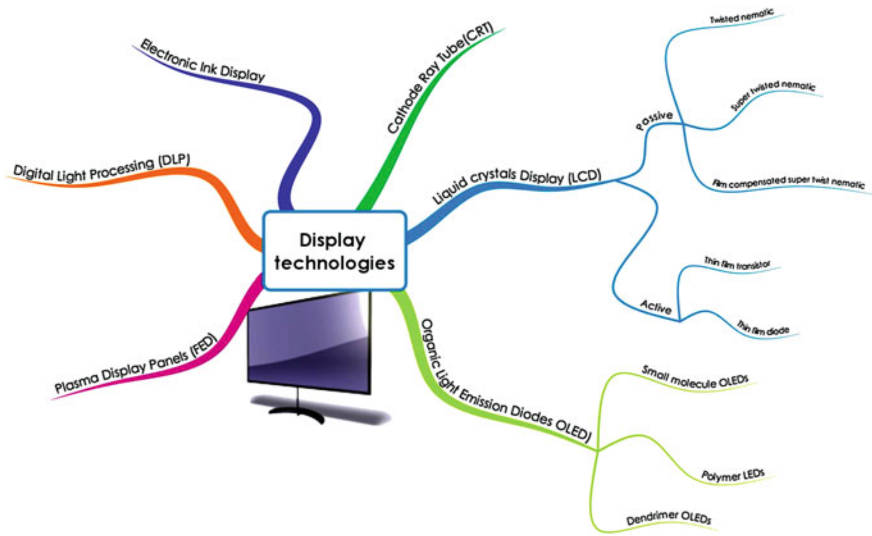


Fig. 7.15 Main display technologies used today

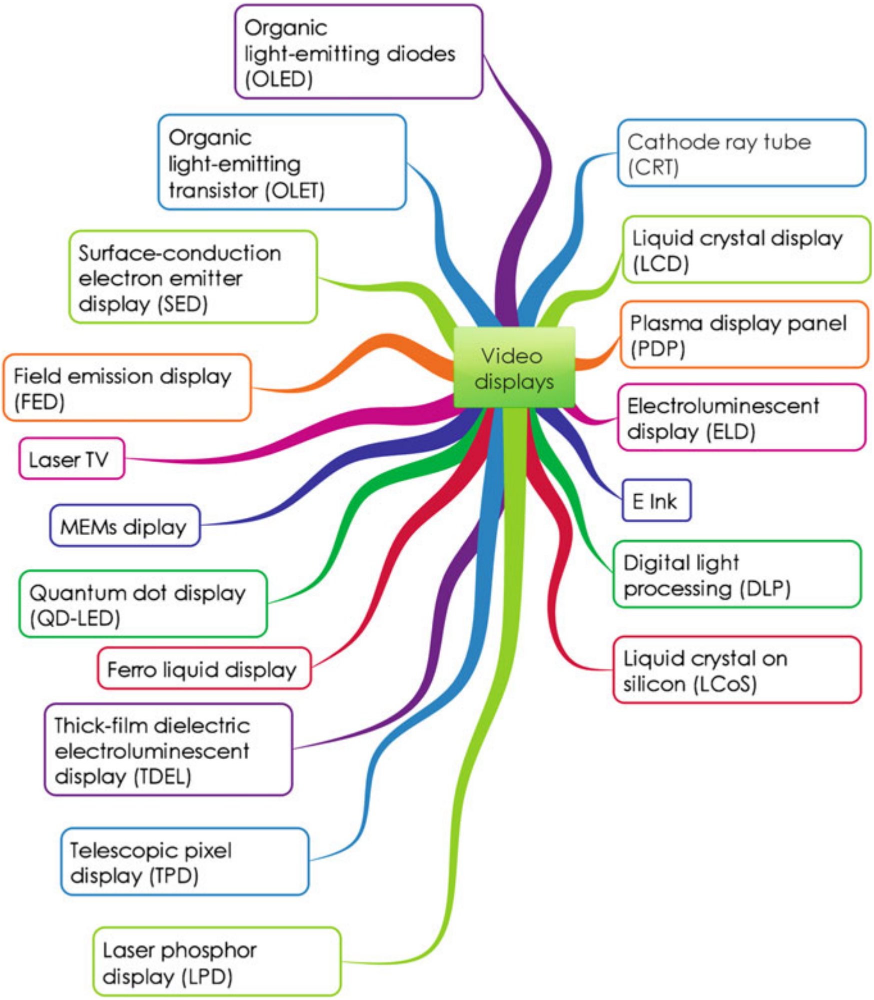


Fig. 7.16 Main technologies for video display

7.8 Displays

Displays are important human-machine interfaces to visualize data, pictures or videos. They are used in computers, TV, command displays, etc. They are widespread in daily life or working places. The technical goal of display manufacturers is to increase space resolution and the display speed of images while giving accurate colors. The economic goal is of course to decrease costs and increase resolution, response and color fidelity. Nanotechnology plays an important role in Organic Light Emitting Diodes (OLED) or Field Emission Displays (FED). More generally nanotechnology is used in the different components of displays: coatings, transparent electrodes, thin film transistors, etc. The main display technologies used today are shown in Figs. 7.15 and 7.16 but we shall just briefly describe the three most important ones.

In the past, cathode ray tubes (CRT) where used. It is an emissive-type technology. CRTs needed an electron gun, a high voltage to accelerate electrons which, when hitting a phosphor screen, produce colored light. CRTs have a fast response time and a high contrast but are cumbersome and need high power. They have been used for a long time as traditional TV and computer monitors. Since the electron beam sweep the screen from right to left and up to down in a raster pattern, this create some flicker.

Liquid crystal displays (LCD) are used in many applications. Their refresh rate is rather slow compared to other technologies and they have a restricted view angle. There are improved LCD technologies such as IPS (In-plane switching), developed by Hitachi in 1996, which provide wide viewing angles and good color reproduction.

LCD is a passive technology requiring backlighting and therefore energy to function. Actually there are three main types of LCD depending upon backlight used: transmissive, reflective and transflective.

Field emission displays (FED) are made of a matrix of cathode ray tubes designed at the microscopic scale. Each nanotube produces one color (red, green or blue). A pixel is made of three subpixel corresponding to the three colors. FEDs require less power than CRTs and about half the power needed in LCDs.

Chapter 8
Major Trends in Nanoelectronics

In the preceding chapter we have described the evolution of microelectronics toward dimensions belonging to the nanoscale area (<100 nm). The progresses in this field follow a road map discussed at the international level. This concerns microprocessors and memories addressed in the preceding chapter. Other aspects complement this domain, using nanotechnology, with other devices or functions giving the ability of treating, processing, and displaying information. There are also new phenomena appearing at the nanoscale which are different from those observed at larger scales. They open new possibilities for applications. Some developments will be briefly presented here but first start with presenting the main trends of the information and communication technologies.

Strong efforts in Research and Development (R&D) are made at the international level in order that microelectronics keeps going on and that new concepts emerge. Following the European Observatorynano project, the R&D in micro and nanoelectronics can be classified in four domains as indicated in Fig. 8.1.

8.1 More Moore

The "More Moore" domain continues to develop CMOS technologies with the goal of satisfying the Moore's law which basically assumes that the cost per transistor should be divided by two every 2 or 3 years. This requires improving several directions (Fig. 8.2):

- Density of transistors,
- Power consumption,
- Reliability and speed of the devices.

In particular, new manufacturing processes and new material developments are needed. We already discussed this area in the preceding chapter and shall just give here some complement.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_8,

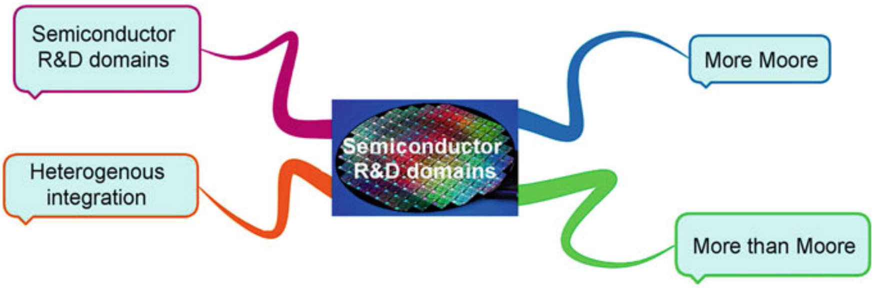


Fig. 8.1 The four main domains of R&D according to the ObservatoryNano project

Fig. 8.2 Different point of improvement in the "More Moore"

The smallest pattern size on a 300 mm silicon wafer which is used to manufacture integrated circuits (substrate) is today around 20 nm. Production at the 14 nm level is expected to start in 2013.

Many technological challenges should be investigated in order that the "More Moore" area continues progressing. Some of them are shown in Fig. 8.3. Indeed, there is a need to have a good basic understanding of the physics of transistors and other components. This requires research in many fields such as transport phenomena, statistical fluctuations, reliability, and the like.

By scaling down the dimensions of transistors, the gate oxide thickness becomes so thin that there is a significant current leakage due to tunneling effect. The gate, usually made of silicon oxide (SiO_2), has to be replaced by high permittivity materials. To accommodate with the new technology gate, silicon electrodes have to be replaced by another metal.

Nowadays, Intel uses metal compounds based on hafnium in its 45 nm node technology and below. With this new technology, the gate leakage is reduced by a factor greater than 100. This is worth since less energy is dissipated and the cooling power of the device can be reduced.

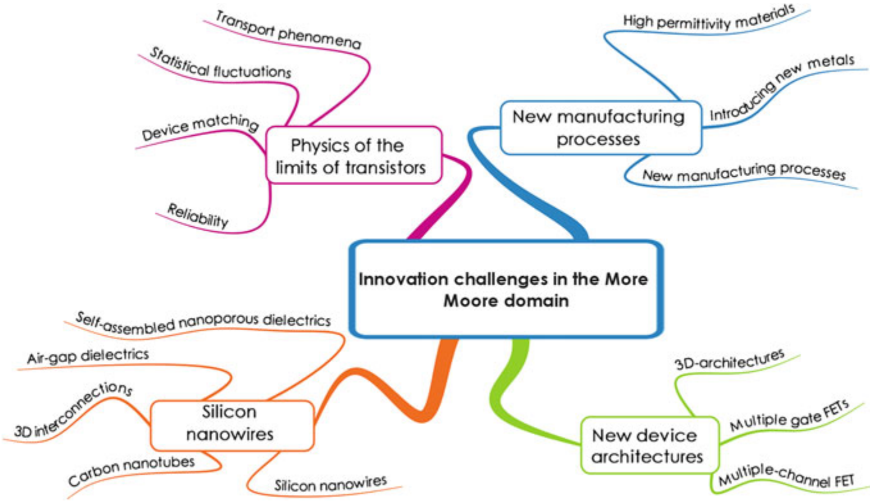


Fig. 8.3 Some innovation challenges that should be investigated for the More Moore domain. Figure built from the results presented in the ObservatoryNano project

New architectures are needed as the dimensions of transistors are scaled down to keep the same conventional functions and compensate for new phenomena appearing as the thickness of the gate decreases.

In order to reduce short channel effects FinFETs and Tri-gate transistors (Intel device structure) have received a lot of attention recently. The basic FinFET structure was introduced by C. Hu and colleagues from Berkeley in the late 1990s. The channel consists of a thin semiconductor (Si, or high mobility materials like Ge or III-V) "fin" surrounded by the gate electrode. This allows for both a better control of short channel effects and for a higher drive current. It is expected that the FinFET technology will be used for the technology generations at 20 nm and below. Figure 8.4 shows SEM and TEM pictures of a FinFET structure with 10 nm width of the fins and 45 nm FinFET pitch. Figure 8.5 shows a schematic view of high mobility FinFETs for the 10 and 7 nm generations.

Interconnections between the transistors are also a serious issue. For example, at very small dimensions, the resistivity of cooper increases. Consequently, the signal is perturbed as it travels through the interconnections.

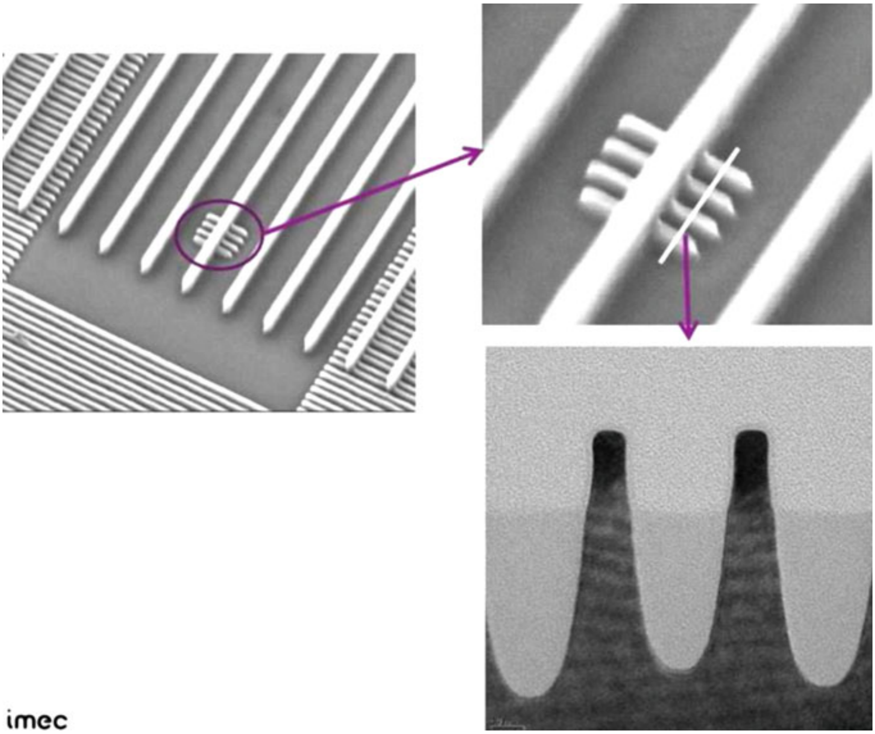


Fig. 8.4 FinFET SEM/TEM pictures (see text). Courtesy of IMEC (Belgium)

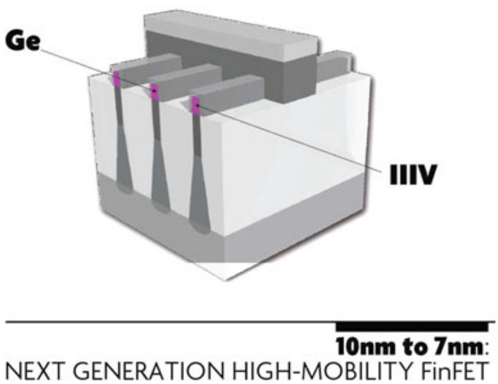


Fig. 8.5 High mobility FinFETs for the 10 and 7 nm generations. Courtesy of IMEC (Belgium)

Connecting billion of transistors

New integrated circuits require interconnecting billions of transistors. In order to do that more and more metal layers are needed and each of them is specially designed to transfer electronic signals over short or long distances. Stacking so many layers was only possible thanks to significant progresses in mechanical and chemical polishing techniques. Many technologies entering the manufacturing of integrated circuits have been improved and some new technologies developed. Let us quote a few of them. Reducing the dimension of a transistor increases the speed of the component because the electrons need less time to travel. This is unfortunately not true for interconnections because the characteristic time constant depends on the product of the resistance time the capacitance which increases as we go down to the nanoscale. This is why aluminum wires insuring the interconnections have been replaced by copper wires in nanocircuits. This change in the technology requires to perfectly encapsulate cooper wires otherwise the Cu atom could migrate and spoil the transistors. Low permittivity materials need to be used to electrically isolate these wires because silicon oxide has not sufficiently good properties at this dimension scale. Leakage current by tunneling through the gate insulator of a MOS transistor is also a relevant issue when the thickness of the gate is very thin (of the order of 1 nm). The insulator, which is usually silicon oxide, has to be replaced by other materials such as HfO_2, for example. Power consumption of transistors in their off-state occurs at low dimensions because of the gate is not able to perfectly control conduction in the channel. Using Silicon On Insulator (SOI) wafer is a solution of this problem.

8.2 More than Moore

The "More than Moore" domain aims to introduce nondigital functions such as those indicated in Fig. 8.6.

These new functions give an extra value to the device but their progress is slower than Moore's law. Among possible new functions, it is interesting to integrate the analog information indicated in Fig. 8.7.

Nanotechnology is expected to play a key role in the "More than Moore" domain. It can be closely involved in the development of sensors and actuators, RF technologies, power and thermal management, user interface, etc. Figure 8.8 summarizes some of the potential subjects where nanotechnology can contribute to a large extent.

Carbon nanotubes are already available commercially in electronic applications. Carbon nanotubes and silicon nanowires give new functionalities within a CMOS technology device.

Sensors and actuators are essentials to measure and monitor environmental parameters. An issue is to make them compatible with the CMOS technology. Nanoscale sensors, based for example on carbon nanotubes or silicon nanowires, have a great

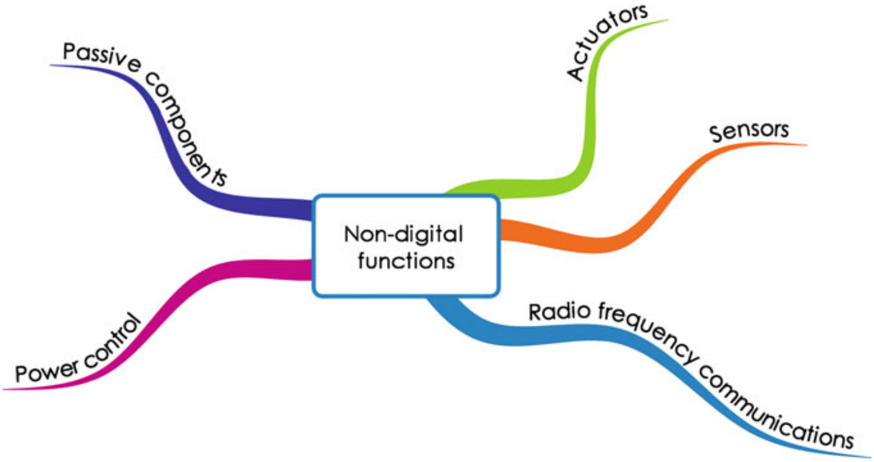


Fig. 8.6 Nondigital functions which should be useful for device integration

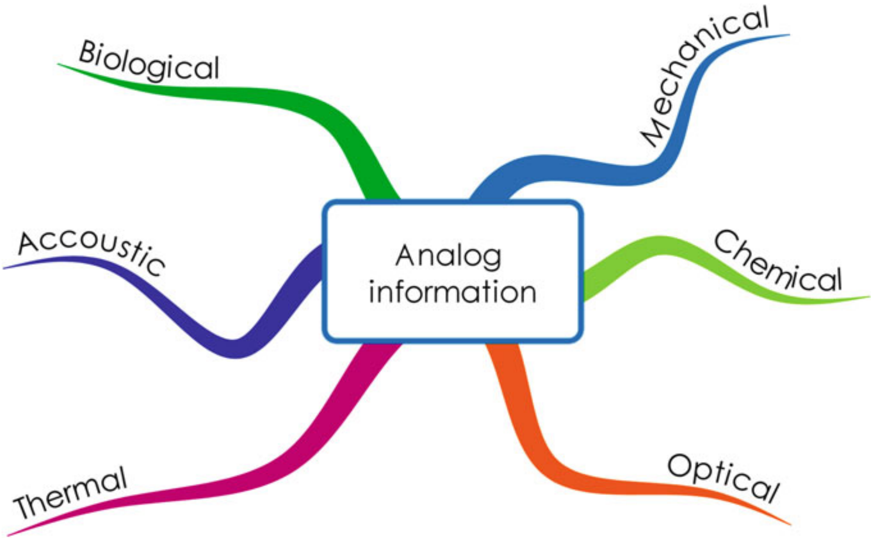


Fig. 8.7 Several analog information are useful to measure using micro and nanotechnologies

potential in terms of strain and deflection sensors. However, nanoscale devices generate small signals and new analog circuits are needed to make them large enough to be treated digitally. These circuits can be complex since one can have to deal with arrays of nanoscale sensors and not only single devices.

Biosensors are the natural complements of physical or chemical sensors with often a high selectivity and accuracy. It is a major challenge to integrate these sensors

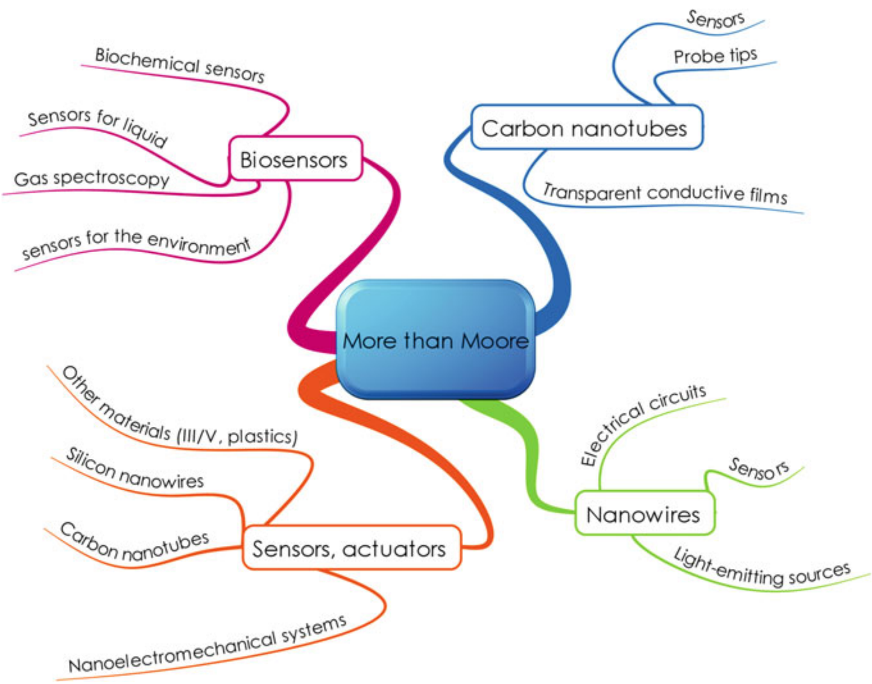


Fig. 8.8 Subjects in the "More than Moore" domain, where nanotechnology can be involved. The main fields are indicated in the boxes, at the first level of the mind map, and some applications are indicated at the second level

in CMOS technology. As far as biosensors are concerned, biocompatibility is an important issue.

8.3 Heterogeneous Integration

The "Heterogeneous integration" domain describes here the combination of the "More Moore" and the "More than Moore" domains. The aim is to integrate digital and analog components in a single integrated circuit. This is an important issue because it opens the way to smart systems linked together in digital networks and possessing several functions. The goal is of course to reduce the cost while increasing the performances. The packaging of such heterogeneous systems is an important issue. Indeed it is necessary to combine digital and nondigital components within a single device.

Heterogeneous systems also include the ability of 3D-integration. 3D-architectures are worth to decrease interconnection lengths and can also increase the speed of information treatment.

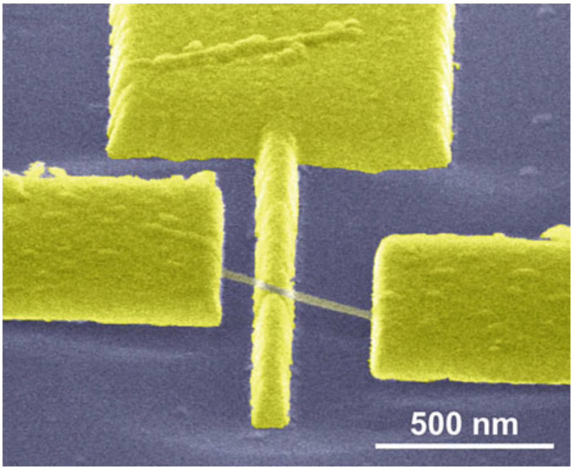


Fig. 8.9 Electromechanical component formed by a nanotube suspended between two gold electrodes. Image courtesy of CEA/LETI (France), Clef CEA n°52

Multifunctional systems linked into digital networks have a wide range of applications including healthcare, information and communication, entertainment, energy, environment, etc.

8.4 Beyond CMOS

The "Beyond CMOS" domain looks at breakthroughs which will either complement or replace today's technologies. Nanotechnology will provide solutions to many of the problems encountered. This is especially the case of molecular electronics which will be addressed in Chap. 10.

There are now several components involving carbon nanotubes or nanowires which have been made at the laboratory level. Resistors, diodes, switches, single electron transistors, electromechanical devices are such examples. Electromechanical devices, such as the one shown in Fig. 8.9, have potential applications in the domain of sensors or as high-frequency oscillators or resonators. A main issue is the ability to move and position the device at the right place on a circuit.

At large dimensions, electrons undergo a sequence of two-body collisions because their mean free path (the typical length separating two collisions) is smaller than the dimensions of the system. This is shown on top of Fig. 8.10. As the dimension of the device decreases and becomes of the order or smaller than the mean free path of an electron, the transport is ballistic and most of the collisions occur with the walls of the device (bottom in Fig. 8.10). If we consider that the electrons form an electron gas, one goes to a classical regime where transport phenomenon is governed by two-body friction to a new regime (Knudsen gas) where transport is dominated by one-body friction (collisions between the electrons and the wall).

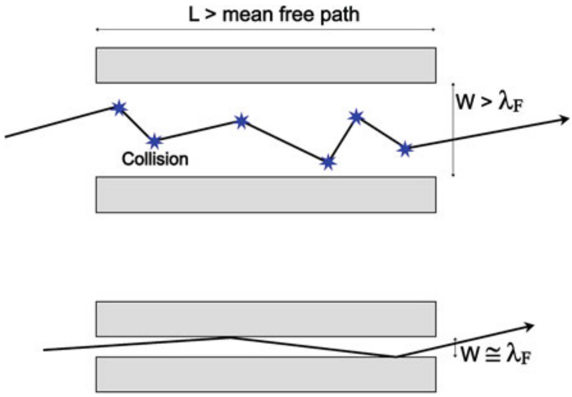


Fig. 8.10 Schematic illustration of the evolution of the mean free path as the dimension of the container decreases. At large dimensions, most of the collisions of a molecule of a gas occur with other molecules. At very small dimensions, most of the collisions occur with the wall of the recipient. We are in the Knudsen or ballistic regime

Controlling the strain of materials at the nanoscale is an important issue because it favors the transport of electrons and holes of small effective mass. A nanotransistor is a device in which the charge carrier transport is ballistic. The mean free path of the electrons, which is about 100 nm, is larger than the channel length of the nanotransistor. If the channel becomes shorter than 10 nm, charge carriers can tunnel from the source to the drain which increases charge leakage in the off-state of the transistor. This drawback can be reduced using Silicon On Insulator (SOI) material and making fully depleted SOI devices. Multigate electrodes are used to reduce this gate leakage. An example of such a structure is shown in Figs. 8.11 and 8.12.

Nanotubes and transistors

The first molecular transistor made of a semiconducting single-walled carbon nanotube was built in 1998 at the University of Delft in The Netherlands. The nanotube was connected to two metal electrodes. An external electrostatic gate allowed a current passing or not. Nanotubes are expected to be involved in several devices as conductors or semiconductors. Indeed, because of their small diameter charge conductors propagate in a ballistic manner giving them interesting electrical properties. It is possible to make field-effect transistors using carbon nanotubes operating in the ballistic regime. Other components can be made such as intramolecular junctions as the one shown in Fig. 8.13. It turns out that, depending upon the nature of the contact with the electrodes and the electrical characteristics of the nanotube involved, it can behave like a classical MOSFET transistor or like a Schottky-type transistor which is another way of functioning.

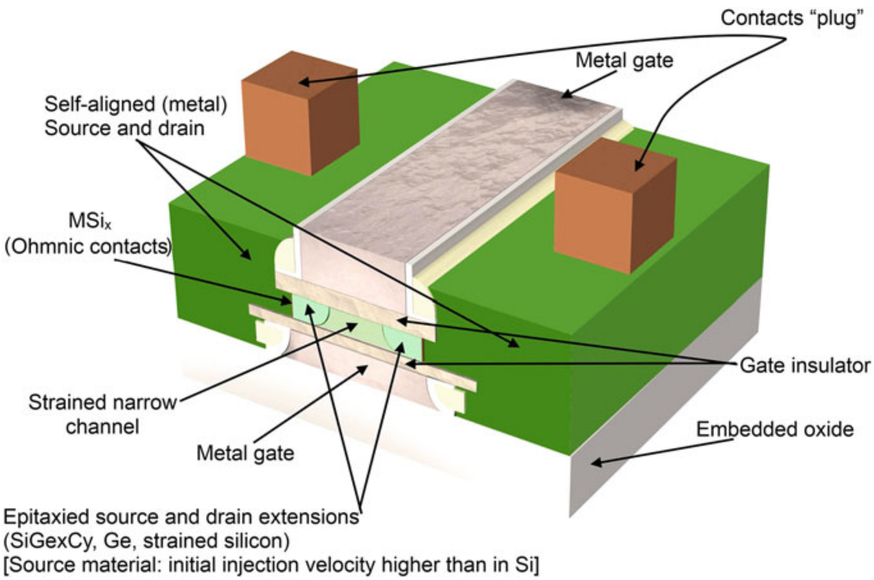


Fig. 8.11 Multigate MOS architecture with metal source/drain carrying extensions increasing the charge carrier injection speed into the channel (CEA-Leti patents). Image courtesy of CEA/LETI (France), Clefs CEA n°52

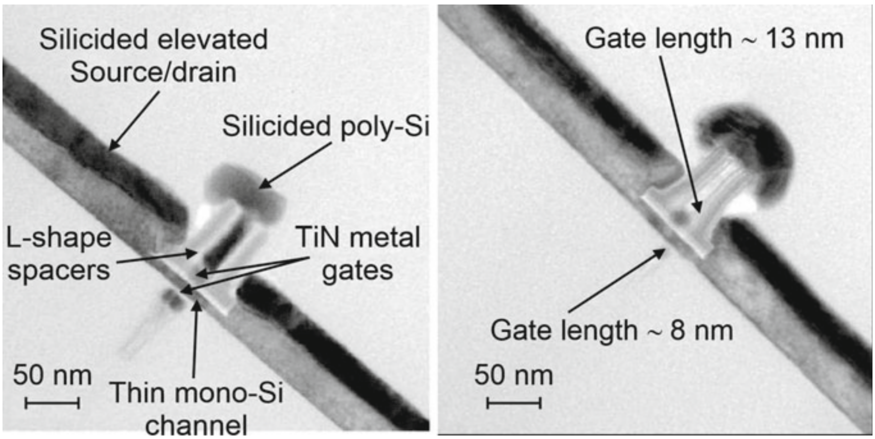


Fig. 8.12 Transmission electron microscope views of a 20 nm (*left* part of the figure) and 10 nm (*right* part of the figure) double-gate transistors fabricated at the Leti to better control leakage current between source and drain. Work of M. Vinet et al., IEEE Electron Devices Letters, May 2005. Image courtesy of CEA/LETI (France), Clefs of CEA n°52

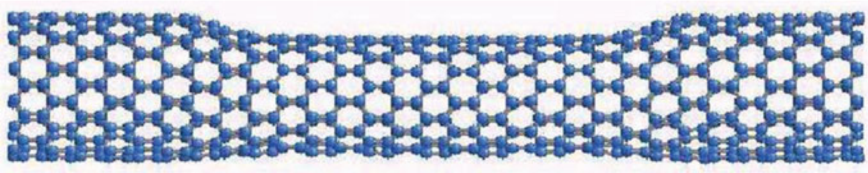


Fig. 8.13 Diagram of a metal/semiconductor/metal intramolecular junction with predicted stability. It consists in three segments of different helicities, Image courtesy of CEA/LETI (France). Clef CEA n°52

Chapter 9
Emerging Quantum Devices

Conventional microelectronic technologies have moved swiftly but continuously—based on a top-down approach—toward the nanometer range. Many commercial microprocessors or memories are now manufactured with minimum dimensions in the 20 nm range. There have been changes in some physical features but basically the architecture of the components remained the same. Outstanding progress in the technology domain has given the possibility to engrave silicon at dimensions which one could not imagine before because of physical limitations. Reducing even further the size of the components poses new problems because the physics can change. Classical physics has to be replaced by quantum mechanics and new phenomena appear while classical ones disappear. We shall now have a quick look to these emerging technologies in the information and communication domain.

The electron, an elementary particle

The electron is an elementary particle with a negative charge $-e$ (where $e = 1.6 \times 10^{-19}$ C is the elementary charge, that is the smallest charge which can be experimentally observed). It has an intrinsic angular momentum called spin which is equal to[a] $s = \frac{1}{2}\,\hbar$.

Spin is a pure quantum property of elementary particles although people try sometimes to make some representation in our classical world. In this case one could think that the electron rotates around one of its symmetry axis like a top. This is of course not true in the real world because an electron is a point particle. Furthermore, even if it would be a tiny sphere, such an object cannot rotate in the quantum world.

[a] $\hbar$ is the Planck constant (h) divided by 2π ($\hbar = \frac{h}{2\pi}$). It is often used as a unit to measure angular momenta. In this case one says that the spin of an electron is $\frac{1}{2}$. Although it is currently said that the spin of an electron is $s\hbar$ or s in units of $\hbar$, this is not the length of the spin vector because of quantum mechanical reasons. Actually, the length of the spin vector is equal to $\hbar\sqrt{s\,(s+1)} = \sqrt{3}\hbar/2 \approx 0.866\,\hbar$. However, the projection of this vector on the z axis can take two values: $\pm\hbar/2$.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_9,

Classically, the projection of the angular momentum (which is a vector) on an arbitrary axis takes values varying continuously between a minimum and maximum value. This is no longer true in the quantum world where discrete values are only possible. Therefore, for the electron, its spin is a vector with only two possible projections on a given axis which we shall refer to as z : $s_z = +1/2\,\hbar$ and $s_z = -1/2\,\hbar$. Because of its spin, a magnetic moment, which is a vector, is associated to each electron. Its value is proportional to the spin but points in the opposite direction. Similarly to the spin, the magnetic vector has only two possible projections on a given axis.

Shrinking the dimensions of microelectronic components has a limit. Below some size the physics governing processes changes and prevent the component to work in the same way as it was the case for a larger size. We are going in a new physical world with surprises and we shall touch a little bit this new area now.

9.1 Beyond the Quantum Wall

All our electronic devices are based on the transport of electrons. However, moving electrons cost energy which is usually supplied by the grid or the battery of the device. Information can be carried from one place to the other (within the digital circuits of a computer, for example) or treated (such as switching a bit from one to zero, for example) thanks to electric signals which are generated by transport of electrons. For instance, a Metal Oxide Semiconductor Field-Effect Transistor (MOSFET) which is a transistor for amplifying or switching electronic signals, needs about 1,000–10,000 electrons to switch from the insulating to the conducting state. Common sense tells you that if you could do the same job with fewer electrons you would need less energy to do it. This is what is observed as electronic circuits are shrunk in successive generations of microprocessor technologies. They consume less energy because transistors are smaller and need fewer electrons to function. That is the reason why the same processor engraved with different feature size has the different energy consumption to do the same job. The ultimate goal would be to be able to switch a transistor with a single electron. This is possible as we shall see below but a different physics is involved and the transistor has a different behavior compared to common transistors. Using fewer electrons to do the same function means also that the component is more sensitive to thermal background.

9.2 Coulomb Blockade

A thin insulating layer (one to several nm thick) between two conducting electrodes is a *tunnel junction*. In classical physics, no electron can flow through the insulating layer: it acts as a barrier against electron flow. However, quantum tunneling takes place in the case of a thin insulating layer (cf. Chap. 3) and electrons can go through the barrier. Applying a bias voltage between the two conducting electrodes generates an electron current and a tunneling current which turns out to proportionally increase with the bias voltage. This means that the insulating layer acts as a resistor. But putting an insulating layer in between two conductors is a capacitor. The thin layer is just the dielectric of the capacitor. Actually, the thin layer has a resistance and a capacitance.

We know that the electric charge is quantized and that e is the smallest amount of charge. Electrons have a $-e$ charge while protons a $+e$ charge. An electric current is just a flow of electrons. If the number of electrons is large, the flow can be considered as continuous. However, for small flows, the quantization of the charge can be seen.

Let us now consider a tunnel junction (thin insulator layer separating two conducting electrodes) at low temperature (typically below 1 K) and assume that the net charge on the electrodes is zero (top Fig. 9.1). Such a system is in its lowest energy state. Suppose that one electron is tunneling from left to right through the barrier. In the final state there will be $-e$ charge on the right and $+e$ charge on the left (bottom in Fig. 9.1). The $+e$ charge means actually that a hole is left as the electron as moved through the barrier. Between the initial and the final state there is a difference of $2e$. Tunneling an electron across the junction increases the energy of the system (the results are such that we have charged the capacitor having the thin layer as dielectric). The voltage difference U induced by the tunneling of an electron is equal to

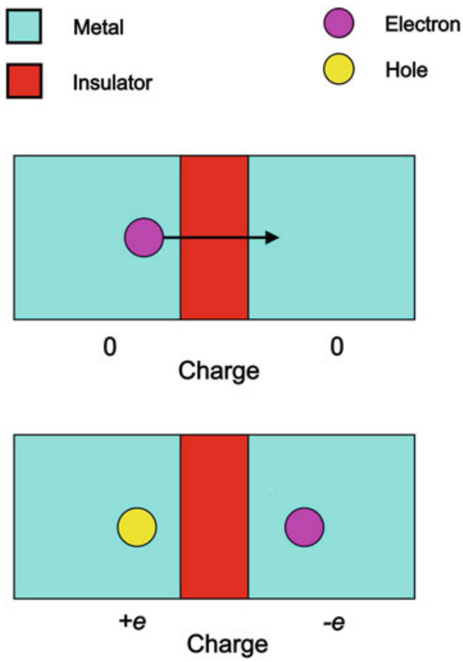


Fig. 9.1 If the two electrodes (*in blue*) are not charged electrically, an electron cannot spontaneously go across the insulator junction (*in red*) because it costs a lot of energy. Inspired from R. Turton, The Quantum dot, W.H. Freeman and Company Limited, 1995

$U = e/C$, where C is the capacitance and e the elementary charge. If the capacitance is very small, U can be large enough to prevent any other electron from tunneling.

We would get a similar situation by considering tunneling of an electron from right to left. Consequently, if no external energy is provided to the tunnel junction, such a tunneling effect is impossible: This is the essence of *Coulomb blockade*. Since there is no electrical current at low bias voltage, the resistance of the thin layer is not constant.

We shall now investigate how it is possible to move an electron across the barrier at no energy cost. For that we shall consider the same schematic device as in Fig. 9.1 but where the initial electrodes have a charge equal to $e/2$. It should be noted that the charge of a particle can only be an integer number of the elementary charge e. However, in a metal the motion of electrons and vibrations of ions induces on the electrodes a fluctuating charge which is not necessarily an integer of the elementary charge and varies continuously. In other words, the average value of an uncharged electrode is zero but fluctuations around this average value make the charge of the electrode to change as a function of time. This occurs for both electrodes. The situation shown on top of Fig. 9.2 can be reached during these fluctuations. In this case, an electron can go across the insulating junction because no energy is required. Look indeed at the situation before and after the electron transfer in Fig. 9.2. The charge on the electrodes has just changed sign but the energy of the system remains the same.

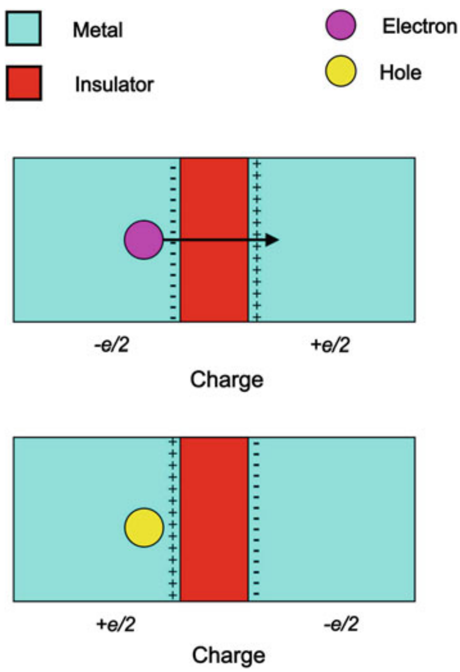


Fig. 9.2 If the two electrodes (*in blue*) are charged electrically with e/2, an electron can go across the insulator junction (*in red*) because it cost no energy. Inspired from R.Turton, The Quantum dot, W.H.Freeman and Company Limited, 1995

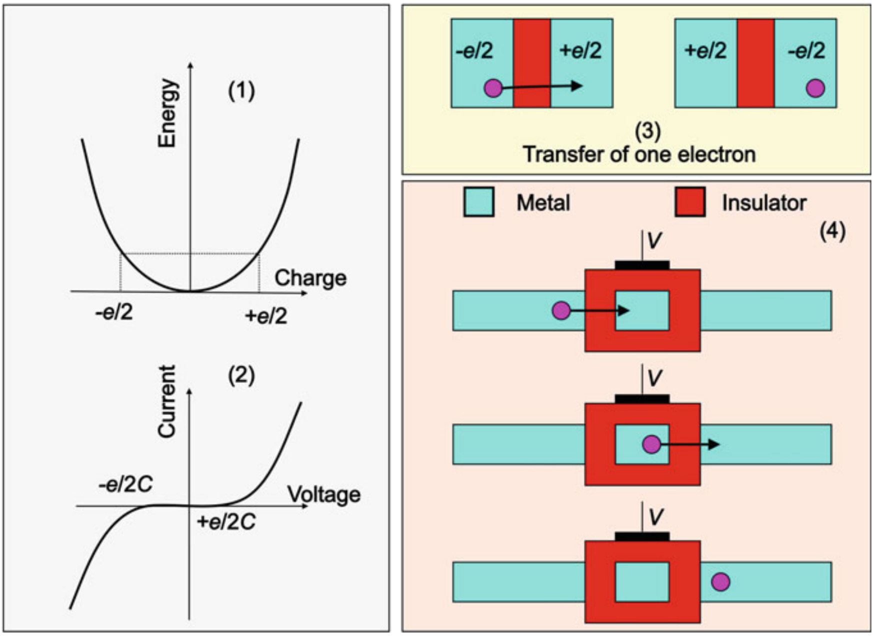


Fig. 9.3 About the 3 parts (*1*), (*2*) and (*3*) of the figure. (*1*) energy as a function of charge of system (*3*). (*2*) Current as a function of the voltage of system (*3*). (*4*) Device allowing the electrons to pass one by one (correlated tunneling). Courtesy of C. Ngô and H. Ngô, physique des semiconducteurs, Dunod, 2007

One electron can go across but not two at the same time otherwise energy would be needed.

A little more complicated device is shown in Fig. 9.3. Here, a small metallic dot (central electrode) is separated from external electrodes by two insulator junctions. A gate (in black) is used to apply an external voltage. Energy can be injected into the device and the charge in the dot can be externally controlled. If there is no charge in the dot, the Coulomb blockade mechanism prevents any electron to go across the junctions. Applying an external voltage allows to change this charge and when we get the situation shown in part (3) of the figure we trigger the mechanism discussed in Fig. 9.2. A second electron can come only if this electron has crossed the second junction using the same mechanism. Such a device allows electrons to go across the central electrode one by one. For this reason one has to deal with a correlated tunneling mechanism.

Conductance quantization

In Fig. 9.4 is shown a two-dimensional electron device fabricated by electron lithography. It is basically an electron waveguide with a constriction of submicron length and a width of the same order as the electron wavelength. The constriction of the device can be continuously changed using the field effect of a gate (see Fig. 9.4). If the width of the contact point is much smaller than the electron wavelength no electron mode is transmitted and the conductance is equal to zero. When the width of the contact point is equal to half the electron wavelength, a first mode is transmitted but the others are reflected. As a consequence, one reaches a plateau in the evolution of the conductance as a function of the gate voltage. The value of this plateau is the quantum of conductance. It equals to 2 times the electron charge divided by the Planck constant. The factor of 2 arises from the 2 possible projections along an axis of the spin of the electron (spin degeneracy). Increasing the gate voltage increases the number of modes that can be transmitted. In the figure, up to 3 modes are transmitted.

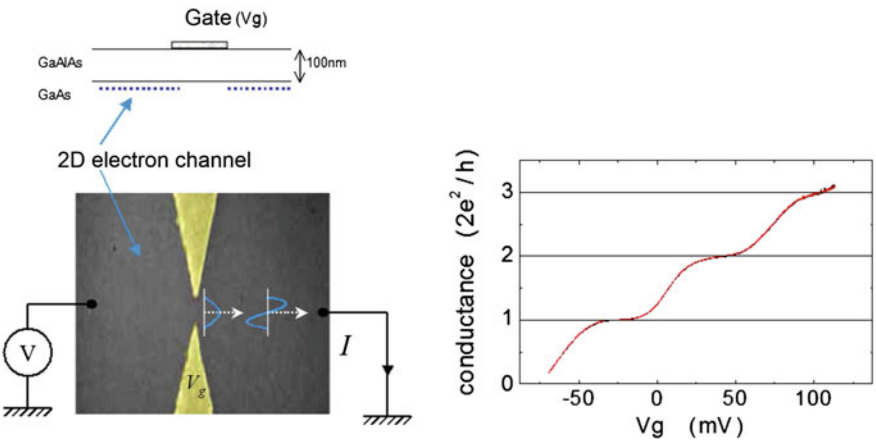


Fig. 9.4 The field effect of two grids, manufactured by nanolithography and evaporated above the surface of a conductor containing an electron layer, can be used to define a constriction of adjustable width. Conductance measures the transmission of electronic modes. Each one has two spin projection possibilities. By increasing the bias voltage, one can see in the figure that the number of modes increases from zero to three. The transmission of a mode is complete when a plateau is reached. Each plateau is an integer multiple of the quantized conductance $\frac{2e^2}{h}$. *The factor 2 comes from spin degeneracy. Image courtesy of CEA/LETI (France). Clefs CEA n°*52

9.3 The Single Electron Transistor

A transistor is a three-terminal device which has several applications such as signal modulation, amplification, voltage stabilization, etc. Depending upon the type of the transistor, an input current or an input voltage allows to control the current supplied flowing through the device.

The Coulomb blockade effect is observed in the single electron transistor device. The idea of making a single electron transistor goes back to the late 1980s. At that time, the technology node was close to 1 μm and about 10,000–20,000 electrons were moved during a switch on/off of a MOSFET transistor. Reducing this number of electrons reduces the energy consumption. The consequence of shrinking the dimensions of the transistor down to the 100 nm is to reduce the number of electrons involved to switch the transistor to a few hundreds. It allows also to increase the density of transistors per unit area. The limit of the game occurs when only one electron is involved. However, we are now going into a new domain of physics where tunneling effect can play a role.

A single electron transistor is similar to a MOSFET but functions differently. It is a switching device that controls electron tunneling to amplify current. It consists in (Fig. 9.5) a source, a drain and a very small island of a few nanometers or less built on a semiconductor substrate. The source and the drain are electrically isolated from the island with a very thin layer of silicon oxide playing the role of a tunnel junction. A tunnel junction consists of two pieces of metal separated by a very thin insulator (typically about 1 nm thickness).

An example of single electron field-effect transistor is shown in Fig. 9.6 as it is observed using imaging techniques.

A gate allows controlling the flow of electrons through the island by electrostatic influence. Indeed, the material separating the gate from the coulomb island is too

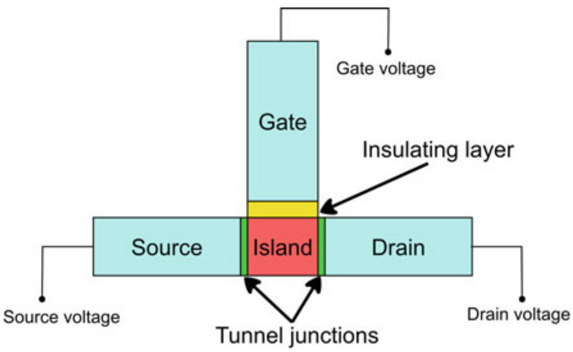


Fig. 9.5 Principle of a single electron transistor. An island (quantum dot, for example), is separated from the source and the drain by a very thin layer acting as a tunnel junction. The gate electrode is separated from the island by a thick material preventing electrons to tunnel through. The gate influences electrostatically the island

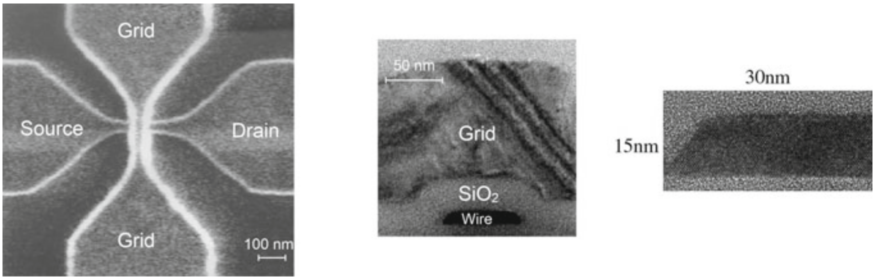


Fig. 9.6 Picture of a single electron field-effect transistor. Image courtesy of CEA/LETI (France). Clefs CEA n°52

thick to be a tunnel junction. The gate is a conductor isolated from the device by an insulator. An electron can only tunnel from the drain to the island and then from the island to the drain but the coulomb blockade may hinder this process which can be monitored by the bias applied to the gate. The number of electrons in the island can be precisely fixed and their flow in and out perfectly controlled. Such a transistor works like a leaky faucet drip where a drop represents an electron. The tap controls the number of drops which flows out. What is different in a single electron transistor is that the electrons flow one by one and at fixed values of the bias applied to the gate. Indeed, tunneling is a discrete process where the electric charge that flows through the tunnel junction occurs in multiples of the charge of electrons. The characteristic curve correlating the bias to the current is no longer an increasing continuous line but the series of discontinuous steps.

A single electron transistor has to be operated at very low temperature in order to get rid of thermal background which would make otherwise thermal excitations and make the device unusable. Other free electrons may also exist and travel over space (we feel static electricity for example with some of our clothes when they rub on a plastic material). In order to be able to use such a device at ambient temperature, a very small island (smaller than about 1 nm) should be made which is difficult today to manufacture in a reproducible manner at an industrial scale. Furthermore, the function done by the single electron transistor is different from the one provided by a MOSFET. This requires having different architectures to treat information. So far the single electron transistor is still studied in the laboratory and not yet ready for industrial use. Single electron transistors have been made using metal, semiconductor, carbon nanotubes, and molecules.

9.4 Applications of Single Electron Transistors

Single electron transistor is an emerging technology. It is still a tool in research and has no extensive applications. In order to be operated at room temperature, the island should have subnanometer dimensions. This is a difficult challenge at the industrial

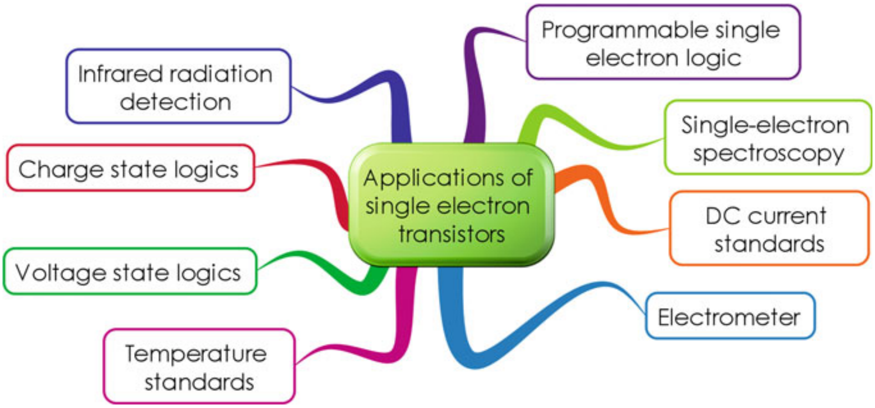


Fig. 9.7 Possible applications of single electron transistors. According to O. Kumar and M. Kaur, Int Journ of VLSI design and communication systems (VLSICS) Vol 1, 4, 2010

level especially to produce quantum dots in a reproducible manner. Small variations in shape can lead to large variations. Larger dimensions of the island require to operate at low temperature otherwise the thermal background prevents using the device. There are also other problems such as the tunneling of several electrons through different barriers at the same time or the background charge coming for example from impurities.

Nevertheless single electron transistors can be useful for specific applications in research. Figure 9.7 shows some of them.

A single electron transistor can be used as a very sensitive electrometer allowing to detect extremely low DC currents ($\simeq 10^{-20}$ A). It can also be helpful in standards (current, temperature). Programmable logic is also possible, thanks to the nonvolatile memory function of a single electron transistor and voltage state logics is also an application because the gate voltage controls the current flowing between the source and the drain part of the transistor.

9.5 Quantum Dots

Semiconductor quantum dots are nano-objects where electrons can be confined in a nanoscale volume. A nanoscale cubic box was an academic example discussed decades ago in quantum mechanics lectures to illustrate the appearance of discrete energy levels for a particle enclosed in a cube of very small dimensions. Two-dimensional or one-dimensional confinement is also possible. The nice thing is that these academic examples are now real objects that can be manufactured in the laboratory.

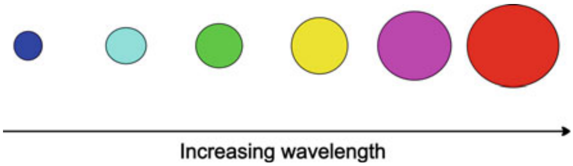


Fig. 9.8 Schematic illustration of the size influence on quantum dot emission. As the size of the quantum dot increases, we move from *blue* to *red*

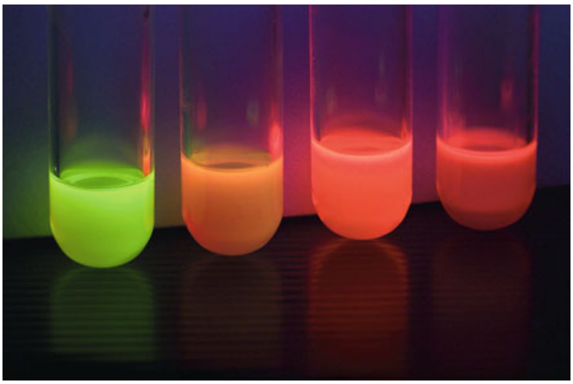
A quantum dot can be seen as an artificial atom, as far as its optical properties are concerned. Indeed; the energy level separation is inversely proportional to the square of the dimension of the confinement. Since the energy difference between two energy levels is directly connected to the wavelength absorption of the light, the color of a solution of quantum dots can be adjusted on demand. Similarly, exciting a quantum dot gives definite wavelength emission and therefore a specific color.

Figure 9.8 shows a schematic representation of the color emitted by excitation of quantum dots of different size. As the size increases, we move from the blue region of the optical spectrum to red.

Quantum dot is a term usually reserved to semiconducting materials. Quantum dots belong to the wider domain of nanoparticles which can be made out of different materials: metals, insulators, organic materials, etc. Nanocrystals correspond to an inorganic crystalline nanosized material. Nanocrystals can be made using a bottom-up manufacturing.

Atoms have discrete energy levels while semiconducting crystals have bands of energy. Semiconductor nanocrystals are intermediate structures and for that reason are called *artificial atoms*. It is possible to tailor their optical properties in such a way that they emit in the visible region or in the infrared region by choosing their geometrical dimension. As an example, Fig. 9.9 shows semiconductor nanocrystals of different size illuminated with ultraviolet light.

Fig. 9.9 Semiconductor nanocrystals of different sizes illuminated with ultraviolet light. Image courtesy of CEA/LETI (France). Clef CEA n°52



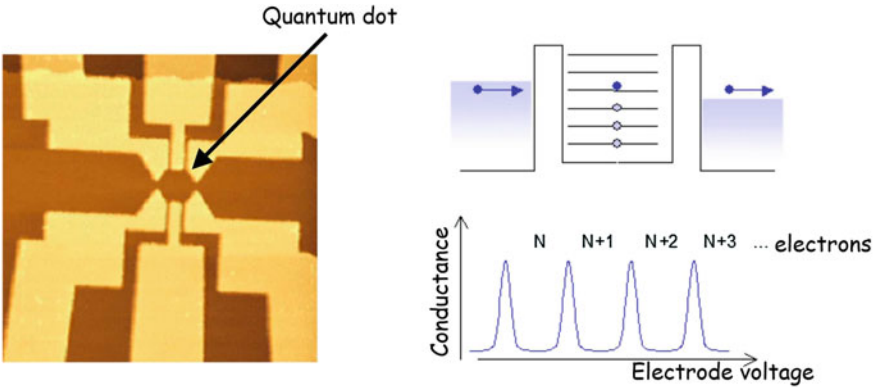


Fig. 9.10 Quantum dot separated from the contacts by a tunnel barrier. The conductance as a function of the gate voltage shows peaks corresponding to the situation where an electron arrives into the quantum dot. Image courtesy of CEA/LETI (France). Clefs CEA n°52

Figure 9.10 shows a real example of what has been presented in Fig. 9.3. A quantum dot is separated from metallic contacts by a tunnel junction. Confinement gives discrete energy levels (top right part of the figure). An electron can go across the barriers if its energy coincides with one of the energy levels. The energy levels can be changed continuously by changing the gate voltage. The Coulomb blockade mechanism discussed above prevents to have several electrons at the same time in the quantum dot. As a result, the conductance shows resonance peaks.

9.6 Spintronics

Electronics devices exploit usually the transport of electric charges. Semiconductor devices are based on the transport of electrons (negative charges) and holes (positive charges arising actually because of a missing electron). Spintronics, called also *spin electronics*, exploits—in addition to the charge of the electron—its intrinsic spin and the associated magnetic moment to develop electronic devices. The nice thing with the spin of an electron is that it can be oriented in one direction or the other. This means that the projection of the spin vector, measured on an axis, can have a different sign: $s_z = +1/2\ \hbar$ or $s_z = -1/2\ \hbar$ (Fig. 9.11). One usually says that we a have a spin-up or spin-down, depending on the sign of the projection with respect to the orientation of the spin vector. Exploiting the spin of an electron rather than its charge to carry or store information has advantages in terms of speed or energy consumption, for example.

The giant magnetoresistance (GMR) is a quantum effect observed in film structures made of alternating ferromagnetic and nonferromagnetic material layers. The thickness of the layers is typically of the order of 1 nm. This effect has been simultaneously discovered in 1988 by Albert Fert and its team in France,

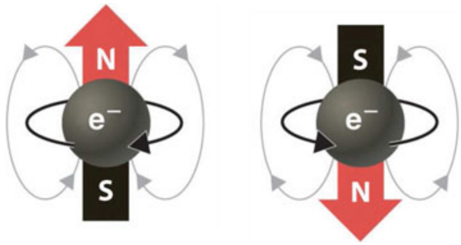


Fig. 9.11 An electron e^- in a magnetic field has two possible orientations associated with different energies, one called spin-up, aligned with the magnetic field, and one with spin-down (antiparallel to the magnetic field)

and by Peter Grünberg and its team in Germany. They were awarded for this discovery the Nobel Prize in 2007.

Magnetization

Spins can arrange in many different ways depending upon the external condition. If they are free to move at ordinary temperature, they are distributed at random as it is illustrated in the left hand part in Fig. 9.12. Applying a strong external magnetic field directed upwards will align these spin as shown in the right-hand part of Fig. 9.12. In a solid-state material, the spin can be oriented at random in a nonmagnetic material or aligned in a magnetic material (Fig. 9.13).

For the sake of simplicity we shall consider only a stack of three layers as shown in Fig. 9.14: a nonmagnetic tunnel barrier (in the order of about 1 nm thickness) sandwiched between two ferromagnetic layers (in real experiments, about 10 layers or more can be used). It turns out that the electrical resistance depends strongly on whether the magnetization of adjacent ferromagnetic layers is parallel or antiparallel (Fig. 9.15, top and bottom). When the magnetizations are parallel, the magnetoresistance is small, i.e., high spin current, while it is larger if they are antiparallel (low spin current). This phenomenon is basically used in hard disk drives.

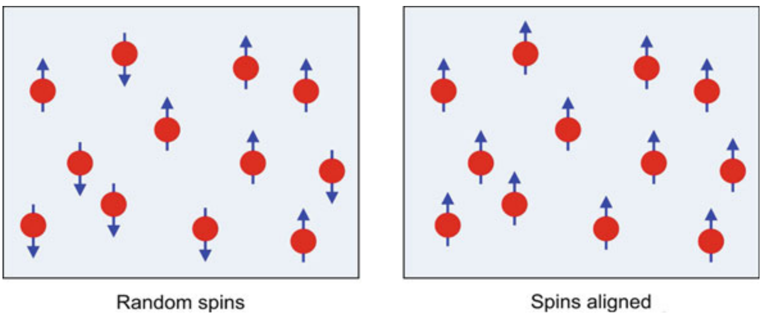


Fig. 9.12 In the *left-hand part*, spins are oriented at random while, in the *right-hand part*, they are aligned along a strong applied external field. Inspired from S. D. Sarma, Spintronics, American Scientist, Vol 89, 516, 2001

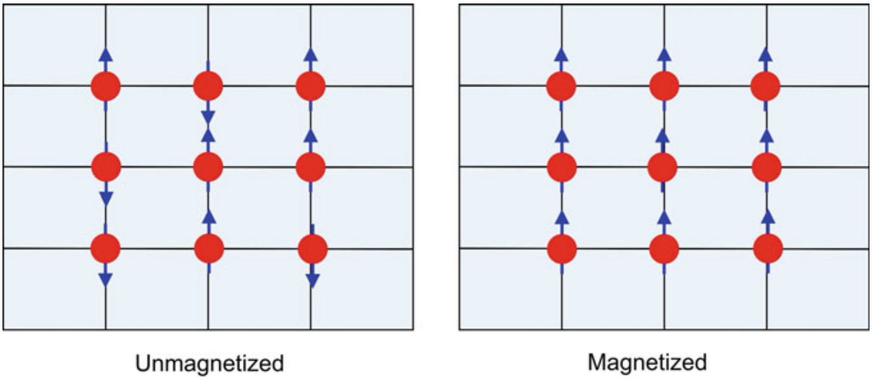


Fig. 9.13 In the case of a crystal where the spins are located at the sites, the spins can be oriented at random in the case of an unmagnetized material or aligned if the material is magnetized. Inspired from S.D.Sarma, Spintronics, American Scientist, Vol 89, 516, 2001

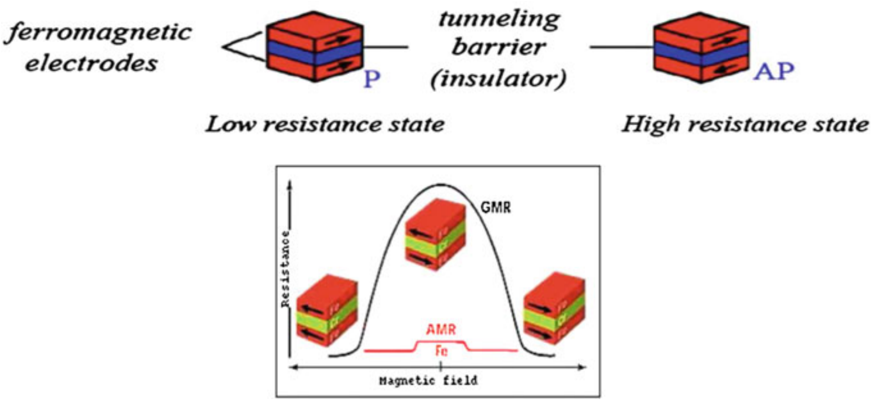


Fig. 9.14 Schematic illustration of magnetic tunnel junction of two ferromagnetic layers separated by a thin barrier layer [A. Fert, Thin Solid Films 517, 2 (2008)] (*left*); magnetoresistance in dependence of external magnetic field (*right*)

Exploiting the spin of an electron rather than its charge to carry or store information has advantages in terms of speed or energy consumption, for example.

Main fields of applications and new directions are the following:

- spin for storage and reading information
- spin for memory, reading and writing (spin-RAM)
- spin field-effect and tunnel junction devices
- spin optoelectronics
- spin galvanics
- spin quantum computing

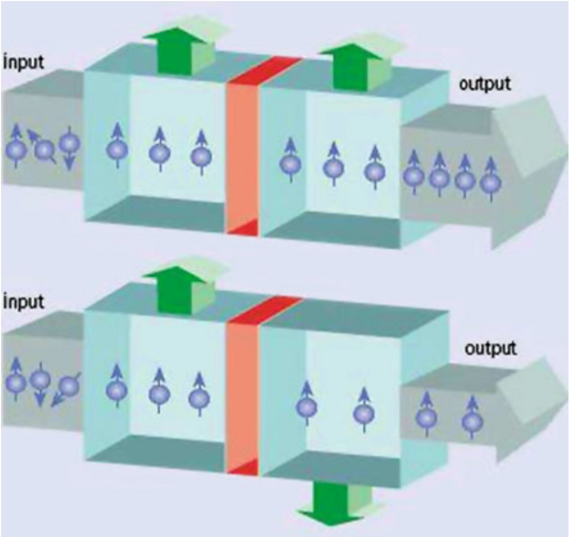


Fig. 9.15 Illustration of magnetic tunnel junction composed of two ferromagnetic layers separated by a thin barrier layer (*red*). When the magnetization of the two ferromagnetic layers is parallel, spin-up electrons can tunnel through the barrier in the second ferromagnetic layer (*top*). When the two layers are antiparallel, however, tunneling is suppressed (*bottom*)

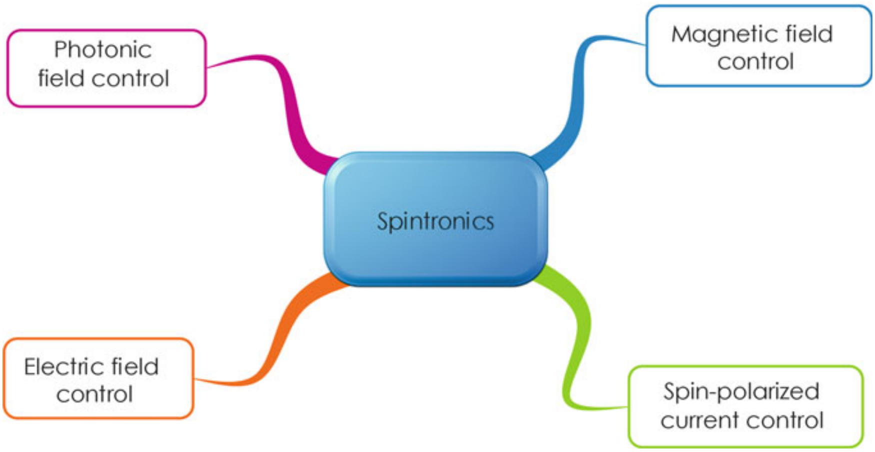


Fig. 9.16 Sectors where spintronics can play a role

We are acquainted to use devices using a magnetic field to control the magnetization orientation of materials and by this process the information stored at that point. Other possibilities of control are now possible with spintronics. They are indicated in Fig. 9.16.

In addition to magnetic field control, it is also possible to control via spin-polarized electric currents, electric fields or photonic fields. This opens a large number of possible applications. For example, it is possible to use a spin-polarized electric current to switch the magnetization of a nanoscale memory cell. Electric fields can change the magnetic anisotropy of ultrathin structures. Ultrafast light pulses are another way to switch the magnetization of nanoscale materials.

Because spintronics devices are very small it is possible to study ultrafast phenomena. This is interesting in the domain of imaging and kinetic studies at a scale of picoseconds or femtoseconds.

Spintronics can be based on semiconductors or metals. Several applications using metal spintronics exist, especially in the storage domain. However, semiconductors spintronics offers a lot of potentialities because of their possible integration in semiconductor electronics.

9.7 Quantum Computing

Quantum computing uses the properties of atoms, molecules, photons, etc., to perform processing and memory tasks. Today's computers manipulate bits which can be in two states labeled 0 or 1. Quantum computers, which are for the moment at the research stage, use qubits (quantum bits) which are not limited to two states. All the possibilities, between 0 and 1 are in principle possible. Indeed, a qubit, which is the unit of quantum storage information, can be a superposition of the two basic quantum states. Starting from quantum states, multiple states can be made giving the potential to manufacture much more powerful computers than today's supercomputers.

Quantum entanglement

If a quantum system like a particle is in an eigenstate, a measurement of an observable quantity can be predicted for sure. For example if we have prepared a particle of spin $\frac{1}{2}$ in a state where the projection of the spin is $+\frac{1}{2}$, we will get for sure $+\frac{1}{2}$ if we measure this quantity. Generally, a system is not in an eigenstate and we can just say that there is some probability to measure a given value of the observable. In the example taken above, if we have a particle with a spin $\frac{1}{2}$ but we do not know the spin projection and if there is no external applied magnetic field, then if we measure this projection it can be either $+\frac{1}{2}$ or $-\frac{1}{2}$ with the same probability. It should be noted that if we have measured $+\frac{1}{2}$ once we shall measure $+\frac{1}{2}$ for any subsequent measurement. If we now consider two independent particles of spin $\frac{1}{2}$ $\boldsymbol{A}$ and $\boldsymbol{B}$, and no external magnetic field applied, we can measure, independently a projection $+\frac{1}{2}$ and $-\frac{1}{2}$ with an equal probability. A measurement of the spin projection of $\boldsymbol{A}$ is completely independent of that of $\boldsymbol{B}$.

Let us now prepare initially a system of two particles $\boldsymbol{A}$ *and* $\boldsymbol{B}$ *in such a way that the total spin of the system is equal to zero. This means that if the projection of the spin is* $+\frac{1}{2}$ *for* $\boldsymbol{A}$ *it should be* $-\frac{1}{2}$ *for* $\boldsymbol{B}$ *and vice versa. The sum of the total projections should be zero indeed. We suppose that the system of the two particles is isolated in the sense that they have no interaction with the medium. Suppose now that the two particles separate (the system decays, for example in* $\boldsymbol{A}$ *and* $\boldsymbol{B}$*).* $\boldsymbol{A}$ *and* $\boldsymbol{B}$ *go away in opposite direction and can reach very large distances. Even if they are separated by large distances the two particles stay correlated (they are entangled). If we measure the spin projection of particle* $\boldsymbol{A}$ *we can get* $+\frac{1}{2}$ or $-\frac{1}{2}$ *with a probability of 0.5. Suppose that in the measurement we find* $+\frac{1}{2}$*. By this measure we fix definitely the value of the spin projection of particle* $\boldsymbol{B}$*. If we measure the spin projection of* $\boldsymbol{B}$ *we find inevitably* $-\frac{1}{2}$*. If, on the contrary the measurement on* $\boldsymbol{A}$ *had given* $-\frac{1}{2}$ *we would have found* $+\frac{1}{2}$ *for* $\boldsymbol{B}$ *since the spin of the total system is zero. This is true (and this theory of entanglement has been checked experimentally) even if the particle is far away. The information is in the system and has not to propagate over the space. It is instantaneous and does not depend on the speed of light. When such a correlation exists one says that the particles are entangled.*

Entanglement is a nonlocal property of quantum objects and has applications in quantum cryptography.

In a quantum computer, the data and the operations to be performed on the data are based on quantum properties such as superstition of states and entanglement just discussed in the box. So far experiments have been made to validate the concept on simple operations and a small number of qubits. We are, however, far from big quantum computers which could solve problems much faster than classical computers.

Quantum cryptography encompasses cryptography but also the possibility to break cryptographic systems. It is an application of entanglement. It can provide unbreakable cryptosystems because it is impossible to measure a quantum system without disturbing it. Consequently if someone has interacted with your message, you know it for sure.

9.8 Nanophotonics

Nanophotonics deals with light-matter interactions occurring at the nanoscale. More precisely the US academy of sciences defines nanophotonics as "the science and engineering of light-matter interactions that take place on wavelength and subwavelength scales where physical, chemical, or structural nature of natural or artificial nanostructured matter controls the interactions".

9.8.1 Controlling Light

The wavelength of visible light goes typically from about 380–780 nm, which is far above the nanoscale limit fixed around 100 nm. More precisely, nanophotonics is concerned when the interactions are controlled by the physical or chemical properties of nanostructures or by their structure.

Nanophotonics can be divided in three main broad areas depending on the nanoscale confinement which is involved. They are indicated in Fig. 9.17. There can be confinement of matter, light, or nanoprocesses.

Finally, nanoscale optical memory or nanoscale conformation dynamics concerns are examples of applications of the nanoconfinement of photoprocesses. The aim of this area of nanophotonics is to control photoprocesses in nanodimensions.

These points are summarized in Fig. 9.18.

Waveguides allow confining and guiding waves such as electromagnetic waves and in particular visible light. Examples are shown in Fig. 9.19. Optical fibers are a common example of waveguides. The photons trapped inside the fiber cannot escape except at the end of the optical fiber. A waveguide has generally a structure made of a material with a high index of refraction surrounded by a material with low index of refraction which constitutes the cladding. Waveguides are useful for optical interconnections. They could replace some of the metal interconnections but it should be kept in mind that even if light is faster to propagate in the material of a wave guide compared to electrons in a metallic wire, the distance over which light has to travel should not be too long otherwise electrons will be faster if the length of the interconnection is much shorter than that of the light interconnection.

A point concerns the conversion of an electronic signal to an optical signal and vice versa which introduces complications, extra energy consumption and delay. A great interest of optical interconnection and treatment is that the energy dissipation of light is negligibly small compared to that of electrons (Joule effect).

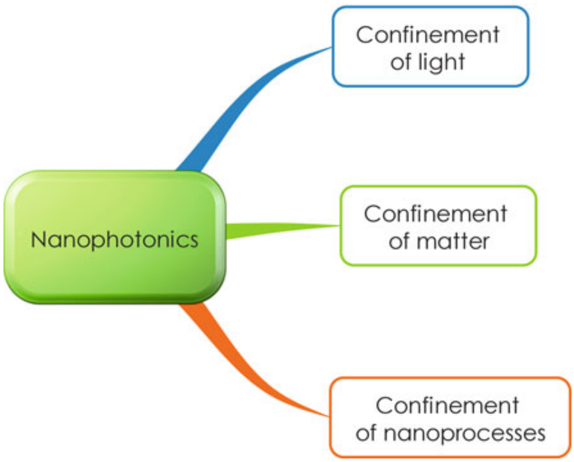


Fig. 9.17 Nanophotonics encompasses several nanoscale confinements indicated in the figure

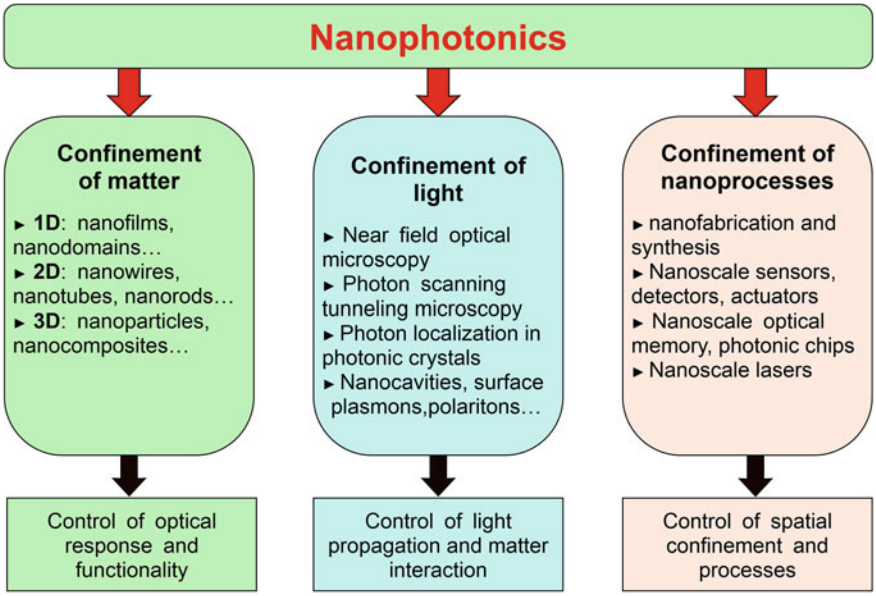


Fig. 9.18 Block diagram representing the main fields and applications in nanophotonics. Image courtesy of Paull Drude Institute, Berlin

Confinement of matter concerns nanoparticles or nanocomposites, for example. Here again it gives the ability to localize matter in nanodimensions in order to control the optical behavior and functionality.

Nanowires have a diameter in the nanometer range. Other Semiconducting nanowires can be made and used in the laboratory. They are usually synthesized by vapor–liquid–solid growth and can be doped to give p or n-nanowires. Nanowires of GaP, GaN, Si, and InP have been made. Field-effect transistors using nanowires have been realized. Si-nanowires are of special interest because they can be more easily used in the electronics silicon industry. An example of nanowires synthesized by vapor–liquid–solid deposition is shown in Fig. 9.20.

Nanoscale optical memory or nanoscale conformation dynamics are example of applications of the nanoconfinement of photoprocesses. The aim of this area of nanophotonics is to control photoprocesses in nanodimensions.

9.8.2 Photonic Crystals

Photonic crystals belong to the nanophotonics domain but are treated separately due to their importance. The first studies on the subject go back to 1887 but a century was needed before substantial progress was made, thanks to the advances in technology and characterization.

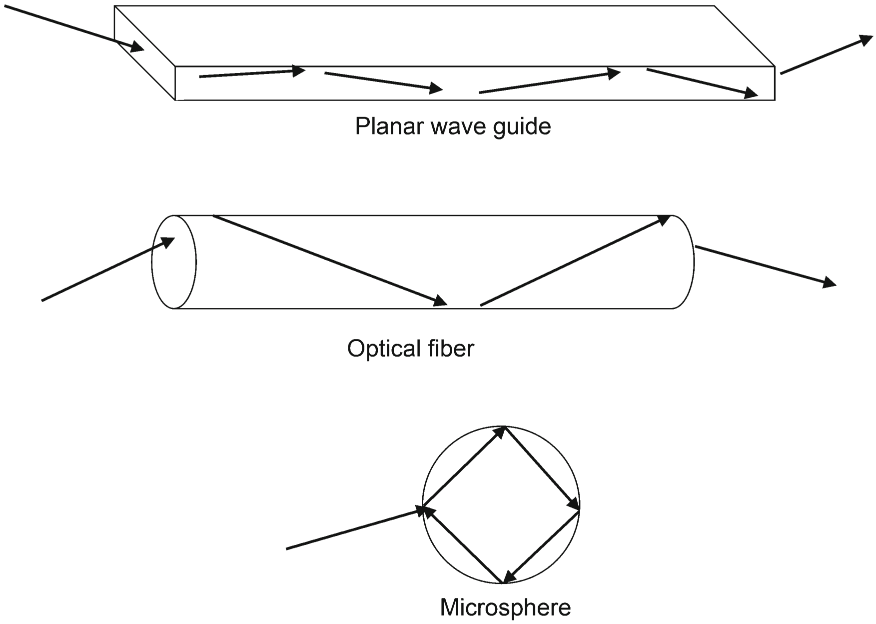


Fig. 9.19 Drawing of different light confinement which can be performed in nanophotonics. A planar waveguide corresponds to 1D confinement, an optical fiber to a 2D and a microsphere to a 3D confinement. Inspired from A. Sharma, Nanophotonics, an overview, NSF-RISE Workshop (2007)

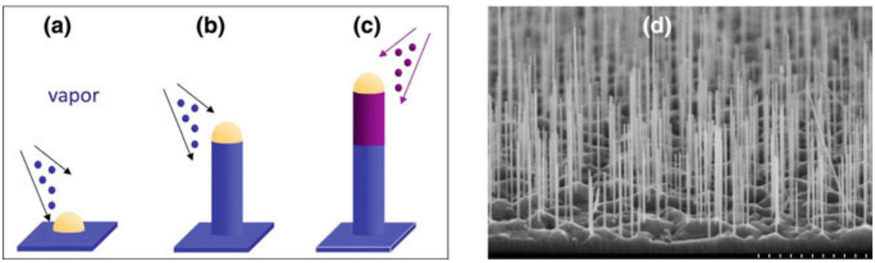


Fig. 9.20 Formation of semiconductor nanowires via vapor–liquid–solid growth mechanism, first introduced by Wagner and Ellis at Bell Labs in 1964. **a** Deposition of catalyst, eutectic formation with vapor. **b** Nucleation at catalyst/substrate interface, growth of nanowires. **c** Formation of axial nanowire heterostructures. **d** SEM image of GaAs nanowires on Si (Image from PDI) Scale bare: 1 µm

Photonic crystals are artificial periodic nanostructures with a period of the order of the optical wavelength. More precisely, the periodicity should be of the order of half the wavelength of the light to be diffracted. This means about 350 nm for red light and about 200 nm for blue light. Photonic crystals have some analogy in terms of structure to a solid-state crystal (semiconductors or insulators). Because of its periodicity, a solid-state crystal has a bandgap (or an energy gap) which is a range of energy without electron states located in between the valence gap filled with electrons in the case of semiconductors or insulators and the conduction band which is empty.

Photonic crystals have bands of photons and a photonic bandgap can be present. It is also possible, with a photonic crystal, to make a localization of light. A photonic crystal is characterized by its dimensionality. It can be 1D, 2D, or 3D.

The photonic bandgap corresponds to energies for photons which are forbidden. It means that photons with incident energy in this gap cannot enter the crystal. On the other hand, electrons cannot emit light in this gap. A photonic crystal acts an optical insulator for certain values of the wavelength. In the same way as an electrical insulator prevents electrons to travel through, optical insulators prevent light to go through.

Semiconductor can be doped. It is possible to do so in the case of photonic crystals. Impurities (atoms or defects) are introduced in the gap to control light propagation and radiation.

From electrons to photons

In optics the goal is to completely control light propagation at any scale and find materials to do it.
Semiconducting materials based on crystal lattices can do that for electrons. A crystal is a periodic arrangement of atoms or molecules. Diamond, for example, is a crystal. A crystal lattice behaves like a periodic potential whose properties depend upon the geometry of the lattice and which can be modified by adding dopants in the crystal. Electrons can behave, under certain circumstances fulfilled inside the crystal, as waves and new properties compared to a classical behavior of electrons happen. For example electron waves meeting certain criteria can propagate without scattering from the constituents of the crystal. There are situations in semiconductor crystals like silicon or germanium, or insulators like diamond, where electrons are forbidden to propagate with certain energies. This is because there is a gap in the energy band structure of the crystal separating the valence band from the conduction band.
The photonic crystal is the optical analogue of the semiconductor or insulator crystal. However, instead of having atoms or molecules at the sites of the crystal, there are pieces of material with different dielectric constant. As a consequence, the periodic potential existing in semiconductor crystals is replaced by a periodic dielectric function, i.e., a periodic index of refraction. By choosing properly the dielectric material and its arrangement, it is possible to make photonic bandgaps. In such a case, light with a certain wavelength cannot propagate in certain directions.

If, in some range of wavelengths, a photonic crystal prevents the propagation of light in any direction and any polarization of light, the photonic crystal is said to have a complete photonic bandgap. Three-dimensional photonic crystals, where the dielectric lattice is periodic along the three axes have this property.
Photonic crystals also allow controlling light in a similar way as metallic waveguides and cavities are used to control microwave propagation. With 1D photonic crystal, for example, it is possible to reflect light incident from any angle and any polarization.
A 1D photonic crystal is periodic in one direction. In a 2D photonic crystal the periodicity is along two directions and a 3D photonic crystal is periodic along three directions. There are photonic crystals in nature for example in the wing of the morpho rhetenor butterfly or in a peacock feather. This structure gives them beautiful colors because of their specific optical properties.

Photonic crystal and complete photonic bandgap systems can be engineered on demand. Several parameters can control that. They are indicated in Fig. 9.21. One can play on the periodicity of the refractive index to design photonic crystals of different dimensionalities (1D, 2D, or 3D). The type of crystal lattice (body centered cubic, simple cubic, face centered cubic, simple hexagonal, or body centered cubic) determines the symmetry of the lattice. A variation of the topology affects the photonic band structure. The lattice parameter is the distance separating the building blocks of the lattice. This distance determines the range of wavelength where the photonic crystal will work. The filling fraction of the lattice, which is the relative amount of refractive material in the lattice, has also an influence on the photonic bandgap. The refractive index contrast is the ratio between the high dielectric constant of the material located at the site and the low dielectric constant of the rest. This parameter

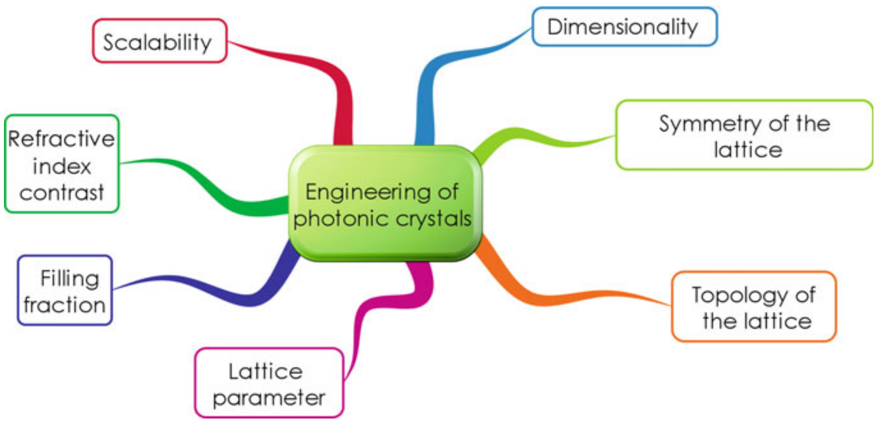


Fig. 9.21 It is possible to play on several parameters to make photonic crystals with required properties

has an influence on the scattering process of light. The scalability allows, by changing some of the length parameters, to have similar properties at different wavelength.

The domain of application of photonic crystals is very rich and we shall just quote here a few of them.

Photonic crystals without complete photonic bandgap can be used as supercollimators or superlenses. The negative index of refraction which can be obtained can be used for these applications. In the same spirit, a super prism effect is obtained with two different photons arriving at the same angle of the crystal but with a slightly different energy. This could have applications in integrated multiplexers.

There is an interest to develop complete integrated circuits where photons carry information instead of electrons. This comprises in particular waveguides based on 2D photonic crystals. As an illustration, Fig. 9.22 shows two examples of wave guide which can be obtained.

Optical fibers based on photonic crystal can already be found commercially. Bragg gratings are an example of a 1D photonic crystal which can be used to measure concrete constraints in dams, for example. A 3D photonic crystal can be either isotropic or anisotropic. Anisotropy is useful to design an optical switch.

Confinement of light includes, for example, near-field and far-field optical microscopies. It comprises also second-harmonic generation microcopies, nanocavities (as shown at the bottom in Fig. 9.23). Basically, the aim is to be able to localize light in systems of nanodimensions and control its propagation and interaction with matter.

Photonic crystals have also applications in the microwave domain. They help to optimize the performance and directionality of microwave antennas.

It is also possible to make microcavities where it is possible to trap light for a long time. Putting defects in crystals trap resonant modes. It is also possible to get tunable cavity modes.

9.8.3 Plasmonics

Metallic structures provide an efficient way to manipulate light at length scales smaller than the wavelength of the photons involved. This is so because at the interface between a dielectric (such as silica glass) and a metal (such as silver or gold) a surface plasmon oscillation can be generated. A surface Plasmon is a coherent (collective) electron oscillation (and they are plenty of electrons at the metal surface) propagating along the interface together with the electromagnetic wave associated with light. Plasmons are the quasiparticles associated to a Plasmon oscillation in the same way as photons are the particles associated with an electromagnetic wave. The nice thing is that the wavelength of surface plasmons is much smaller (of the order of ten times less) than the wavelength of photons. For example, using a He-Ne laser to excite a silica-silver interface with a wavelength of light at 633 nm excites a surface plasmon oscillation at 70 nm. Tuning the laser wavelength around the Plasmon resonance decreases the surface plasmon wavelength down to the nanometer range. This gives

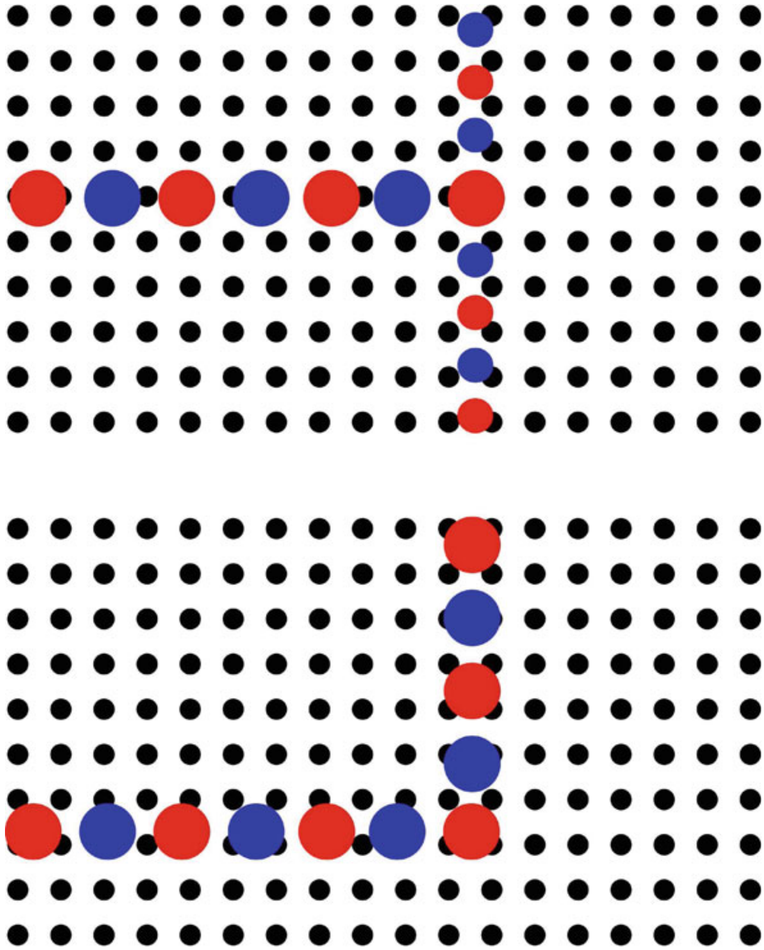


Fig. 9.22 Two schematic examples of waveguides using photonic crystals. On *top* a wide-angle splitter is shown and at the *bottom* a lossless sharp bend wave guide. The lattice is represented by the *small black dots* which correspond to high dielectric material. The light wave is represented by alternating *b*lue and *red dots*

the possibility to make plasmonic nanocircuits to treat light at dimensions smaller than the wavelength.

It is possible to put a light source, such as a quantum dot, close to the metal and excite surface Plasmon oscillations. If it is a light-emitting diode (LED) put in the plasmonic structure, it is possible to electrically excite surface plasmon oscillations. Conversely, it is possible to enhance LED emission by surface plasmon waves.

Arrays of metal nanoparticles can be used as optical waveguides because plasmon waves can linearly propagate along nanoparticles chains.

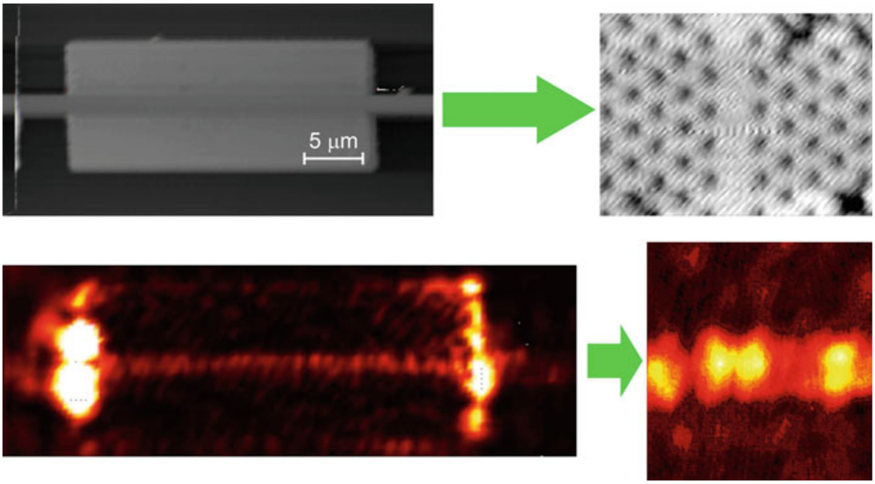


Fig. 9.23 Local probe view (known also as a near-field image) of the optical wave propagating in a photonic crystal waveguide. The image on *top* is a topographic view of the guide while the image at the *bottom* is a near-field image. Image courtesy of CEA/LETI (France). Clefs CEA n°52

Fig. 9.24 Possible applications of metamaterials

9.8.4 Metamaterials

Metamaterials are artificial materials which are engineered composites. This gives them physical properties different from what can be found in nature. They are made from conventional elements such as metals, plastics, ceramics, etc., engineered in such a way that they exhibit new properties due to the arrangement of the individual elements rather than due to the properties of the individual elements only. In other words, the behavior of metamaterials is determined by the sum of the elements rather than by the elements themselves.

Photonic crystals have a lattice size of the order of the wavelength of light in order to have a photonic bandgap. Metamaterials have a lattice constant much smaller than the wavelength because the diffraction phenomenon is avoided contrarily to photonic crystals where it is required to build a photonic bandgap. Some metamaterials can have a negative refractive index.

A fascinating application of plasmonic metamaterials is trying to make an invisible cloak. To be invisible one needs at least that the refractive index of the invisible body is equal to the refractive index of air. This can be achieved in some range of frequencies using plasmonic metamaterials.

Metamaterials have many possible applications as shown in Fig. 9.24.

Chapter 10
Molecular Electronics

Another way to make nanoscale devices is the bottom-up approach. The starting point is single molecules rather than macroscopic pieces of matter containing an extremely large number of atoms and molecules. This field, called *molecular electronics* or sometimes *moletronics*, started in 1974 when A. Aviram and B. Ratner first proposed the idea of a molecular rectifier. Today, prototypes of active electronic devices are made with a single molecule or a molecular layer. In molecular electronics, it is possible to make components with tens or hundred molecules only. First commercial applications concern organic solar cells or organic LEDs.

The advantage of the bottom-up approach is the wide choice of organic molecules and the fact that their properties can be adjusted on demand by chemical synthesis. Compared to the fabrication of nanoscale CMOS transistors, self-assembly or chemical synthesis is cheaper to perform although other difficulties exist. The application of single molecules gives a high reproducibility due to their chemical synthesis process. Consequently, a large number of identical molecules can be exactly fabricated by chemical reactions. A key issue is based on the capability to assemble them to create more complex systems or larger functional devices. In order to do that, self-assembly processes can be used because it would be impossible to make very large structures molecule by molecule.

Some of the advantages in developing molecular electronics are sketched in Fig. 10.1.

Organic molecules are often used in molecular electronics because of the wealth of possibilities.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_10,

Organic molecules

Most organic compounds contain carbon atoms combined with hydrogen, oxygen, nitrogen, sulfur, and phosphorus atoms. Sometimes other atoms are involved such as metals (iron in the case of hemoglobin, for example). A large variety of organic molecules can be synthesized or found in nature. Some of them can be used in nanoelectronics devices or materials having a large number of applications. Carbon can form four covalent bonds thanks to its four outer shell electrons. If one pair of electron is shared with another atom we have a single bond while if two or three pairs of electrons are shared two or triple bonds are formed. Ethane (CH_3–CH_3) is an example of a molecule with one single carbon–carbon bond. Ethylene or ethene (CH_2=CH_2) has a double carbon bond and acetylene or ethyne (CH≡CH) is a simple triple bond molecule (see Fig. 10.2). An organic compound is said to be saturated if it contains single bonds only. It is classified as unsaturated if the molecule has one or more multiple carbon–carbon bonds. Single bonds involve so-called σ electrons and double and triple bonds involve, in addition to σ electrons, also π electrons. As we shall see below, conjugated molecules are of great importance in molecular electronics. A conjugated molecule is a molecule formed by alternating single and multiple bonds. Such a configuration lowers the energy of the molecule and increases its stability but increases it chemical reactivity. Furthermore π electrons can move at very high speed under the influence of an external electric field leading to an efficient electron transport. This is due to a delocalization of π electrons over the part of the molecule which is conjugated because there is an overlap between the atomic orbitals where these electrons initially belong. It gives the ability to make high frequency devices.

Another important thing about organic molecules is that the different atoms forming it have different electronegativities. This means that when a bond is formed between two different atoms, electrons are shared unequally and one atom has a partial positive charge while the other has a negative charge. The bond is said to be polarized and has a dipole moment. Atoms having a large electronegativity have a tendency to attract electrons. For example, in hydrogen chloride (HCL), chlorine is more electronegative than hydrogen and carries a small charge $-\delta$ while hydrogen carries a $+\delta$ charge (the whole molecule is of course uncharged). Hydrogen chlorine is a polar molecule and behaves as a small dipole. In more complex molecules, the elementary dipoles sum up and if the resultant vector is nonzero, the molecule is polar (Fig. 10.3). For example the water molecule H_2O is a polar molecule because the angle between the O–H bonds is 105°. On the contrary the CO_2 molecule is nonpolar because the C=O bonds are aligned and the corresponding dipole moment point in opposite directions. Polarity is an important characteristic of a molecule because it governs solvation processes and is involved in the coupling to an external electric field such as the one carried by a light wave, etc.

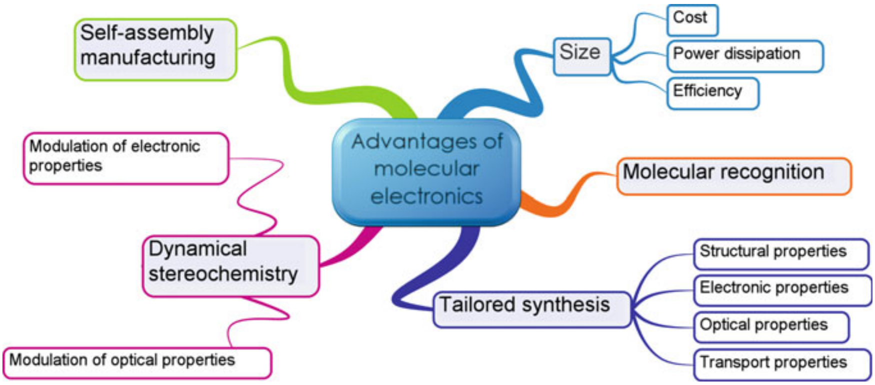


Fig. 10.1 Some advantages of molecular electronics

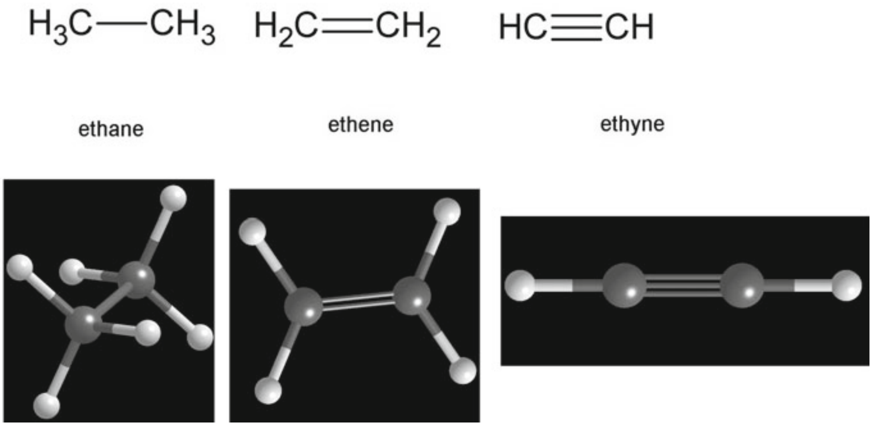


Fig. 10.2 Ethane, ethene, and ethyne molécules. On *top* of the figure the chemical formula is displayed. At the *bottom*, a schematic three-dimensional structure of their formula is shown. *Dark spheres* stand for carbon atoms and *light spheres* represent hydrogen atoms. In the ethane molecule there is a single carbon–carbon bond and the angle between bonds is about 109° (each carbon is at the center of a tetrahedron). The ethane molecule is planar. There is a double carbon–carbon bond and the angles between the bonds equals 120°. The ethyne molecule has a triple carbon–carbon bond and is linear. In ethane each carbon is said to be hybridized sp^3; in ethane it is hybridized sp^2 and in ethyne it is hybridized sp

10.1 Electronic Conduction

Basically two things are needed for electronic conduction in a material. The first one is to have a large number of atomic orbitals interacting strongly with each other because this allows the formation of band structures. The second condition is that there is an insufficient number of electrons to fill these band. This happens in metals or semiconductors (inorganic materials). In the case of a molecule, delocalized electronic states over the whole molecule are necessary. Most of organic materials are

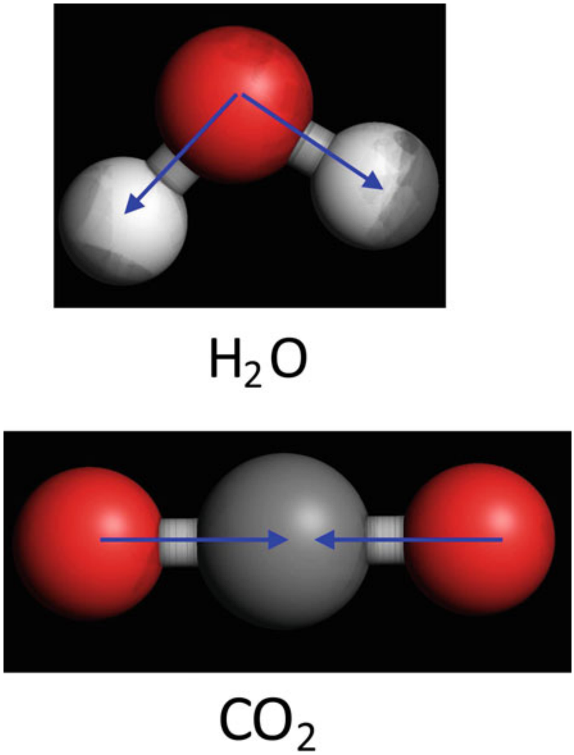


Fig. 10.3 Stick-and-ball models of H_2O and CO_2 molecules (*blue arrows* indicate polarization vectors)

nevertheless nonconducting. It is also the case of conjugated polymers unless they are doped.

Bandgap

A single atom has discrete levels of energy as indicated in the left hand part of Fig. 10.4. Each level can be occupied by an electron. Because quantum mechanics fully applies in this case, only discrete values of the electron energy are allowed. The ground state of the atom corresponds to a situation where the levels are filled up from the bottom with electrons while satisfying the Pauli principle (there is a maximum of two electrons per level, one with the projection of the spin-up and one with the projection of the spin-down). If we now consider a perfect crystal with atoms put on each of the sites of the lattice, the energy levels transform in bands as indicated in Fig. 10.4. A band contains a huge number of levels and can be considered as continuous. Typically, a one centimeter cube of a silicon crystal contains of the order of 10^{23} levels. Electrons can only have energies belonging to a band and, similar to atomic levels, there are forbidden regions. It means that an electron of the crystal cannot have an energy located in the forbidden region. In the same way as the energy levels of an atom are filled up from the bottom, the bands are filled up with the available electrons starting from the bottom.

The highest energy band containing electrons is called the *valence band*. The lowest unoccupied band is called the *conduction band*. The distance in energy separating the top of the valence band to the bottom of the conduction band is called the *energy gap* or *bandgap*. At zero absolute temperature, the highest energy occupied by an electron is called the *Fermi energy*.[a] Figure 10.4 is of course a very schematic representation of what really occurs but is enough to basically understand the difference between insulators and metal, for example.

In the case of insulators, the valence band is completely filled with electrons (blue color in Fig. 10.4) and there is a large gap separating the valence band to the empty band located above. A huge amount of energy would be necessary to promote valence electrons to the conduction band and such a material behaves like an electrical insulator.

In a metal, several situations may occur. Either the valence band is incompletely filled or there is an overlap between the valence and conduction bands. The first case corresponds to alkali metals such as sodium or potassium, for example. The second case corresponds to alkaline earth metals such as calcium or magnesium.

There is the case where the energy gap is small: the material has the behavior of a semiconductor. For example, silicon has a gap of 1.12 eV (1 eV = 1 electron-Volt = 1.6×10^{-19} J) at 300 K and germanium of 0.67 eV. This is much smaller than the gap of diamond (5.5 eV) which can be considered as an insulator.

[a] This definition of the *Fermi energy* is used in solid state physics. Scientists from semiconductors often design by *Fermi energy* what is in fact the *chemical potential*. This latter quantity is equal to the *Fermi energy* at zero temperature only.

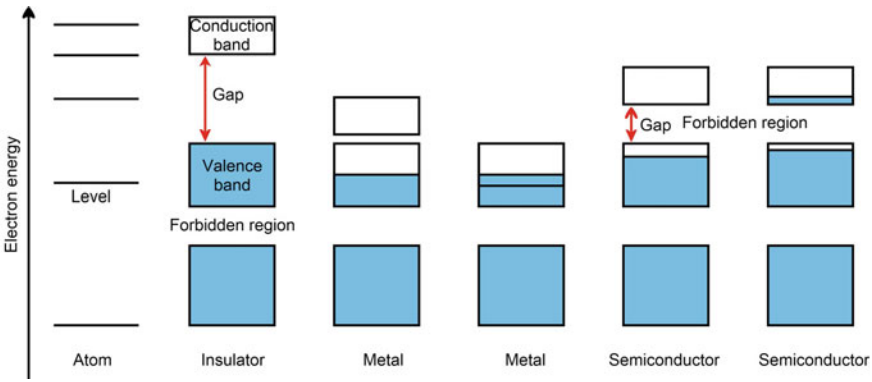


Fig. 10.4 Schematic representation of the band structure of metals, insulators and semiconductors. In the *left-hand side* of the figure is indicated the level structure of a single atom. See text for more details

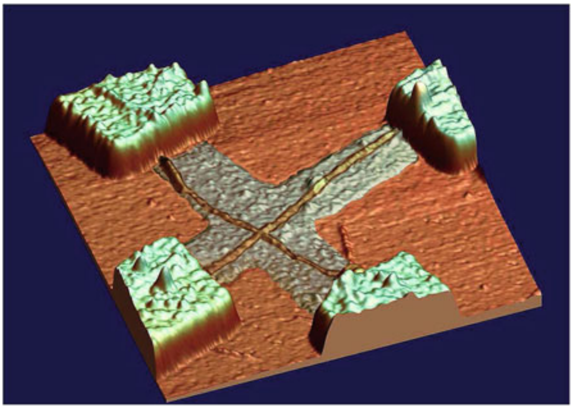


Fig. 10.5 Crossover of two carbon nanotubes deposited on silica, illustrating the production of nanotube circuits by self-assembly. The *gray strips* are molecular glue to allow positioning of the nanotubes (joint work by CEA and Motorola). Image courtesy of CEA/LETI (France), Clef CEA n°52

10.2 The Electrodes

A key difficulty is to connect electrically a molecule or molecular devices to the external world in order to study its electrical properties and build complex electronic devices. Conventional techniques cannot be used to do that at this scale and imaging techniques are useless in most of the cases to test the quality of the contacts. Only indirect proofs can be used to check that a contact between an electrode and a molecule is correct. Artifacts in the measurements often occur making the measurements difficult. Figure 10.5 shows an example of a homemade experiment to investigate the crossover of two nanotubes.

10.3 Nanowires

Wires are an essential part of electronic circuits because they have the ability to transport electric charges. Molecular wires are molecules which can do the job. In order to do that they have a structure enabling electrons to circulate from one end to the other. The simplest structure to do that is a chain consisting of alternating single and double bonds. Electrons involved in the conduction are π-electrons which are delocalized over the entire system (Fig. 10.6). But more complicated structures, with aromatic building blocks, can be used provided conjugation of single and double bonds occurs allowing π-electrons to extend over the whole molecule.

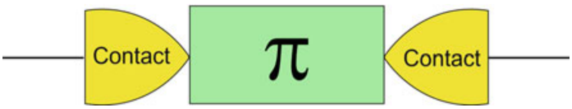


Fig. 10.6 Principle of a molecular wire. The *green rectangle* named π corresponds to the molecular wire which is a molecule with delocalized π-electrons

Some organic molecules can conduct current with different mechanisms such as quantum tunneling or hopping conduction, for example. It is interesting to note that the conductance of some organic molecules can vary with the intensity of an applied external electric field.

Carbon nanotubes, which we have been already introduced in Chap. 8, have conductivities ranging from metallic to semiconducting depending on their structure. One asset of carbon nanotubes is their high mechanical strength and their length which can be very long compared to their transversal dimensions. Because of that, they can be easily connected to electrodes. Semiconducting carbon nanotubes have been used to make field-effect transistors in the laboratory. They are used as the channel connecting the source and drain electrodes. The main issue of this technology is reproducibility making difficult to develop large-scale manufacturing. Furthermore, the amplification factor of such a device is still too small for applications.

Nanowires have a diameter in the nanometer range. Other Semiconducting nanowires can be made and used in the laboratory. They are usually synthesized by vapor–liquid–solid growth and can be doped to give p or n-nanowires. Nanowires of GaP, GaN, Si, and InP have been made. Field-effect transistors using nanowires have been realized. Si-nanowires are of special interest because they can be more easily used in the electronics silicon industry. An example of nanowires synthesized by vapor–liquid–solid deposition is shown in Fig. 10.7.

Molecular resistors can also be made. Electric isolating molecules are easier to find and can be included in molecular devices. Alkanes are an example of insulating molecules. For example, they can be put in between two conducting molecules.

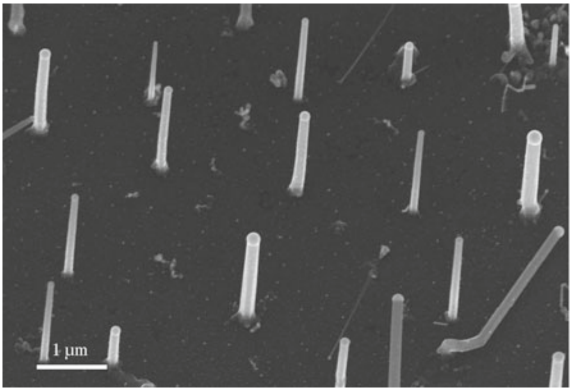


Fig. 10.7 Scanning electron microscope image showing silicon nanowires with a diameter in the range 30–100 nm synthesized by the vapor–liquid–solid technique. Nanodrops of gold used as catalyst in the process are shown at the end of the nanowires. The position and the size of the nanodrops of gold tailors the position and the diameter of the nanowires. Image courtesy of CEA/LETI (France), Clef CEA n°52

Conjugated molecules

In molecules, electronic conduction is observed if there is a set of overlapping orbitals allowing a delocalization of electrons over the entire molecule. This occurs in organic conjugated molecules with alternating single and double bond structure. In this case π electrons are involved. They are issued from the hybridization of p atomic orbitals. A simple example of a molecule with delocalized electrons, although it cannot be used in practice for electronic conduction, is benzene. In this planar molecule, π electrons are delocalized above and below the ring. Usually, benzene rings are associated with other functional groups and the delocalization of electrons extends to other adjacent atoms.

10.4 Molecular Diode

A molecular diode is one of the simplest two-terminal devices. It is used as a rectifier in electronics. This device conducts electricity in one direction only. One possible solution is to use a molecule which has a donor part and an acceptor part separated by a nonconducting region (spacer). The donor part is analogous to a n-type semiconductor while the acceptor part is analogous to a p-type semiconductor. The spacer plays the role of a junction barrier preserving the energy difference between the acceptor and donor parts but allowing electrons to go through with some probability. The acceptor and donor part of the molecule have delocalized π-electrons while the spacer part has σ-electrons only, which means saturated chemical bonds. The basic principle is shown in Fig. 10.8.

There are other possibilities to make a molecular diode using a rod-like molecule connected to two gold electrodes at both ends. In addition of having the characteristics of a diode, it has a negative resistance behavior. This means that if the applied voltage takes values within some range, the electric current decreases as the voltage increases. This property can be used to make resonant tunneling diodes which are useful devices because they can be used in high-speed electronic circuits.

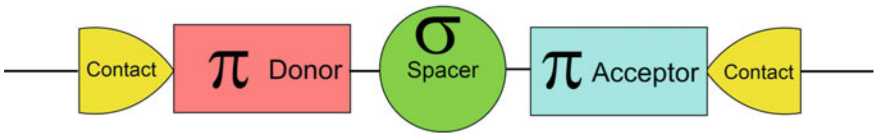


Fig. 10.8 Basic principle of a molecular diode

10.5 3-Terminal Device

A transistor is the most widely known 3-terminal device. These devices are widely used in electronic circuits because they have the ability to amplify or commute electronic signals. 3-Terminal devices are necessary to design electronic circuits with the same functionalities as those developed in micro- and nanoelectronics. Three nanosized contacts have to be made to connect the device to other components. This is a hard job if the aim is to go to an industrial stage in the future.

There are two ways to make 3-terminal devices.

- The first one is to assemble a molecule which already has three different ports. Each port is connected to three different electrodes.
- The second approach is to attach a third terminal at a distance which is close but not in contact with a two-port molecule. Applying a potential to this terminal modifies the electrostatic state of the two-port molecule. This type of device has to be operated at low temperatures because single electron effects are used. Consequently, thermal background has to be strongly reduced which is done by lowering the temperature. In such a 3-terminal device, the third port (terminal) plays the role of a gate. The potential applied to the gate enables to switch the single electron transistor from the coulomb blockade regime to the conducting regime.

In a molecular transistor, the molecule is inserted between two conducting or semiconducting electrodes.

10.6 Conducting Polymers

Conjugated polymers are a class of organic materials widely used in molecular electronics. The reason is that they can become conductive when partially oxidized or reduced. Polymers are usually cheap to manufacture and are good insulators of heat and electricity. Oxidation can be made by doping the original polymer. For example, a 10^8 increase of the conductivity of polyacetylene is observed by an oxidative doping with iodine. A.J. Heeger, A. MacDairmid, and H. Shirakawa were awarded the Nobel Prize in chemistry in 2000 for the discovery and development of conducting polymers.

Several conducting polymers are known. The simplest ones are polyacelylene, polypyrrole, polythiophene, polyaniline, etc. They are difficult to process, some of them are toxic, and they have a poor solubility in solvents. However, nanostructured forms of conducting polymers can be more easily processed and give them better properties. Therefore, they are more useful for developing applications.

Light emission can be produced when a voltage is applied to a thin layer of conducting polymer. Applications are found in the domain of flat panel display or solar cells. A main concern of conducting polymers is their resistance to external conditions. Their packaging to protect them against oxygen or aging is one of the key points to be addressed.

The electrical conductivity of conjugated polymers comes from the existence of completely delocalized π electrons over the molecule.

Bandgap engineering

The properties of the bandgap of conjugated polymers have important consequences with regard to their electronic properties. There are several ways to customize the properties of bandgaps.

- An increase of the degree of polymerization decreases the value of the bandgap.
- The bigger the alternating structure of single and double bonds, the larger is the bandgap
- Polymers have often, in their structure, aromatic parts characterized by resonant configurations. This increases their stability and the bandgap is larger.
- By playing with the conformation of molecules composing the polymer, it is also possible to modulate at will the bandgap. Substituent groups on the molecules are another tool to modify bandgaps.

In summary, chemists have at their disposal a lot of possibilities to tailor the bandgap of conducting polymers to specific applications. The development is driven by research on organic field transistors, light-emitting devices and organic solar cells.

10.7 Oligomers

Oligomers are often used in molecular electronics. They are made of a few monomer units while polymers are made of a large number of monomer units. The length and morphology of polymers can be tailored but oligomers allow a more complete design because each step of the synthesis is under control. Polyphenylene or polyphenylene-based molecules are example of conjugated oligomers.

An important property of the oligomers is that the electrons are delocalized over the whole molecule. In mineral semiconductors, such as silicon crystals for example, there is a band structure formed because a great number of atomic orbitals strongly interacting with each other. In general, these bands are responsible for the conducting, semiconducting or isolating properties of these crystalline materials. Similarly, for conjugated oligomers, the electronic transport properties are governed by the occupation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This is analogous to the valence band and conduction bands in crystals, respectively. In the same way as the energy difference between the valence and conduction band is called the gap of a semiconductor material, the difference of energy between LUMO and HOMO is referred to as the gap of the organic materials.

10.8 Polymer Conduction

Most conjugated polymers do not conduct electricity and they have to be doped to acquire this property. Semiconductors, such as silicon are also doped to make electronic devices such as field-effect transistors or other components. The conductivity mechanism is, however, different in the case of conjugated polymers compared to semiconductors. In doped conducting polymers, transport occurs by the motion of charge carriers between localized states or between new states created in between the energy gap (polarons, bipolarons, solitons, soliton bands). Carriers can hop across or tunnel through barriers created by these isolated states and this depends on the temperature.

We shall not go into the details of this matter which is quite complex but just summarize, in Fig. 10.9, the main conductivity mechanism which are expected to happen for nanoscale molecular wires. This picture is made according to the classification of Chen et al., Yale school of engineering, based on measurements or simulation. The mechanisms presented below can be modified by changing the molecular or electronic structure as well by varying the external conditions such as the solvent, for example.

Nonresonant coherent electron motion occurs when there is no strong dissipation or trapping effect during transport which takes place without loss of energy along the nanowire.

On-resonance coherent electron motion occurs when the tunneling effect takes place and that the energy of the tunneling electrons is resonant with the conduction band of the wires.

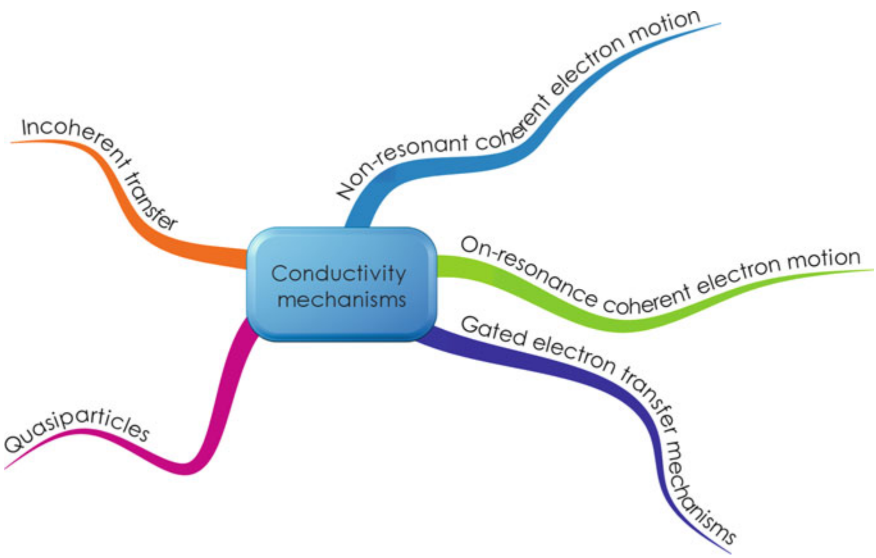


Fig. 10.9 Different charge transport mechanisms in molecular wires made of organic materials

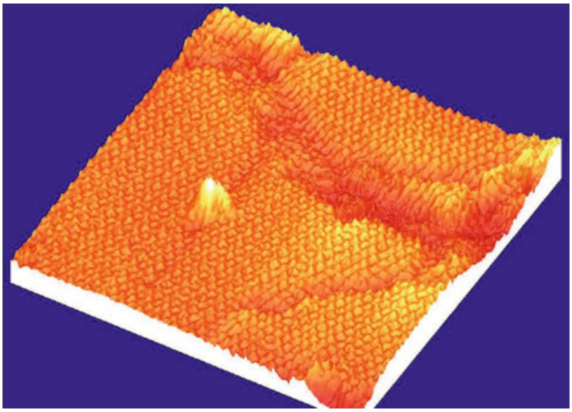


Fig. 10.10 Self-assembled monomolecular layer of dodecanethiol on a single gold crystal viewed by tunneling microscopy. Each bump in the relief corresponds to a molecule of dodecanethiol. The bright protuberance is a molecule of bisselenoltertiophene inserted in the monolayer. It has a greater ability to conduct electricity and for this reason it looks brighter and higher than dodecanethiol molecules although it has about the same geometrical size. Image courtesy of CEA/LETI (France), Clef CEA n°52

Inelastic scattering of the electrons is important in the case of incoherent transfer. The nanowire behaves like a resistive wire with conductivity inversely proportional to its length.

Conduction by quasiparticles such as polarons or bipolarons can have a large contribution to conduction in long molecular wires.

Gated electron transfer occurs when molecules can undergo stereochemical changes (such as a cyclohexane ring which transforms from the boat configuration to the chair configuration). Depending upon the geometry, electrons can flow or not through the nanowire.

Tunneling microscopy allows to see changes in the conductivity of molecules as it is exemplified in Fig. 10.10.

10.9 Self-assembled Monolayers

We have already discussed, in Chap. 2, the Langmuir-Blodgett technique to make monolayers. Another route to make ordered monolayers is the self-assembled monolayer technique (Fig. 10.11). These two-dimensional structures are formed by adsorption of a solution—or a vapor—of surface active molecules on a solid surface. These molecules will spontaneously orientate toward the substrate surface and arrange in an ordered layer corresponding to a thermodynamic equilibrium state. Actually, the functional end groups of the molecules chemically react and are absorbed by the substrate material forming a two-dimensional assembly of molecules. The energy minimization process governing monolayer formation eliminates any error appear-

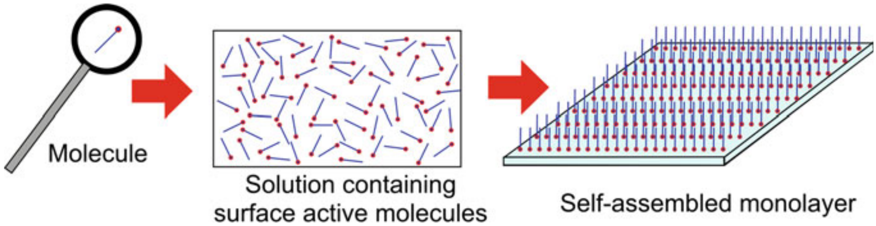


Fig. 10.11 Illustration of self-assembled monolayer deposition via surface active molecules

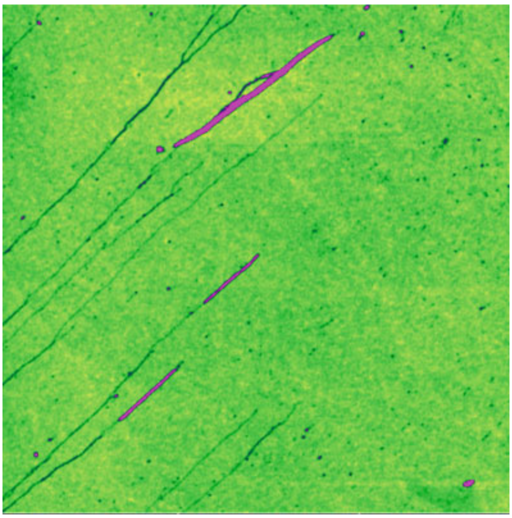
ing during the process. This technique has the advantage of being cost-effective and simple.

With self-assembled monolayers it is possible to make very dense functional systems such as switches or memories. Nevertheless scientists are far from being able to make similar complex systems as those obtained by top-down techniques.

10.10 Conclusion

Molecular electronics is a very exciting domain since it allows to make systems starting from molecules. However, even if elementary functions have been realized in the laboratory, we are far from applications at the industrial stage. Such studies are also interesting because they provide a good understanding of the underlying mechanisms where molecules are interacting or subject to external interactions. Building blocks on demand gives also the ability to graft these blocks onto inorganic materials such as silicon. In another interesting domain of research biological objects, such as DNA strands, can be used to build nanostructures in a bottom-up

Fig. 10.12 Carbon nanotubes (*pink*) linked to DNA strands (*black*). The combing of DNA strands allows to align carbon nanotubes. Image courtesy of CEA/LETI (France), Clef CEA n°52



manufacturing. Figure 10.12 gives such an example where the combing of DNA strands linked to carbon nanotubes allow them to align.

Part III
Nanotechnology for Information and Communication Technologies

Conclusion

Microelectronics has naturally moved toward the nanotechnology domain. Commercial microprocessors and memories available today are based on components manufactured with a precision better than 100 nm. The evolution from the micron domain to the nanometer domain accuracy has been continuous, thanks to an enormous and fast technological progress. The driving force for this evolution is the international road map followed by all the actors in microelectronics. As a consequence, the cost to manufacture single transistors has dropped dramatically, enabling opening the use of powerful microprocessors, large memories, and other sophisticated electronic devices in daily life. *Smaller, faster, and cheaper*, which is the motto of microelectronics, also applies to nanoelectronics and more generally to nanotechnology.

The top-down approach which is the basis of microelectronics has been extended to the nanoelectronics domain with great success. Functionalities of the components have remained the same but with a smaller number of electrons at work. One advantage of this evolution is lower power consumption; the drawback is a higher sensitivity to background noise. Critical layers of many structures are now of the order of the nanometer and about 100 electrons are sufficient to control the operation of a MOSFET. Manufacturing and research require increasing improvements in control for deposition, patterning, characterization as well as purity and clean rooms in the manufacturing environment.

Moore's law still governs today the evolution of micro and nanoelectronics. However, there is a need to go beyond this evolution by introducing new technologies based at least partly on nanotechnology. It is necessary to build heterogeneous micro and nanosystems borrowing technology from other fields. In particular, a coupling to living and biological systems is a promising path to obtain more efficient and powerful devices.

In reducing even further the dimensions of components, below about 10 nm or so, we are faced with the appearance of new physical phenomena: pure quantum effects. The bad thing is that it is no longer possible to use the same architecture of

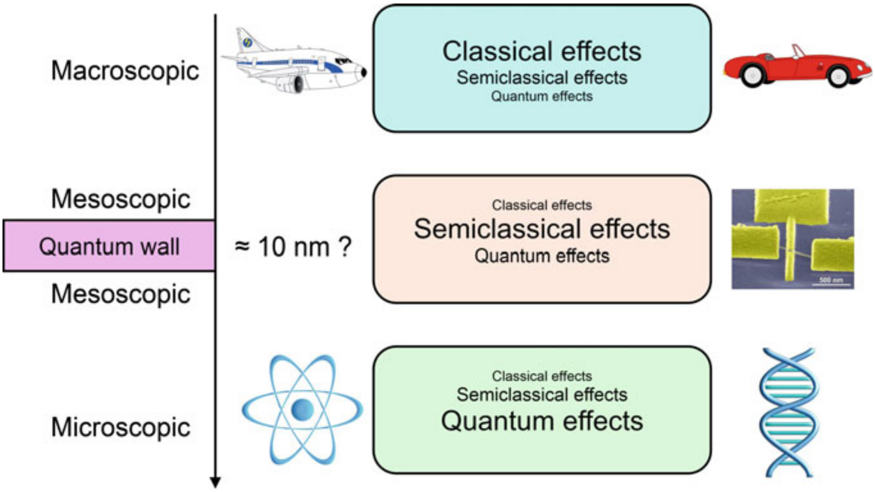


Fig. III.1 Evolution of the physics as we go from macroscopic systems to microscopic systems. See text

devices as at larger dimensions to perform the desired function. The good thing is that new phenomena pave the way to new functionalities. Graphene electronics, nanomagnetics, spintronics, nanophotonics, and plasmonics are new areas leading to many innovations today as well as in the future. Information and communication technologies are likely to be very different tomorrow compared to what we are used today. Figure III.1 summarizes this evolution of physics as we go from macroscopic dimensions to microscopic ones. The size of the letters is just to show their importance at the different scales.

It is also possible to make nano-object or nanostructures starting from atoms and molecules and using self or directed organization. Nature does that every day and it is worthwhile to learn from it as well as to imagine new concepts to make nano-objects from elementary building blocks. This is the path followed by the bottom-up approach. Molecular electronics is heavily based on this approach.

Weaknesses are still present, for example, the compatibility to the well-established Si technology, compatibility in growth processes, hybrid heterostructure formation; many nano-objects are only available on non-Si substances. This compatibility is missing and problematic for graphene, carbon nanotubes, or in case of molecular electrons. The potential directions for future nanoelectronics developments are based on Fig. III.2:

- a low dimensionality of active regions: for instance, layered graphene or one-dimensional semiconductor nanowires. The low dimensionality can also be a result of reducing the size (single electron device).
- "non-charge" driven devices (not electrons/holes) as it is discussed in the field of spintronics where the spin is used for manipulation, or in biomolecular

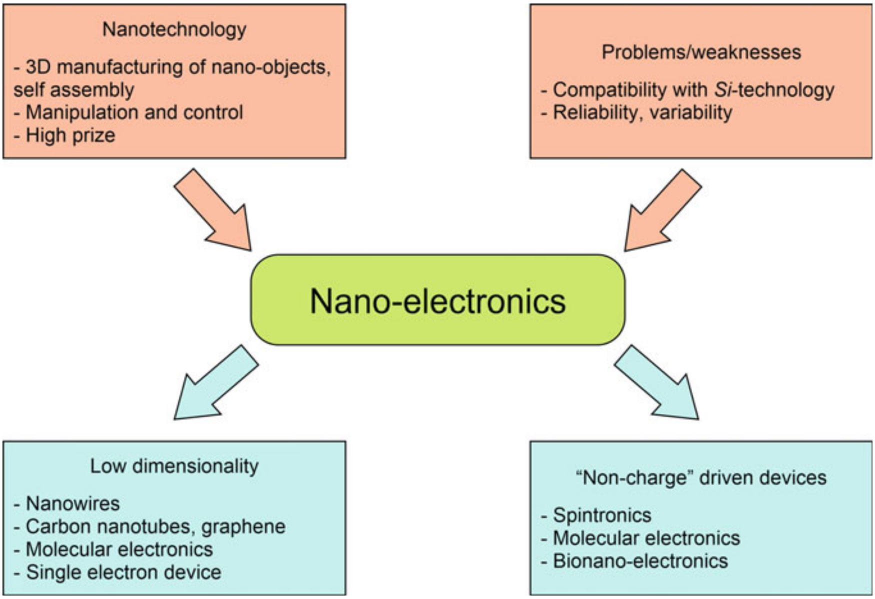


Fig. III.2 Highlights of the potentials and weaknesses in nanoelectronics. Courtesy of Paul-Drude-institute, Berlin

electronics where other properties (e.g., conformation, quantum state) are used for signal processing.

The potential impact and breakthroughs of nanoelectronics in other technologies are:

- in medicine: engineered tissues covered by designed nano-objects can be integrated in the nervous system or as sensing systems to develop in vitro diagnostics;
- in energy: a reduced energy consumption during manufacturing is expected and the chips will consume less energy.
- in textiles, agriculture, transport,...and most industrial technologies and daily life. The aim is to improve efficiency, reduce cost, operate environment-friendly, create jobs, and improve the standard of living.

Part IV
Healthcare

Introduction

People are living longer than a century ago. For example, in France, life expectancy which was below 30 years in 1800, and about 50 years in 1900, has now reached 80 years. The overall population of many countries, especially developed countries, is aging as life expectancy increases and birthrate declines. Improvements in medical care and related technologies have certainly played a key role in this evolution. It is not only important to live longer but also to improve the quality of life. People are also becoming more sedentary, which leads to further healthcare problems. A major challenge is therefore to upgrade the healthcare system while keeping the costs affordable so that everybody can reap the accompanying benefit. What are the promising technologies that will drive the benefits for individual citizens? A solution to these rather complex problems is nanomedicine. Figure IV.1 represents the length scale from meters to nanometers for human cells and molecules with an indication of bioproducts along the scale and the associated biotechnology disciplines.

Medical and life science applications may become the most lucrative markets for nanotechnologies: lab-on-a-chip devices are already showing the way toward the miniaturization of diagnostics, but once these are fashioned using nano-objects, an altogether smaller scale of operation will become realized. Opportunities will widen further to simplified use by the patient, with diagnosis and monitoring eventually becoming combined with therapy in integrated systems. Targeted drug therapy with selective routing of individual drug payloads to a diseased organ or tissue is already under development.

Especially attractive are the relatively low costs compared with the development of entirely new drugs. While nanotechnologies will contribute to a decrease in costs and an improvement in healthcare, this approach will require a multidisciplinary effort. Furthermore, nanotechnology for medicine will have to take into account regulations, rules, ethics, and societal concerns. Care must be taken

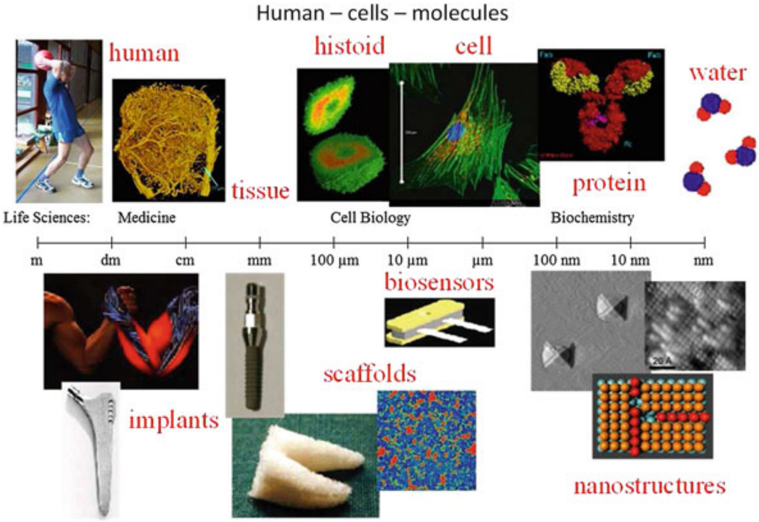


Fig. IV.1 Overview of nanotechnology in life sciences. Image courtesy of University of Basel

that the complex approval processes in nanomedicine does not delay the health benefit to patients and economic benefit to companies.

"*Test*, *treat*, and*repair*" is a three-pronged approach to maintaining health.

1. **Test** It is valuable to see inside the human body using minimally or noninvasive techniques. This can help in the prevention of serious disease onset and progression. This approach covers the entire diagnostics domain including analysis and imaging.
2. **Treat** It is important to deliver the right quantity of a drug, at the right time and to the right place, to reduce the risk of side effects. This encompasses the therapeutics area with dedicated application of drugs.
3. **Repair** With a longer life expectancy, the medical profession is increasingly called upon to provide support in the repair of tissues (including bones, teeth, etc.) to ensure people live a comfortable life. This wide domain includes surgery, implants, coatings, and regenerative medicine.

The expected advantage of using nanotechnologies and nanomaterials in medicine is to improve diagnostic efficiency and give better efficacy to treatments. If a smaller amount of a drug is required to achieve the same effect on the patient, fewer side effects result and individualization of therapy is achieved. Further, outcomes include biological screening that is performed faster and at lower cost, better quality implants and prostheses, and reactive materials that can last longer inside the body. For some applications (Fig. IV.2), it is not necessary to go down to the nanometer scale, as phenomena on the micrometer scale sometimes provide enough benefit. For many systems exploiting electronics, the evolution will very likely be toward hybrid systems containing both micro and nanometer scale

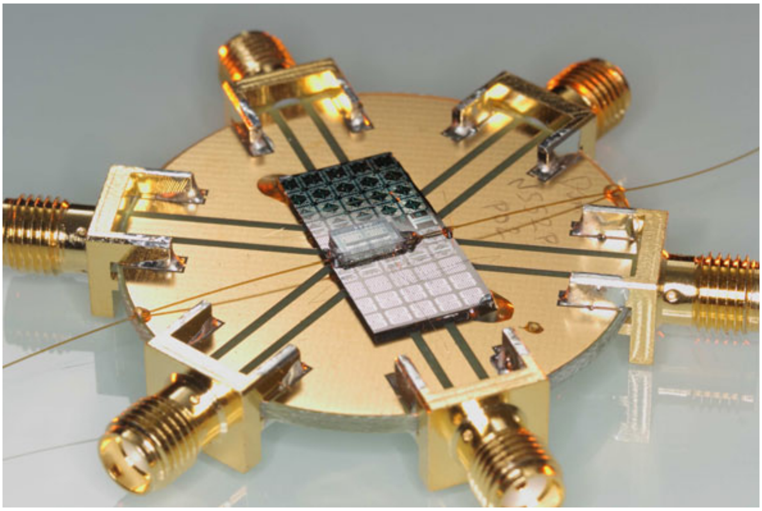


Fig. IV.2 Packaged NEMs (nano-electro-mechanical) sensors. Image courtesy of CEA/LETI (France)

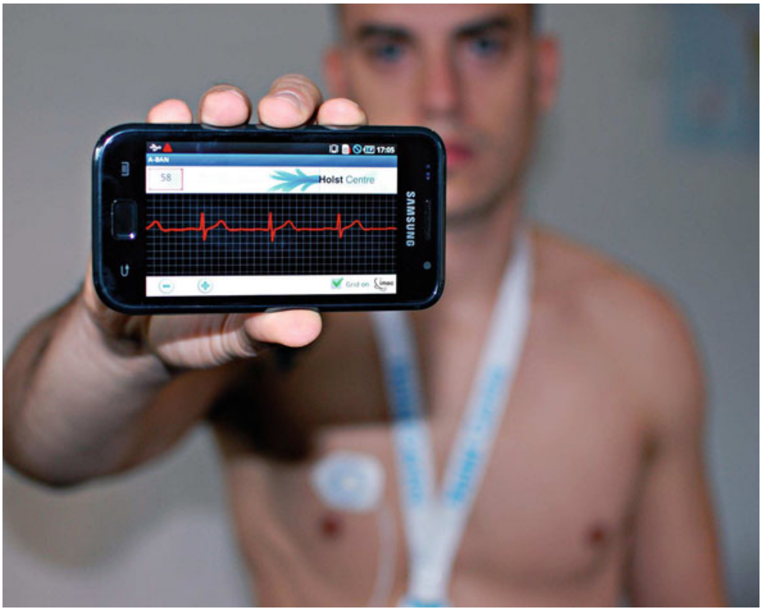


Fig. IV.3 Wireless transmission of an ECG signal. Image courtesy of Holst Center (Netherland)

components. It is notable in this regard that the size of biological cells our body consists of is in the range of 10 microns. Wireless transmissions are going to play a more and more important role in health monitoring devices. For example, Fig. IV.3

shows an ECG signal wirelessly transmitted to an android mobile phone via a low-power interface.

Human healthcare may be regarded as being concerned with those three main strategies of *test, treat,* and *repair*. Thus, it is valuable to see inside the human body using noninvasive techniques; these can help in the early detection of serious diseases. It is also important to deliver the right quantity of a targeted drug to treat a disease while minimizing side effects. The drug has to be administered at the right time, to the right place. Since people are living longer and longer, some types of repair are required more and more frequently, e.g., for bones, teeth, and organs, to ensure people have a high quality of life. These three domains will be further developed in the next two chapters.

For materials in the medical domain, there is a continuous transition from macroscopic objects to objects of smaller and smaller size, down to the molecular scale. This is because it may be necessary to deliver tiny systems with the ability to travel to various parts of the body exploiting small-dimensional scales. Micro and nanosystems, due to their small size, have the ability to match the size of functional units of living organisms. They can thus have specific interactions with biological entities from cell organelles and whole cells through to tissues and organs. Furthermore, multiple functions can be concentrated in a very small volume allowing for complex therapies that are minimally invasive. One further possibility would be to effect painless operations by minimizing disruption to normal tissues. Several microsystems have been developed to examine parts of the body and the evolution is now toward nanometer size systems. As well as accessing smaller parts of the body, a size reduction would achieve a reduction of the energy consumption, always the Achilles heel of electronic systems. Many of the microsystems dedicated to health consist of both micro and nanoparts, with the simplest example being a component which is further coated with a nanometer thick material conferring specific valuable properties.

Smaller than human cells

Nanotech's promise comes from the fact that objects designed at such remarkably small scales operate at just within the size range at which the natural machinery of biology operates. To put this into perspective, the nanoscale is thousands of times smaller than a human cell and similar in size to biomolecules such as enzymes and cell receptors. For example, hemoglobin, the molecule that carries oxygen in red blood cells, is approximately 5 nm in diameter, DNA is 2.5 nm, while a "quantum dot" is about the same size as a small protein (<10 nm) and some viruses measure less than 100 nm. Nano-objects and devices around 50 nm can enter many types of cells unassisted, with even wider cell access and body distribution possible for 20 nm objects, including the inside and the outside of the circulatory system. Because of their small size, nanoscale objects can also readily interact with large biomolecules on both the surface of cells and the interior of cells. The access gained to so many parts of the body, and the facility for selective molecular interaction, means that nano-objects can be used both for detecting change as well as for modifying cellular processes. It is this fundamental, and *unique, capability that will allow tailored nanostructures to be our next generation of designer treatment and diagnostic systems.*

Nanomedicine is not a standalone domain but is immersed in the vast domain of biomedicine. Nanoscale technologies will only be used when they offer a significantly better solution to a medical problem. They can even provide solutions for problems unsolved so far. Given the current pace of development, this is likely to occur. They will be of increasing importance in order to better understand cell mechanisms and to develop tailored treatments to various serious diseases including cardiovascular diseases, cancer, and skeletal degeneration.

Chapter 11
Diagnostics

Some diseases affect a significant proportion of the population. The most important are shown in Fig. 11.1.

A relatively small group of noninfectious diseases have a major impact in modern society. Cardiovascular diseases, for example, are the primary cause of death in the European Union, whilst cancer is today the second cause of death in developed countries and requires complex therapies. Neurodegenerative diseases such as Alzheimer's and Parkinson's are also becoming a serious problem in society with an increasing incidence. Degenerative joint disease, notably osteoarthritis in the aging population, inflammatory joint disease, and disorders associated with repetitive movements in the workplace are expressions of the major disease burden presented by musculoskeletal disorders. These diseases lower the quality of life and demand long-term medication. The occurrence of type II diabetes is also increasing, mainly due to dietary and lifestyle factors and it demands especially close monitoring and medication.

Bacterial and viral infections also pose an important problem due to their infectious nature and so should be quickly identified and dealt with appropriately. This is going to be an increasing challenge with the continuing increase in antibiotic resistance.

Diagnostics include *in vivo* and *in vitro* methods as well as imaging techniques which are more and more used to detect any heath anomaly or disease. Nanotechnology offers several assets in this domain. Beside the fact that it can dramatically decrease the cost of some diagnostic techniques, it can increase the sensitivity compared to conventional methods, offering lower detection limits, and decreasing the size of the detectors. New sensors will be able to detect nano- and even femto-concentrations of chemical markers, allowing early detection of diseases. Carbon nanotubes or nanofibers and nanowires can be used as sensitive sensors thanks to their good electrical properties. As far as imaging techniques are concerned, nanotechnology allows development of new contrast agents for improvement of magnetic resonance analysis, quantum dots can be used in molecular imaging, and so on.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_11,

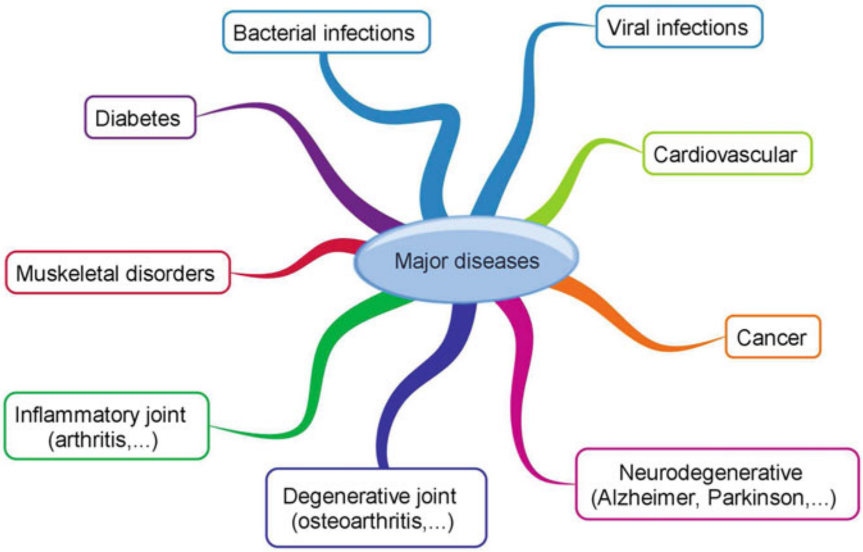


Fig. 11.1 Major diseases touching a large proportion of the population

Nanotechnologies in cancer research

Nanoscale devices and processes offer great medical potential for development:

- Imaging agents and diagnostics that will allow detection of cancer in its earliest stages;
- Agents that can give predictive monitoring of molecular changes and prevent healthy cells from becoming malignant;
- Systems that provide better predictive assessment of therapeutic and surgical outcomes for acceleration of clinical uptake;
- Multifunctional, targeting devices capable of bypassing natural biological barriers and giving selective delivery of therapeutic agents directly to cancer cells and tissues in the microenvironment that plays a role in tumor growth and cancer metastasis;
- Novel treatment methods to reduce the symptoms of cancer that adversely impact the quality of life;
- Research tools that enable rapid identification of new therapeutic targets for clinical development and for prediction of drug resistance.

A typical example is given by multifunctional iron oxide nanoparticles designed for magnetic drug guidance in the body, for theranostics, a combination of therapeutic and imaging functionalities is shown in Fig. 11.2.

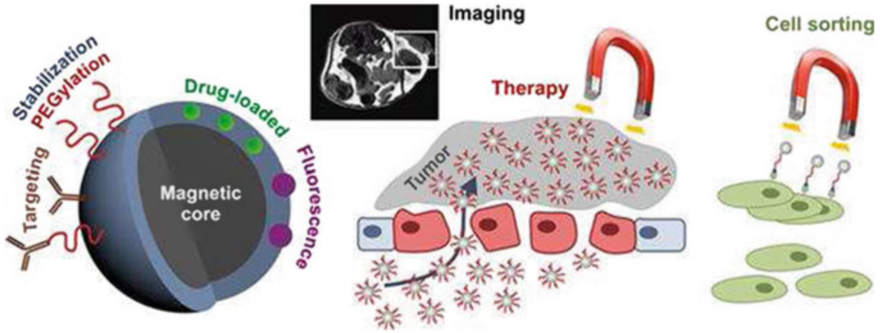


Fig. 11.2 Magnetic nanoparticles: Design and characterization, toxicity and biocompatibility, pharmaceutical, and biomedical applications. Harivardhan Reddy L., Arias, J.L., Nicolas J., Couvreur P., Chem Rev., 112, 5818-5878; 2012. American Chemical Society

11.1 Diagnosis and Imaging

Keeping people in good health requires reliable monitoring, e.g., using imaging techniques to anticipate and identify any dysfunction of parts of the body. Microanalysis is a part of this diagnosis strategy. Its evolution is the same as for microelectronics: *smaller, faster, and cheaper*. Microanalysis today covers molecular, structural, and cellular biology. Micro and nanotechnologies can be used in medical diagnosis in three main areas: *in vitro* and *in vivo* diagnostics, and embodied in medical devices. A prospective example is given in Fig. 11.3 for heart and brain scanning.

In vitro diagnosis of blood, tissues, and other body fluids needs sampling and analysis time, typically ranging from hours to days and sometimes even weeks to realize the results. Miniaturization allows an increase in speed which can be even greater using parallelization of the tests (where several analyses are done at the same

Fig. 11.3 Solutions for human attacks: heart and brain scanning

time). By using the techniques of microelectronics, various micro and nanodevices have been developed or are under development.

Nanotechnologies have a special role to play in preventive medicine by providing new diagnostic tests for biomarkers associated with a particular disease. This allows assessment of the risk to a given individual with respect to a particular disease before any symptom occur. People with a greater than average risk can have regular check-ups and monitoring of their biomarkers. Prevention, or at least early intervention, reduces the medical and treatment cost which is an important economic goal for society in general.

Microsystems dedicated to medicine are a growing field and many applications will be available in the future. *Biochips* and *microarrays* are tools that are especially suited to test cellular samples, and can reveal the presence of specific genes, proteins, etc. A *lab-on-a-chip* uses microfluidics to transport nanoliter volumes of biological sample to a measuring, detection, or separation/dilution component. Biological tests require microsystems containing highly integrated electronic and optical components made using microelectronic techniques. A natural extension of these devices is the *cells-on-a-chip* where living cells are coupled to a transducer. Cheap *in vivo* diagnosis can be developed and used by nonspecialized medical staff at the patient's home or doctor's office. These kinds of microsystems will be presented below.

Let us now go swiftly through the diseases we have just highlighted.

Noninvasive or minimally invasive 3D-imaging techniques for the cardiovascular system will soon appear based on micro and nanoscale components. Furthermore, telemedicine for heart monitoring using surface nanostructured nanosensors is under development.

Cancer presents a complex disease challenge. Early diagnosis is, of course, important because it is far more difficult and costly to treat patients if a late stage has been reached, especially with metastases. Nanotechnologies can help in diagnosis by identifying specific biomarkers flagging up a predisposition to or an early indication of a particular cancer. The lab-on-chip technology will be very useful for pattern recognition in body fluids of proteins, small metabolites, DNA methylation states, and other discriminators between healthy and affected individuals. Nanotechnologies can also be useful in reducing the toxicity of drug carriers used in medical imaging, while minimally invasive tools such as endoscopes and catheters for diagnosis and therapy will be a more direct application of nanotechnologies. Molecular imaging will soon help in radiation therapy by showing those parts of a cancer which are more resistant to radiation and those which are more sensitive. This would allow delivery of a smaller dose of radiation to radiation-sensitive parts and a higher dose to radiation-resistant parts, so reducing the damage to healthy parts around the cancer and decreasing side-effects.

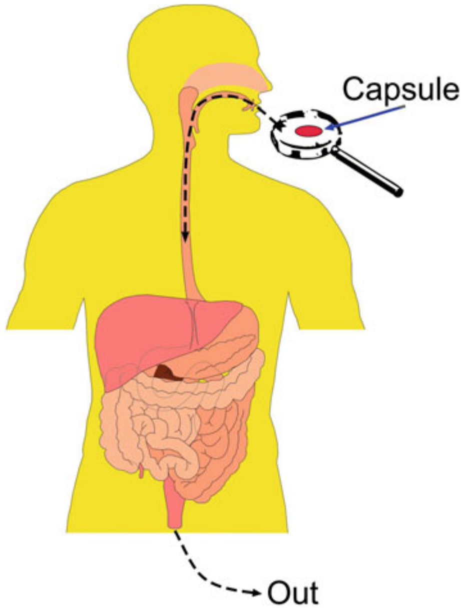


Fig. 11.4 Schematic example of using a wireless capsule to perform endoscopy

Wireless capsule endoscopy

Examples of a microsystem dedicated to medical imaging are those used in the form of capsules for endoscopy (Fig. 11.4) www.givenimaging.com. It is, for example, amenable for the detection of colon cancer at an early stage, thus increasing the likelihood of a good surgical outcome. This microsystem, containing many components, has dimensions of just over 25 by 10 mm and weighs about 4 g. There is a small color video camera coupled to an integrated circuit allowing signal processing and radio-wave transmission of the data to an electronic circuit contained in a belt worn by the patient. A light source and optics produce a camera image; the electronic circuit contained in the belt stores the data. Compared to conventional endoscopy, the preparation of the patient is similar. Fasting is necessary from about 8 h before the operation and some drugs are taken by the patient to clean the bowel. However, there is less disruption to the patient, and potential coverage of the gut is increased.

Gastroscopy is used to check the upper part of the digestive track, and colonoscopy for the lower part (colon and rectum). However most of the small intestine (about 7 m long) is not checked by these methods, while this is achieved using the capsule. Other methods, such as radiographic imaging, are not reliable. It took 20 years to develop this technology. This type of technique also provides an indication of what might be achieved through nanotechnology, both in reducing the size of the probe element and in generating more complex on-board functionalities such a chemical detection.

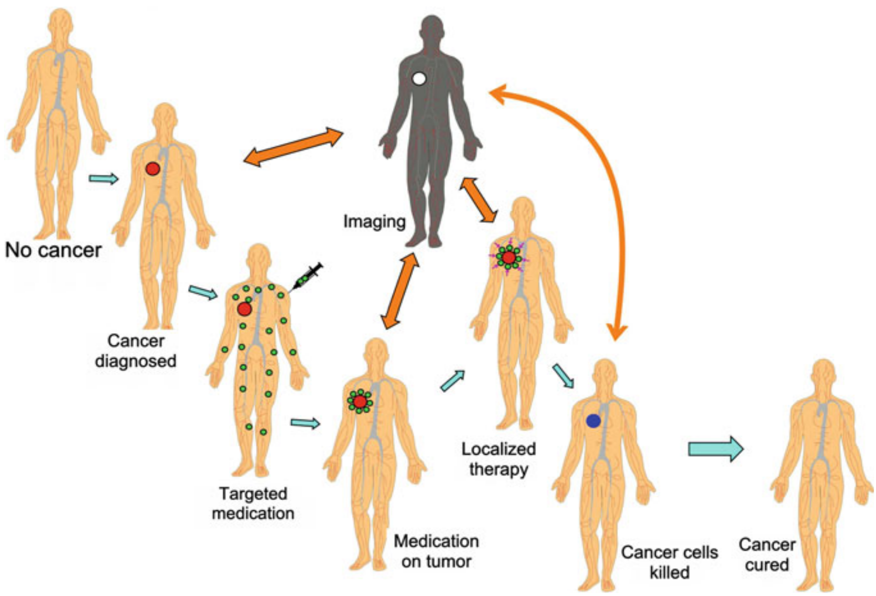


Fig. 11.5 Different steps which can be used to cure cancer

A cancer develops if a small number of genes are modified. A modification of five genes can be sufficient to start an anarchic proliferation of cells and induce a cancer, followed later on by metastases. Molecular imaging working on the nanoscale will be able to identify an over- or under-expression of the modified genes inside the organ where it takes place. Molecular imaging is now possible because biomarkers can be fabricated which are specific to some particular cell component and can bind selectively to it.

As shown schematically in Fig. 11.5, it is important to diagnose early the presence of any cancer. A targeted medication, like chemotherapy, for instance, can destroy cancer cells and in most cases radiation and/or surgery are required. Another way is, as in Fig. 11.5, to provide a dedicated medication which can specifically go to the cancer region and stick to it. If it cannot destroy cancer cells by itself, it can be helped by an external source of radiation providing a localized therapy because of its specific interaction with the molecules of the medication. For example, to cure a specific and dangerous form of breast cancer, functionalized carbon nanotubes can be used. They can be localized inside the body, stuck to cancer cells, and then local application of a laser operating at a specific wavelength can disrupt cells by changing the wavelength of the laser to another specific value.

Neurodegenerative diseases such as Alzheimer's and Parkinson's are slow to progress and difficult to detect. Probes or marker molecules able to cross the blood-brain barrier for imaging (and in the future for drug delivery) and allowing for rapid identification of damage, will rely on nanotechnologies.

In the case of diabetes, noninvasive or minimally invasive measurements of glycaemia are needed in which nanosensors may well play a part.

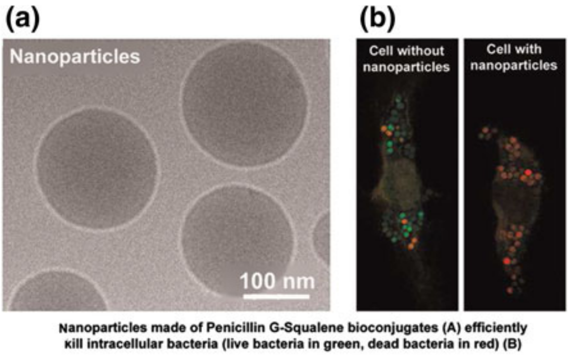


Fig. 11.6 Self-Assembled Squalenoylated Penicillin Bioconjugates: An Original Approach or the Treatment of Intracellular Infections. Semiramoth N., Di Meo C.; Zouhiri F., Saïd-Hassane F., Valetti S., Gorges R., Nicolas V., Poupaert J., Chollet-Martin S., Desmaele D., Gref R., Couvreur P., ACS Nano, 6, 3820–3831; 2012 Copyright American Chemical Society

Nanotechnologies will also be used to develop systems for rapid and early diagnosis of bacterial and viral infections. Furthermore, nanoparticles of penicillin can be used to fight resistant intracellular infections. The use of nanoparticles loaded with penicillin allows this antibiotic to reach the intracellular bacteria and to kill them (Fig. 11.6).

11.2 From Biochips to Cells-on-Chips

Keeping people under healthy conditions is an important goal. In case of illness it is important to identify the right pathology, to choose the best therapeutic treatment and to monitor its effect. In some cases, it is also worthwhile identifying a genetic predisposition to certain diseases to watch for any precursory symptom and take the right decision sufficiently early to ensure the success of the treatment. Looking at a genetic predisposition should nevertheless be performed according to ethical rules. Indeed it is of no help simply to predict a greater probability than the average to suffer from an incurable disease, as this can lead to stress and mental trauma. For all the above reasons, it is important to develop low-cost, fast, and efficient micro and nanosystems for biological analysis. This is now possible using the progress of micro and nanotechnologies.

11.2.1 A Need for Biosensors

Biosensors and biochips are very powerful devices used in analysis because of the high selectivity of biological recognition systems. The detection system consists of a bioreceptor which produces a change measured by a transducer. The bioreceptor, based on a biochemical mechanism for recognition, can be a biological species such as an antibody, an enzyme, a protein, a strand of DNA, etc. It can also be a living biological system like cells, tissue, etc. The transducer converts the information into a measurable quantity such as a fluorescent response or an electric signal. Biochips are usually an array of biosensors which can each detect a different entity and can be monitored individually. The transducers are often based on integrated circuits.

Biochips have developed rapidly since the 1990s thanks to the rapid development of semiconductor technology. The principle is to arrange biosensors in a two-dimensional network (microarrays). Biosensors act independently of one another and each of them is designed to detect something different. The biosensors forming the microarray are arranged on a solid substrate. One of the advantages of microarrays is the ability to perform parallel sensing and thousands of biological reactions in just a few seconds.

11.2.2 Biochips

Biochips are the simplest microsystem that can be developed. They are, for example, able to rapidly decode genes. In a genetic biochip, each sensor consists of short strands of DNA. By immersion in the solution under investigation, it is possible to detect where the sample hybridizes with the strands of DNA fixed on the microarray. This method has been used in the human genome project to identify the genes in human DNA (about 80,000). Apart from genetic applications, biochips can also be used in toxicology or protein research. They can be used to better understand cell mechanisms and develop tailored treatment to various serious diseases.

Detecting oral cancer with nanobiochips

More than 300,000 persons develop an oral cancer each year. Usually discovered by dentists or oral surgeons, a biopsy of the cheek has to be performed; the sample is sent to a laboratory for analysis and several days are needed for the results to be released. Although 95 % of the lesions are not cancerous or premalignant, those which are have to be quickly treated. Indeed, if the oral cancer is detected sufficiently early, the 5-year survival rate is 90 %, while it drops down to 60 % if it is detected later on.

A nanobiochip has recently been developed in the United State (Cancer Prevention Research April 2010 3; 518) and it still undergoing test with patients. Diagnosis is found to be 97 % sensitive and 93 % specific in detecting malignant and premalignant lesions, results that compare well with biopsy tests. It is a painless analysis and results can be obtained in 15 min. One has just to touch the tongue or the cheek of the patient with a brush at the place where the lesion is located.

A sample often does not contain enough biological material and detection would be difficult with the initial concentration. Fortunately, there is a powerful technique allowing multiplying initial pieces of DNA: PCR (Polymerase Chain Reaction). The principle of the technique is described in the frame below.

PCR (Polymerase Chain Reaction)

The Polymerase Chain Reaction (PCR) is a molecular biology technique allowing for multiplication of a single or a few pieces of DNA by several orders of magnitude. Thousands to millions of copies of a particular DNA sequence can be obtained by this amplification technique. This process was enhanced in its operation by Kary Mullis in 1983 and is now extensively used in medical and biological research. The amplification process consists of a series of repeated cycles of heating and cooling. The vessel where the PCR takes place contains the DNA target to be amplified, the oligonucleotides (primers) specific to the sequence investigated, the DNA polymerase (Taq polymerase, for example) and a mixture of the 4 bases making the DNA. A PCR cycle consists of 3 different steps and lasts a few minutes:

1. The denaturation step takes place at around 95 °C. DNA melting occurs, meaning that the double helical state of the DNA unwinds and separates the DNA target into single strands (it is like opening a zipper).
2. The second step corresponds to hybridization or annealing. It takes place at a lower temperature (50–65 °C). The goal is to bracket the part of the DNA region to be amplified. For that, the right and left primers anneal (base pair) to their complementary sequence in each of the DNA strands.
3. In the third step, the temperature is raised a little bit allowing the polymerase to attach each end of the primer site and extend, that means synthesize, a new DNA strand complementary to the DNA template strand.

The trick is that the synthesized products at each cycle are reused in the next cycle. There is an exponential growth of the number of copies and the number of copies is doubled at each cycle.
It should be noted that after the first cycle, the length of the copy is larger than needed (long strand) but at the end of the third cycle there appear copies of the exact required length (short strands). The number of long strands increases linearly while the number of short strands (the desired strands) varies exponentially.
The PCR works like a copying machine. It allows the choice of a particular piece of the DNA and copies (amplifies) this sequences a large number of times so that it becomes visible at the macroscopic scale.

A DNA chip consists of thousands of different nucleotide sequences tied in a regular way (distributed according to a two-dimensional array) to the chip. Each nucleotide sequence acts like a specific sensor (probe) sensitive uniquely to a particular DNA or RNA sequence.

One basic application of DNA chips is to rapidly determine the genes expressed by a cell or a tissue. This method can be useful to detect some cancers like cancer of the breast or of the prostate, for example. Indeed, by comparing the gene expression of a normal tissue and a cancerous tissue, it is possible to see if there is any difference and reveal a way to detect a cancerous tissue if this is the case. Let us illustrate this

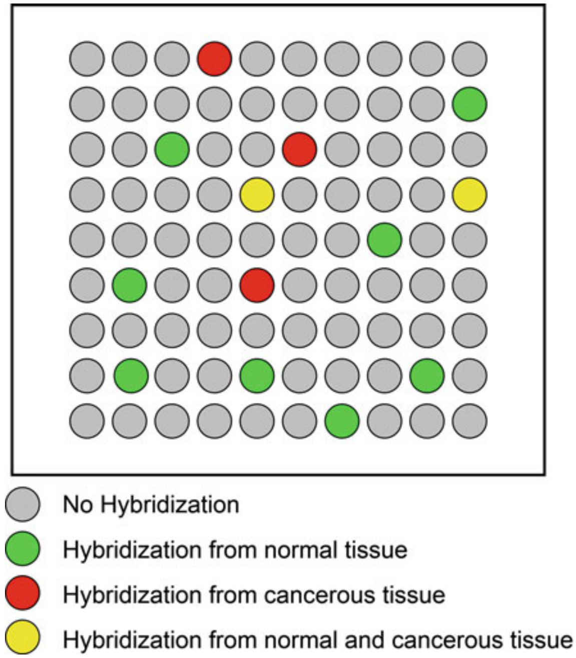


Fig. 11.7 Schematic illustration of a DNA chip array (see text)

point on a simple and schematic example (Fig. 11.7) where we compare a normal and cancerous tissue. When a gene is expressed, it is transcripted into mRNA (messenger RNA). The mRNA of the two tissues is isolated and, using the reverse transcriptase enzyme, converted into complementary strands of DNA (cDNA). In order to be able to differentiate between the two tissues, the cDNA is fluorescently tagged with a color maker. Suppose, for the sake of illustration, that the color is red for the cancerous tissue and green for the normal tissue. After removing the mRNA and mixing the cDNA of the two tissues, the DNA chip is used to compare the two cDNA samples. A DNA chip is an array which can have a hundred thousand or so different probes which are each a unique DNA sequence. A sequence is a single-strand containing typically 20 nucleotides representing a small region of a particular gene of the genome. The part of a gene which is complementary to a probe binds to it: we say that they hybridize. This occurs at a well-defined position of the array indicating which probe is involved in the hybridization process. Afterward, the unbound cDNA is washed away to retain only the hybridized probes. The DNA chip is read by scanning its surface with a fluorescent light, revealing which probes are hybridized and the nature of the tissue. Figure 11.7 shows the method schematically for a very small array; we see different colored spots indicating the probes which have been hybridized. The red and green correspond to genes of the cancerous and normal tissue, respectively. The yellow color indicates that the genes of both tissues are hybridized (there are many identical probes located at a point of the array and not just a single-strand of DNA). The existence of red spots indicates that the cancerous tissue gives different

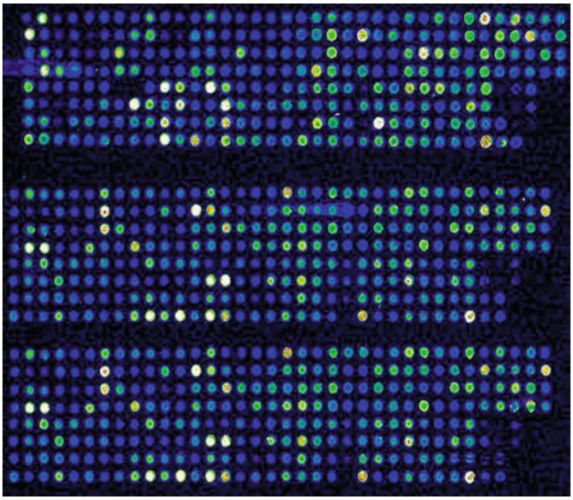


Fig. 11.8 Example from fluorescence scanning of a DNA chip. Clefs du CEA n°52. Image courtesy of CEA/LETI (France)

signals than the normal tissue and this information can be used to detect or monitor the particular cancer.

Real experimental results are shown in Fig. 11.8 obtained by the CEA (Commissariat de l'Energie Atomique et aux Energies Alternatives), which looks very similar to the schematic in Fig. 11.7 illustration of a DNA chip array (see text). Working with two-dimensional arrays allows making many reactions in parallel which strongly increases the speed of analysis.

The process is automated and computer driven. Figure 11.9 shows an experiment where nanodrops are placed using a robot on a glass plate, to perform a high-speed screening of genes: the experiment is part of the ICANCERODROPS project, a collaboration between CEA and INSERM financed by the "Ligue Nationale Contre le Cancer." The aim of the study is to contribute to work studying the involvement of DNA-repair in the resistance of malignant glioma to chemotherapy.

In the CAPUCINE project (Fig. 11.10), the chip consists of a sequence of several hundred biological molecules—DNA, peptides, or proteins—linked to the inside wall of a capillary glass tube having the size of a hair. Each element occupies a specific cylindrical section. This configuration allows analysis of a biological sample of only a few hundredths of a microliter. The capillary is linked, through a microfluidic connection to a lab-on-chip, a capillary electrophoresis system, or to a mass spectrometer.

11.2.3 Labs-on-Chips

Labs-on-chips are devices that integrate, in a single chip, one or several chemical and biological analytical functions. The total size of a lab-on-chip can range from

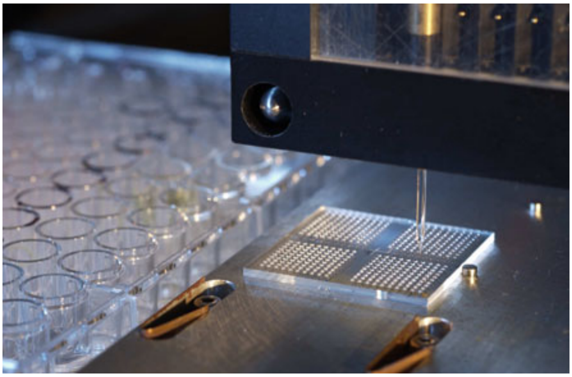


Fig. 11.9 Several cells where many cellular phenotypes can be recorded in biological reactions made in parallel on the biochip. Nanodrops of 50 nl can be dispersed using a robot on a glass plate of 4 cm^2 and analyzed by microscopy. Image courtesy of CEA/LETI (France) (project ICANCERO-DROPS)

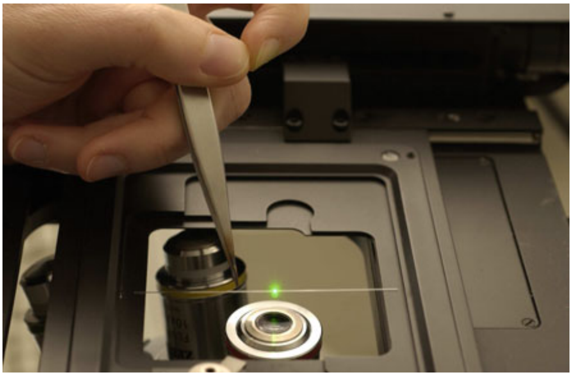


Fig. 11.10 In this biochip, there are hundreds of biological molecules fixed on the internal wall of a capillary. With this one-dimensional arrangement, it is possible to analyze biological samples of hundredths of microliters using a lab-on-chip and a capillary electrophoresis system coupled to a mass spectrometer. Image courtesy of CEA/LETI (France) (project CAPUCINE)

a few mm^2 or cm^2 and it will contain elementary micro and nanodevices. While MEMS (microelectromechanical systems) use mechanically movable structures to measure physical parameters like pressure (pressure sensor) or acceleration (airbag sensors, for example), labs-on-chips manipulate fluids to perform chemical or biological analyses analogous to those made in conventional laboratories operating at the macroscopic scale. The first lab-on-chip system, developed in 1975, was a gas chromatograph microsystem, but researches in this field have only really strongly started at the end of the 1980s and the beginning of the 1990s.

Some devices can perform a complete chemical or biological analysis. They contain micro and nanocomponents and are a macroscopic laboratory scaled down to a chip-size. For that reason, they are sometimes called *micro total analysis systems. A lab-on-chip* can perform only part of the total sequence of the chemical or biological analysis, perhaps one or two laboratory functions. In this sense, DNA chips, discussed above, can be considered as simple lab-on-chip systems. One advantage of a lab-on-chip is the ability to make on-site analysis and bring the sampling location and the analysis nearer to each other. A lab-on-chip is a microsystem which associates a user, reagents, and a protocol to produce information which can be read with a specific instrument.

The packaging is also an important issue, especially if the labs-on-chip has to be implemented inside the body of a patient. There are several advantages to using lab-on-chip devices compared with conventional analysis. Mass production allows production of low-cost and disposable labs-on-chips. Because of the small size of elementary analysis units in each chip, it is possible to make massive parallelization analysis with a high output rate. Because of the small size of the diagnostics volume, low fluid volumes of reagents as well as sample are needed and less waste is then produced.

A lab-on-chip can be used to make *in vitro* diagnostics, to monitor the environment, or to make analysis in chemistry or life science. The sampling and sample preparation are two critical steps before using the lab-on-chip technology. The size of the sample should in particular be significant.

Because of the small volumes involved, the chemical reactions are faster, giving a faster time for analysis and a smaller response time, allowing a better control of the process. The low-cost and high-speed analyses of labs-on-chips make analysis simpler but, on the other hand, these devices are far more difficult to make. The accuracy of the measurement is often not as good as that obtained in a conventional laboratory, but the advantage is in obtaining the results quickly and almost at any location. The main problem in scaling down a process working at the macroscopic scale is the appearance of new chemical and physical effects which may require modification of the process to obtain the same result. In particular, the surface-to-volume ratio of the reagent becomes extremely large, and capillary forces, for example, become important compared to gravitational forces. Surface roughness also has to be controlled. The dimensions of the different parts of the lab-on-chip have to be precisely mastered.

Microfluidics concerns the behavior, the control, and the manipulation of fluids corresponding to volumes with dimensions in the submillimeter scale. Surface tension, viscosity, and fluid resistance play a key role: in lab-on-chip devices, nano and picoliter volumes are handled.

The BioChipLab is an example of a project of integrated microsystems for the preparation of protein samples for mass spectrometry identification. These microsystems are designed to increase the sensitivity of protein identification by mass spectrometry. This technology leads to higher yields and faster kinetics of protein digestion, requires low sample volumes, and allows a direct interfacing with the mass spectrometer. Figure 11.11 shows the silicon microcomponent for liquid chromatography. It has an electrospray pen coupled to the mass spectrometer.

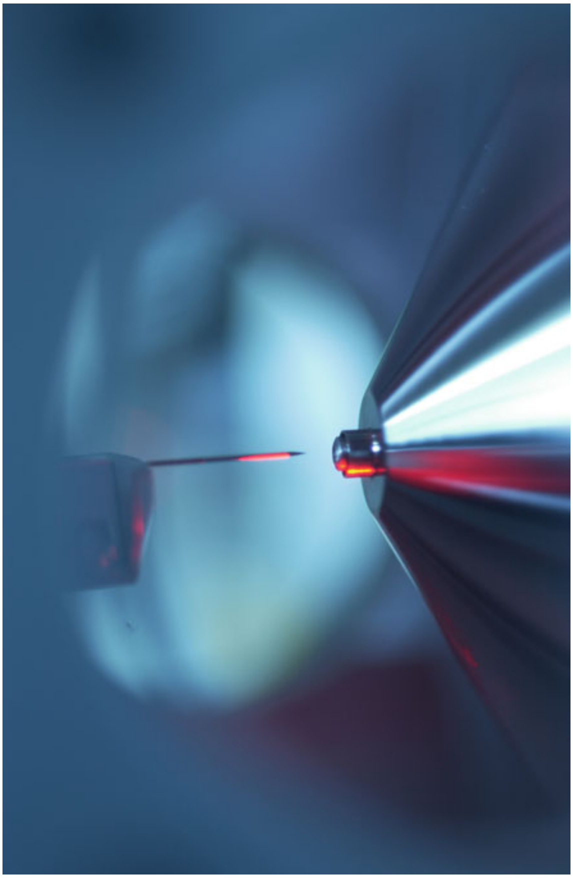


Fig. 11.11 Silicon micro-component for liquid chromatography. This device has an electrospray pen coupled to a mass spectrometer. Image courtesy of CEA/LETI (France) (Biochiplab project)

In labs-on-chips, several functions can be performed. Figure 11.12 shows a commercial device developed by CEA and ST-Microelectronics dedicated to genetic diagnosis. It offers an integrated DNA amplification and detection system on a single chip. This monolithically integrated system performs a PCR-based amplification and a microarray-based detection using microfluidics functions.

Manipulating nanoquantities of liquid is a big challenge in the fabrication of microsystems dedicated to the life sciences. Nanodroplets can be displaced using electrical forces. Figure 11.13 shows a microsystem allowing manipulation of 100 nanoliters by electrowetting. Droplets are moved by a current applied on different electrodes. A droplet is moved by a current sent through the electrodes one by one.

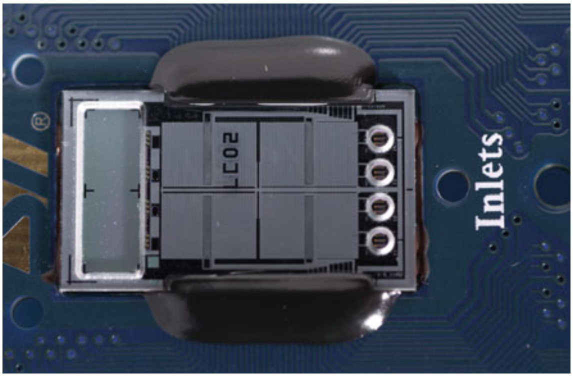


Fig. 11.12 Device developed by CEA and ST-Microelectronics dedicated to genetic diagnosis. The device includes the preparation of the sample using PCR and its analysis using hybridization on oligonucleotide probes. Image courtesy of CEA/LETI (France)

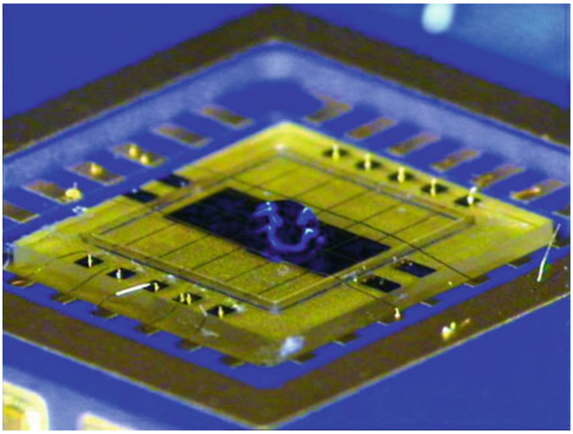


Fig. 11.13 Microsystem allowing to manipulation of 100-nanoliter droplets by electrowetting. The sample droplet is moved by a current monitored applied on the different electrodes. Clef CEA n°52. Image courtesy of CEA/LETI (France)

11.2.4 Cells-on-Chips

Coupling living organisms with artificial-based technology opens a broad field of possibilities. Sensors can exploit a natural extension of biological response and physical or chemical sensors. Cells are able to respond to a change in their environment with high sensitivity due to the biological receptors located at their surface. The sensitivity and selectivity with respect to some species goes far beyond what can be done with chemical and physical sensors. Therefore, it is worthwhile investigating and exploiting changes in cell metabolism or morphology in response to external environment or stimuli. This can be done in cells-on-chips where these changes are transduced and analyzed using electronic micro or nanostructures disposed in an array in order to perform high-speed screening taking advantage of the large number of parallel measurements.

Genome, proteome, transcriptome and metabolome

The genome contains all the genetic information of a living organism. This information is contained in DNA or, for some viruses, in RNA
The proteome is the set of expressed proteins in a cell under given defined external conditions. More generally, it is the set of proteins expressed by a genome.
The transcriptome is the set of transcripts in a cell in given condition, expressed in the form of all RNA molecules. More generally, the transcriptome is the set of all RNA molecules in a given organism under particular external conditions.
The metabolome is the set of the organic compounds (metabolites) present in a cell which has been produced by its enzymes or which derives from the environment.
The proteome, the transcriptome and the metabolome change as a function of time. One of the aims is to develop analytical methods to get as much as possible information about them.

There are various ways to interface living organisms with active inert materials. It is possible to interface neurons with electronic transistors. One can also manipulate single cells using electrical, optical, or acoustic signals. One can also grow cells in microdroplets, making a two-dimensional network on a microarray. Each droplet can be used as a biological sensor for high-speed screening of drugs, genes, RNA, etc.

The COCHISE project, a European research project, developed biosensors able to detect single cell-to-cell interactions. This project applied several technologies simultaneously: electronics, microfluidics, and cell management. The applications of these sensors are to provide a better monitoring and treatment of cancer but several other applications can be foreseen in the environmental engineering, defense, and so on. A lab-on-chip device that acts as a cell sorter which can identify and isolate circulating tumor cells from a blood sample is shown in Fig. 11.14.

An interesting application of CMOS (Complementary Metal Oxide Semiconductor) technology, which is commonly used in microprocessor manufacturing, has been made by the CEA, INSERM, and Silicon Biosystems. An array of more than 100,000 individually controlled electrodes is used to manipulate each cell. Above each elec-

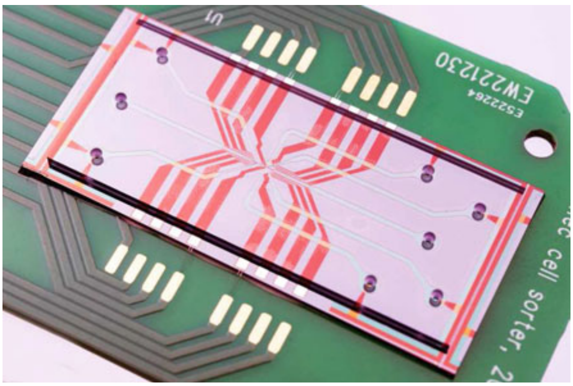


Fig. 11.14 Lab-on-chip device that acts as a cell sorter. Image courtesy of IMEC (Belgium)

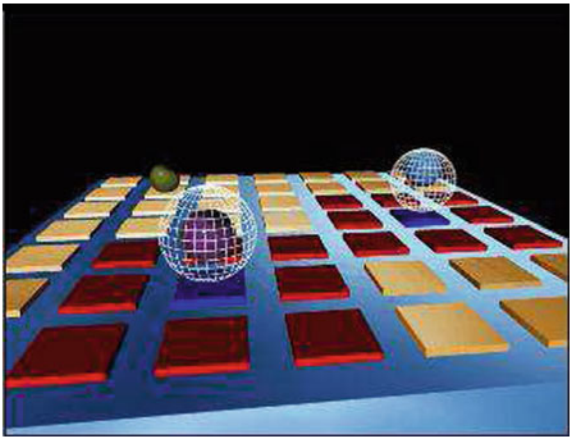


Fig. 11.15 Section of an electrode network in which electric potential traps have been designed to trap particles. From Clef CEA n°52. Image courtesy of CEA/LETI (France)

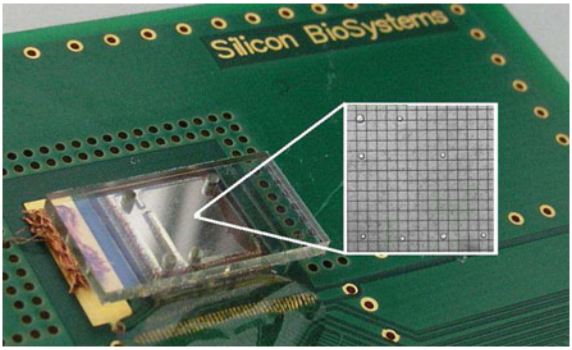


Fig. 11.16 Chip with cells organized in the trap (insert). Each cell is individually manipulated, allowing one to sort populations of rare cells. From clefs CEA n°52. Image courtesy of CEA/LETI (France)

trode, cells self-organize in each of the electric potential wells (traps) with only one cell per trap. Cells are localized using on-chip optical and electronic sensors. Each cell can be displaced at will and moved from one position to another. Such a technology has several applications such as sorting stem cells or the manipulation of therapeutic cells.

In Fig. 11.15, a section of an electrode network is shown. Each electrode measures 20 μm squared. Electric potential traps have been designed in order to be able to trap cells, here represented by spheres.

In Fig. 11.16, the MeDICS chip is displayed with cells trapped in the array (insert). By individually manipulating each cell, it is possible to sort rare cells. This technology can be used, for example, to sort stem cells or find anomalous cells during the analysis of biopsies.

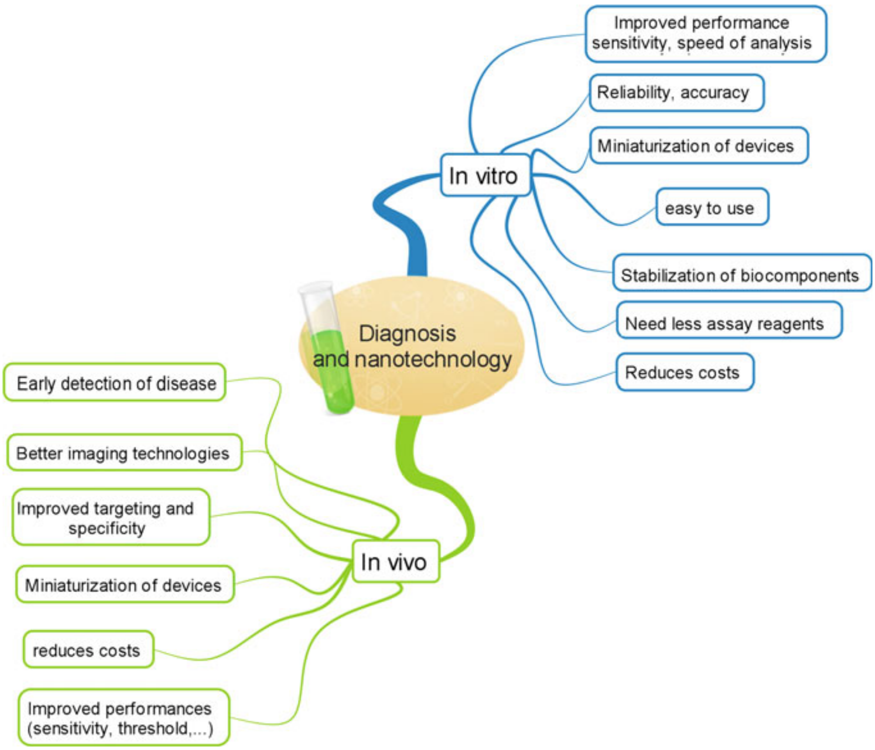
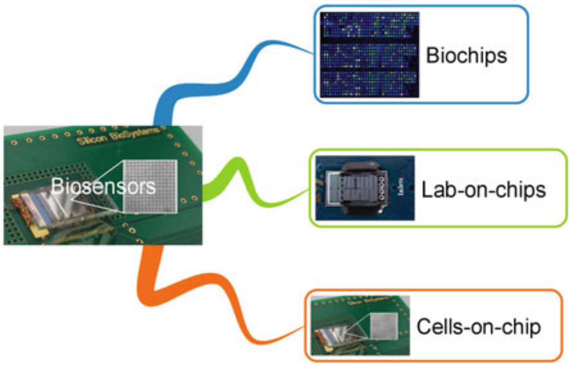


Fig. 11.17 Main benefits that nanotechnology can bring to diagnosis

Fig. 11.18 Categories of biosensors relying on micro and nanoelectronics and micro and nanotechnology



11.3 Conclusion

The evolution of healthcare is toward tailored medicine. This is possible thanks to a continuous and rapid technological progression where nanotechnology has an important role to play. Diagnosis is the first and most important step in patient care.

It can be made *in vitro* or *in vivo*. Figure 11.17 summarizes some of the main benefits expected from nanotechnology in the diagnostics sector.

Diagnostics can benefit from micro and nanoelectronics as well as from micro and nanotechnology (Fig. 11.18). Biochips give the ability to make parallel high-speed analysis at low cost. With labs-on-chips it will be possible to quickly perform complex analysis in any place at low cost. With cells-on chips, by coupling inert and living, additional possibilities will appear using the advantages of both.

Chapter 12
Therapeutics and Regenerative Medicine

The history of medicine shows that drug-based treatments have been a mainstay of patient management throughout the millennia. Many of the active ingredients that modern day medicines contain have dimensions on the scale of nanometers or they interfere with biological molecules that are at the nanometer scale, yet their production is not considered as a “nanotechnology.” Nanotechnologies usually refer to processes where objects are manufactured or manipulated at the nanoscale, typically at dimensions between 1 and 100 nm. The production of passive or active nanoscale packaging also belongs to the field of nanotechnology, but the therapeutically active drug molecules themselves do not. As far back as the mid-1970s, investigations into soft capsules to encapsulate the active ingredients of a drug had started, and encouraging results were obtained a decade later.

There is more and more demand for personalized medicine. With conventional treatments, this is costly and there is a hope that nanotechnology will substantially lower these costs, making them available to a greater number of people. This may disturb the model of the pharmaceutical industry where a single (blockbuster) drug can be ordered for a large number of patients.

12.1 Therapeutics

12.1.1 Improved Drug Delivery

Targeted delivery and smart release of drugs is becoming a challenge in pharmaceutics. In the treatment of severe diseases, like cancer for example, there is a multidisciplinary approach to deliver the most efficient drug cocktail in chemotherapy sessions. The challenge is to decrease the global amount of a drug delivered to a patient while delivering it at the right place and at the right time. It is also important to minimize drug degradation and loss before it reaches the disease site. Indeed, in classical methods, like oral delivery, an excess amount of drug may be required

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_12, © Atlantis Press and the authors 2014

to compensate for extraneous losses and this can be associated with side effects to the patient. Therefore, nanotechnology can help in reducing the quantity of a drug while keeping the same efficacy. At the moment, mostly existing drugs are used in a nanotechnology delivery. However, in the future, new drugs are expected to be introduced better fitted to a nanotechnology delivery. Furthermore, nanotechnology can help in providing better understanding of intracellular function in order to develop new drugs and new delivery techniques.

Nanodrug delivery

Drugs need: (i) to be protected during their transit through the body to the target, (ii) to maintain their biological and chemicals properties, and/or to stop them from damaging the parts of the body they travel through. Once a drug arrives at its destination, it needs to be released at an appropriate rate for it to be effective; one way of achieving this is to encapsulate the drug.

Nanotechnology can improve both the permeability and degradation characteristics of the encapsulation material, allowing the drug to travel efficiently to the target and to be released in an optimal way. Nanoparticle encapsulation is being investigated for the treatment of cancer, neurological disorders, and to deliver therapeutic molecules directly to the central nervous system beyond the blood–brain barrier, as well as to the eye beyond the blood–retina barrier. Applications could include treatment of Parkinson's, Huntington's chorea, Alzheimer's, amyotrophic lateral sclerosis (ALS), and diseases of the eye.

Several drugs are not used because they have a poor solubility and, because of that, are difficult to administer. Nanotechnology can help in this respect, by "clothing" the drug in such a way that the solubility is increased.

The advantages offered by nanotechnology drug delivery are summarized in Fig. 12.1.

The way drugs are released is important for better efficiency (Fig. 12.2). There can be continuous or pulsed delivery. In the case of continuous delivery, the drug is released, for example, by diffusion out of a degradable polymer, at a controlled rate. For pulsed delivery, the drug can for instance be trapped within a polymer and be released using an external stimulus (light, pH, temperature, etc.). The delivery of a

Fig. 12.1 The main expected advantages of nanotechnology delivery of drugs

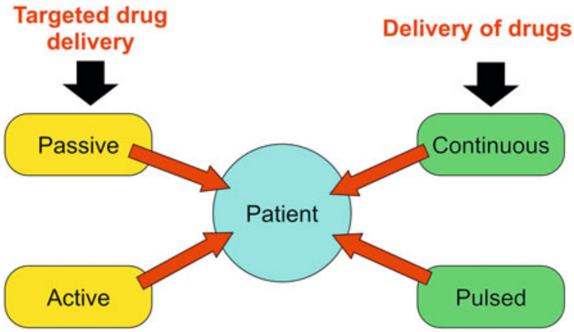


Fig. 12.2 Methods of drug delivery

drug can be passive (degradation of a polymer, for example), or active (a second-generation transdermal patch, for example, where the delivery is triggered by an applied electric field).

Colloidal systems are good drug carriers. They can comprise micelles, liposomes, nanoparticles, etc. Micelles are formed with molecules having a hydrophilic head and a hydrophobic tail (Fig. 12.3). They form a hydrophilic shell around the micelle protecting the contents: inside they can contain the drug. In this way, the drug concentration is sometimes greater than its intrinsic water solubility. The shell of the

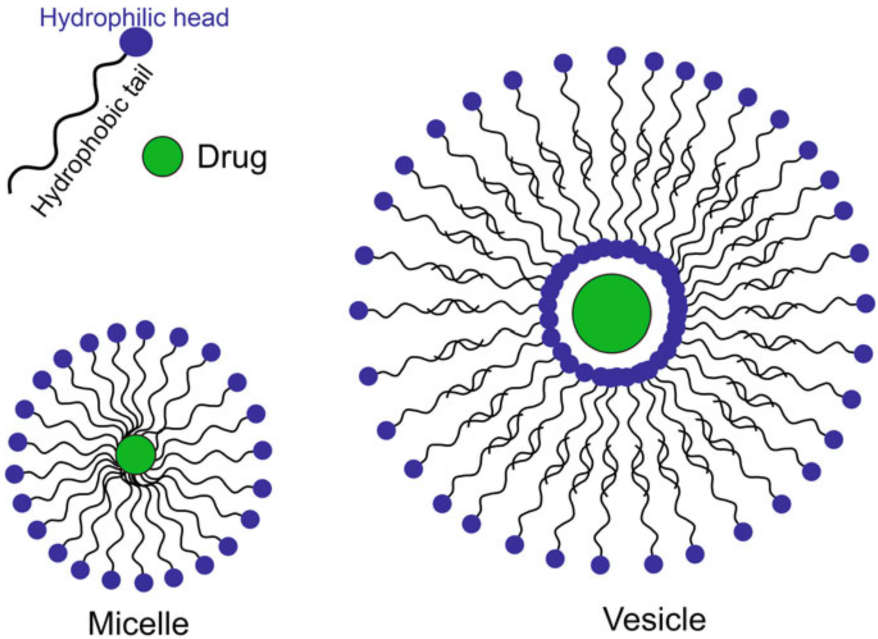


Fig. 12.3 Schematic representation of a micelle and a vesicle

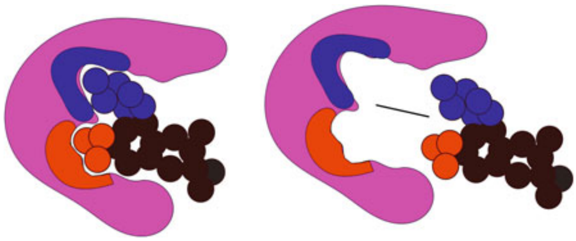


Fig. 12.4 Principle of imprinted polymers: a molecular template is used to have a molecular imprint for selective binding of equivalent molecular structures

micelle protects the drug until it is delivered. Liposomes are vesicles (see Fig. 12.3) where drug molecules can be encapsulated inside a bilayer of molecules.

Other methods exist using dendrimers, liquid crystals, hydrogels, or molecular imprinted polymers, for example. A molecular imprinted polymer has properties similar to active biological molecules: it has a greater affinity with molecules having a complementary geometrical shape (the system behaves like a lock and key). In this sense, it behaves like a plastic antibody. This is schematically shown in the Fig. 12.4. Because of these specificities, molecular imprinted polymers have great potential for smart drug delivery. Functionalization of synthetic polymers with biological molecules, such as peptides or proteins, are also techniques which can improve drug delivery by better targeting the drug and protecting it before it reaches its target.

In the future one may have micromechanical systems (in particular containing nanocomponents), made using microelectronic technologies, able to deliver several kinds of drugs on demand and at the right place. In situ forming implants are also less invasive and less painful than conventional implants. They can be delivered, for example, by subcutaneous injection.

12.1.2 Delivery Routes

The delivery route of drugs is also a key point in disease treatment. The very nature of the molecule sometimes puts a constraint on the delivery possibilities. The most common way to deliver drugs is via the oral route. It is a convenient and cheap but part of the drug can be lost and lead possibly to side effects. Routes such as intravenous, intramuscular, or subcutaneously injections are more efficient but less convenient. This is an area where nanotechnologies can play an important role. Nanoscale drugs have a great potential in nasal and sublingual delivery. Because nanoparticles are able to cross some physical barriers like the blood–brain barrier, this opens the way for more easily treating brain diseases.

Other routes of drug delivery exist such as pulmonary delivery (aerosols, inhaler systems, nebulizers, etc.) where nanostructured drugs can be used. Transdermal drug delivery can also benefit from micro and nanosystems. The delivery can be passive, by diffusion, or active, by being directed by some external agent. Gene delivery is also a new development in medicine for treatment of diseases resulting from a genetic malfunction or disorder. Nanotechnologies will especially play a role in transporting modified genes to their targets.

Subcutaneously implanted chips are being developed to monitor key body parameters continuously, including pulse, temperature, and blood glucose; optical microsensors are implanted subdermally or in deep tissue to monitor tissue circulation after surgery; while a third type of sensor uses MEMS and future NEMS (micro/nanoelectromechanical system) devices and accelerometers to measure strain, acceleration, angular rate, and related parameters for the monitoring and treatment of paralyzed limbs, and to improve the design of artificial limbs. Implantable sensors would ideally be used to work with devices that administer treatment automatically, e.g., fluid injection systems to dispense drug. Opportunities here include chemotherapy that directly targets tumors, e.g., in the colon, and are also programmed to dispense precise amounts of medication at specific times, to optimize therapeutic effects or to be less intrusive, such as when a patient is not physically active, e.g., asleep. Sensors that monitor the heart's level of activity can also work with an implantable defibrillator to reverse abnormal heart activity.

Nanotechnology offers many therapeutic possibilities which are summarized in Fig. 12.5. We shall highlight some of them as follows.

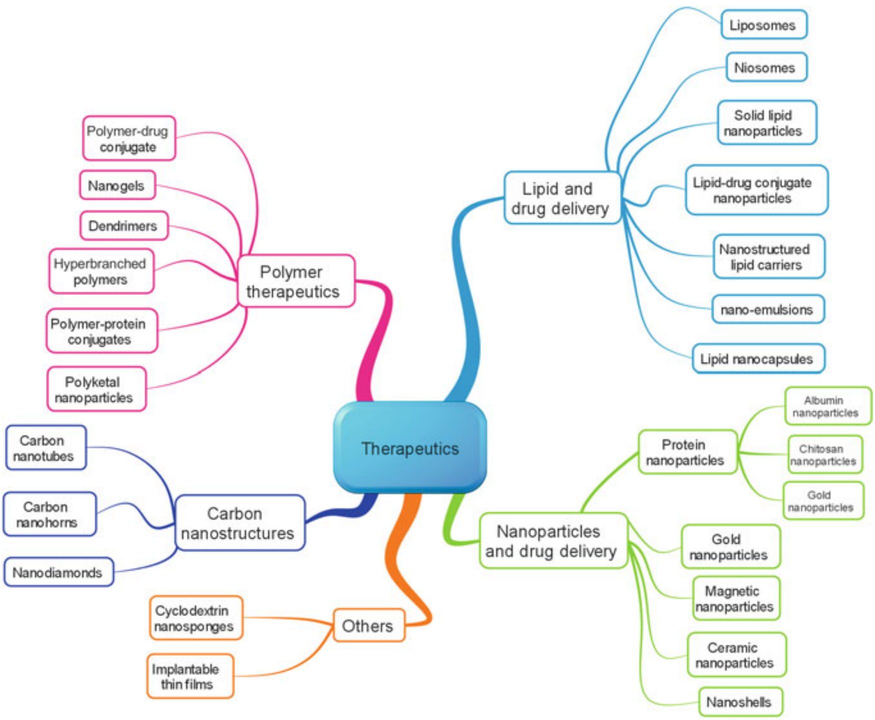


Fig. 12.5 Some therapeutics based on nanotechnology. Figure built from the results of the observatoryNano project

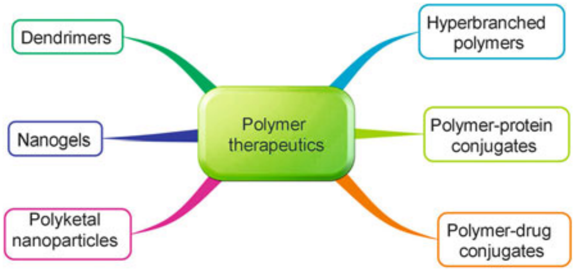


Fig. 12.6 Different fields of polymer therapeutics

Polymer Therapeutics

Polymer therapeutics includes many techniques which are shown in Fig. 12.6. The advantage of polymer therapeutics in drug delivery is that it is possible to precisely customize the properties of the therapeutics for the drug delivery requirement. Furthermore, polymer therapeutics provides high biocompatibility and increases the stability of volatile drugs. A high concentration of the drug can be delivered to a desired location. Applications can be found in cancer therapy, for example, but also in antibiotics targeting.

Dendrimers are molecular nanostructures which we presented in Chap. 2. They provide a nanoscale container that can carry molecules like drugs. The exterior surface can be functionalized. One of the advantages of dendrimers is that they can have a size similar to many proteins and biomolecules such as insulin or hemoglobin. They can be used for targeted drug delivery. Dendrimers are also efficient in treatment of bacterial and viral infections. Hyperbranched polymers are basically irregular dendrimers and are less expensive to prepare. Their surface can be multifunctionalized.

Polymer–protein conjugates increase protein stability and solubility. They improve the targeting ability, reduce toxicity, and overcome drug resistance. They are already used to treat some cancers, and hepatitis B and C. Nanogels are made of flexible hydrophilic polymers cross-linked at the nanoscale. They are soluble in water and are used to incorporate drugs, inorganic molecules, and so on. Nanogel particles have been used to cross the blood–brain barrier to deliver oligonucleotides to the brain. They have also been used to carry insoluble anticancer drugs.

Polymer-drug conjugates can improve targeting ability, reduce toxicity, and overcome drug resistance. They are used in cancer treatment. Polyketals[1] can form nanoparticles for encapsulation of hydrophobic drugs and proteins. They are used in the treatment of some lung diseases, in imaging techniques, etc.

One example is terpenes-based nanoparticles: synthetic terpenes loaded with anticancer compounds have been obtained by living radical polymerization leading to nanoparticles with dramatic anticancer activity (Fig. 12.7).

[1] Polyketals are polymers with ketal linkages in their backbone.

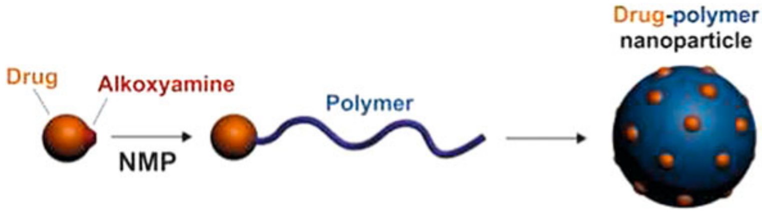


Fig. 12.7 Nanoparticles with *in vivo* anticancer activity from polymer prodrug amphiphiles prepared by living radical polymerization, Harrisson S., Nicolas J., Maksimenko A., Trung Bui D., Mougin J., Couvreur P., Angewandte Chemie Int. Edition, 10.1002/anie.201207297; 2012. *Copyright* Wiley-VCH Verlag GmbH and Co. KGaA

Lipids in Drug Delivery

Liposomes are vesicular structures (Fig. 12.3) with an inside core surrounded by a lipid bilayer. They have been used in drug delivery and cosmetics since the 1970s. Liposomes protect the drug that is enclosed in the core during its transport inside the body of the patient. They are particularly useful in the delivery of insoluble drugs, and targeted molecules can be grafted at the surface, thus allowing one to better reach the desired zone of the body where the drug has to be delivered. Liposomes can deliver several kinds of drugs or biological molecules: antibiotics, antioxidants, vitamins, genetic material, etc. It is even possible to incorporate magnetic particles, allowing improved monitoring in magnetic resonance imaging. Liposomes can also be used in controlled gas or drug delivery using ultrasound, for example.

Micelles are spherical lipid nanostructures with no inner cavity (Fig. 12.3). Thanks to their small size, they can penetrate into tumor cells more easily. Micelles are often conjugated with ligands to increase their efficiency, especially in cancer treatment.

Solid lipid nanoparticles are oily droplets of nanometer dimensions. They are solid at room temperature and are stabilized by surfactants. They are used in controlled drug release and provide a protection from water. They also have applications in cosmetics.

An improved lipid nanoparticle technology is based on mixing solid and liquid lipids to make nanostructured lipid carriers, and even to synthesize lipid–drug conjugate nanoparticles, as this considerably increases loading capacity compared to solid–liquid nanoparticles.

Nanoemulsions are dispersions of nanodroplets of one liquid within another. They are more efficient in drug delivery than larger scale emulsions and are well suited for drug delivery of drugs with very low water solubility. Lipid nanocapsules are in between liposomes and nanoemulsions. They can be functionalized at the surface and the delivery can be better controlled. These capsules have an oily core and have been used to deliver drugs and radionuclides across the blood–brain barrier.

Nanoparticles in Drug Delivery

There is a major interest in using nanoparticles in drug delivery because they provide a number of advantages compared to conventional methods. There are very stable, highly specific, and can carry a high load of treatment agent with a facility for release on demand. One important use is drug delivery for cancer treatment. Indeed, drugs can be enclosed inside the nanoparticle and binding molecules linked at the surface, giving the nanoparticles the ability to preferably reach a tumor region, for example. After reaching the target site, the drug is released using different techniques. In passive delivery, the drug is released using local physical or chemical processes such as diffusion, degradation, swelling, etc. In active delivery, the drug payload is released by an external agent such as light, a magnetic field, or ultrasound.

Protein nanoparticles are one route for drug delivery. These include albumin nanoparticles where drugs or biomolecules can be grafted on the surface. This technique is, for example, used by the Abraxis Bioscience Company, to treat some breast cancers using a solvent-free formulation of Paclitaxel. An advantage is that the toxicity of the drug is reduced because most of it is administrated at the right place.

Chitosan is a natural product derived from the shell of crustaceans. An interesting property of chitosan is that it has the ability to clot blood. Chitosan nanoparticles can be used in bandage and hemostatic agents. A derivative of chitosan is also used for nonviral gene delivery.

Lecithin is a lipid mixture used extensively as a food additive, extracted from egg yolk or soy beans. It is also a basic product in liposomes and micelle production. If chitosan is coated on the surface of lecithin nanoparticles, its stability and adhesive properties are improved.

Gold nanoparticles have been known for a long time, much before nanotechnology became fashionable. They are used in the treatment of rheumatoid arthritis or multiple sclerosis. Gold nanoparticles can be easily manufactured, have a good biocompatibility and can be easily functionalized. If they are of small size, typically with a diameter smaller than 50 nm, they are able to cross the brain–blood barrier.

Magnetic nanoparticles such as iron oxide nanoparticles are used as contrast agents in magnetic resonance imaging and for drug delivery. Because they are sensitive to an external magnetic field, they can be used in cell separation techniques or to label cells.

Magnetic nanoparticles coated with molecules permit the targeting of tumor sites, for example, and can carry drugs having the ability to destroy malignant cells.

Nanoparticles of silica, alumina, etc., of a size of about 50 nm are easy to prepare and are relatively stable. It is possible to tailor their physical characteristics and properties such as size, porosity, and also biomolecules can be linked on their surface. These nanoparticles, often called ceramic nanoparticles, can be used to encapsulate hydrophobic drug molecules.

Nanoshells have a nanospherical core made of silica or of another material with an external metal coating such as gold, for example. These structures have a plasmon resonance (a collective motion of valence electrons) that can be excited by external electromagnetic radiation (light) of the right frequency (see Chap. 5). The value of the resonance frequency depends upon the thickness of the gold coating. A change of the frequency can be made by changing the thickness of the coating, allowing a fine tuning of the system. Nanoshells have applications in cancer therapy (prostate cancer, for example). Antibodies or biomolecules are linked to the surface in order to specifically target the nanoshells toward the cancer site. The idea is to destroy the tumor cells by irradiating this area where the nanoshells have stuck using near-infrared light producing heat locally (thermoablation).

Aptamers are nucleic acid-based binding species which can bind tightly to target ligands. Early aptamers used DNA or RNA strands to bind to small molecule ligands such as soluble proteins (thrombin, polymerases, ATP, etc.). Aptamer-nanoparticle conjugates have advantages compared to antibodies. They can be used to treat age-related macular degeneration or prostate cancer.

Colloidal dispersions of nanoparticles (Nanosuspensions) are used for intravenous delivery of insoluble molecules. Because the drug is ultimately delivered in a solid state, the delivery load can be large, allowing a decrease of the duration of treatment.

Nanocrystals are aggregates of ordered atoms. They have a size ranging between 10 and 400 nm and are produced by sonication. They have the ability to deliver insoluble drugs. Nanodiamonds can also be functionalized and used to deliver drug molecules. Fluorescent nanodiamonds can penetrate inside cells and can be used for tracking and imaging.

Carbon nanotubes or nanohorns (nanotubes closed at one end) can transport molecules, proteins, and nucleotides. They can enter cells without harming them. Their surface can be functionalized. They are useful for the delivery of insoluble and toxic drugs having a tendency to cluster.

Cyclodextrin nanosponges, which are mostly used to remove organic impurities from water, can also be used to deliver drugs. Thin films, with a thickness of about 150 nm manufactured with several layers, can be tailored to release drug when a small voltage is applied, acting in this way as an active patch for the patient.

12.2 Regenerative Medicine

The population is aging, and the probability of a deficiency in some part of the body increases throughout the population as a result. Accidents can also lead to severe injuries of the body, and destroy or weaken some functions. Additionally, some people suffer deficiencies at birth. The increasing demand for repairing the body has led to advances in regenerative medicine. In order to be effective, one needs smart biomaterials, active cells, and bioactive signaling molecules.

Nanotechnology offers the opportunity to study processes at molecular and cellular scales in real-time, and during the earliest stages of the development of a disease. Since nanocomponents can be made to share some of the properties of natural nanoscale structures, there are great opportunities to develop artificial nanostructures that sense and repair damage to the cell or tissue, just as a naturally occurring biological nanostructures might do.

12.2.1 The Quest for Biomaterials

Almost half a century ago, the first generation of biomaterials were used inside the human body to replace a limited range of tissue parts. It was clear then that they had to be biologically inert in order not to be rejected by the body and needed to avoid cell-based disruption. Around the late 1980s, bioactive components were introduced, having a controlled action on the body of the patient. This corresponded to a second-generation of biomaterials. Applications of this type exist in the orthopedic and dental domains. Resorbable materials (some polymers for example) were also developed at that time.

Now, new materials are being developed with regenerative properties that help the body to heal itself. This represents the third-generation of biomaterials. Such regenerative tissue engineering (Fig. 12.8) is a growing domain where nanotechnology can be of great help. The idea is usually to use a resorbable scaffold and specific cells to regenerate diseased or damaged tissues; for example, applications include skin, cartilage, and bone regeneration. Stem cells are an important source of regenerative cells. There is also a possibility of using of cell-signaling molecules to produce regeneration messengers useful for driving tissue reconstruction. One of the advantages of nanotechnology for regenerative medicine is the possibility to achieve requisite functional properties in situ and to decrease cost, providing a real advantage in allowing these methods to be used on a large scale. Damaged tissues and organs are often replaced by artificial substitutes, and nanotechnology offers a range of new biocompatible coatings for implants that improves cell adhesion, as well overall materials durability and lifespan. Many new types of nanomaterials are planned as implant coatings to improve interface properties, such as nanopolymers to coat devices in contact with blood (such as artificial hearts or catheters) to disperse clots or to prevent their formation. Nanomaterials and nanotechnology fabrication

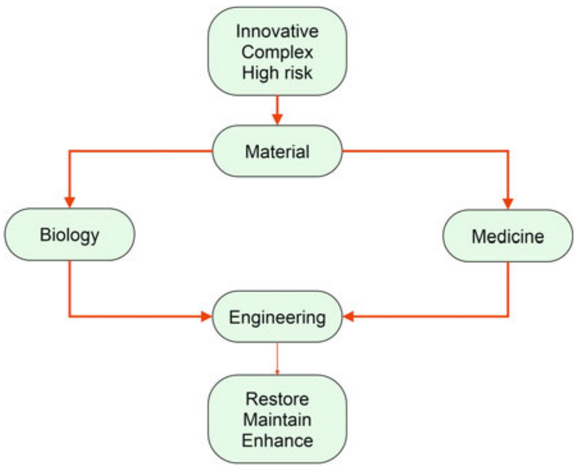


Fig. 12.8 Basic steps toward regenerative tissueengineering

techniques are being investigated as tissue regeneration scaffolds. The ultimate goal is to grow large complex organs, examples include nanoscale polymers molded into heart valves, and polymer nanocomposites for bone scaffolds.

Commercially viable solutions are scheduled for the next 5–10 years, based on likely technological advances related to a better basic understanding of molecular/cell biology and of fabrication methods for production of controlled 3D scaffolds.

Nanostructures are promising for temporary implants, e.g., that biodegrade and do not have to be removed in a subsequent operation. Research is also being carried out on flexible nanofiber membrane meshes that can be applied to heart tissue in open-heart surgery. Such a mesh can also be infused with antibiotics, painkillers, and other medicines in small quantities and applied directly to internal tissues.

12.2.2 Biomimetics

One technique in regenerative medicine involves mimicking what nature does (biomimetics). Tailored resorbable polymers at the molecular level can be used as a matrix for tissue regeneration. These materials are "smart" in the sense that they can react to their environment and trigger a molecular response at the cellular level in order that they may, for example, operate by changing their conformation depending upon the physical conditions of their environment (temperature, pH, electrical stimuli, etc.). Nanotechnologies come into play because they allow production of tailored macromolecular structures at the nanometer level. Manufactured structures with different morphologies are now achievable and could be used to produce resorbable scaffolds.

Bionanomaterials can improve the longevity and the functionality of implanted materials. Nanomaterials could also enhance the mechanical properties of materials and be used to reinforce some weak parts of the body. A bioactive coating of an implant with nanomaterials can make a better bond with the neighboring tissues, and so help to increase the lifetime and integration of the implant. It will be also possible, with an active nanocoating, to build a barrier preventing immune rejection mechanisms from the host. Because of their small size, nanosystems could be used in neural prostheses.

12.2.3 Cell Therapy

Cell therapy is bringing hope for a new era of regenerative medicine. Cellular differentiation naturally occurs in the normal cell, and turnover and repair follow any injury. Turnover is different, depending on the nature of the tissue. It is fast for blood or epidermis, much slower in bone or cartilage, and can be extremely slow or nonexistent for some tissues such as brain tissue. Adult stem cells have a great self-repair potential that can be used in regenerative medicine, and nanotechnologies could be useful in developing delivery vehicles based on smart nanomaterials. Nanotechnologies are also needed to better understand natural healing mechanisms, and in decoding communication between cells based on different types of cell signaling.

Cellular signaling

Cellular activity and relationships with neighboring cells in a tissue are governed by a complex communication system which is partly based on direct cell-to-cell signaling and signaling by diffusible biomolecules. A single cell should indeed take account of its close environment in various ways during the development of a tissue, and its repair following an injury or after a challenge to the immunity system. Therapies based on bioactive signaling molecules are under development. The need here is a complex one because sequential signaling is involved in the natural formation and repair of tissue. The sequence is in most cases unknown and has to be understood. Nanotechnologies can help in the development of systems able to make a sequential delivery of signaling biomolecules (proteins, peptides, genes, etc.) at controlled rates which will in turn activate cells to produce growth factors and initiate the growth and self-assembly of a tissue. Nanotechnologies can also contribute to the understanding of the communication system of cells within a tissue.

The basics ingredients necessary in regenerative medicine are summarized in Fig. 12.9.

12.2.4 Implants

The major problems with implants are that they can be rejected by the body or wear out and require replacement in the future. Nanotechnology is expected to improve biocompatibility either by coating implants with nanomaterials or by having implants manufactured from nanostructured nanomaterials. Coatings can be chosen to protect against bacterial or fungal infections. When applied on synthetic vascular grafts, the

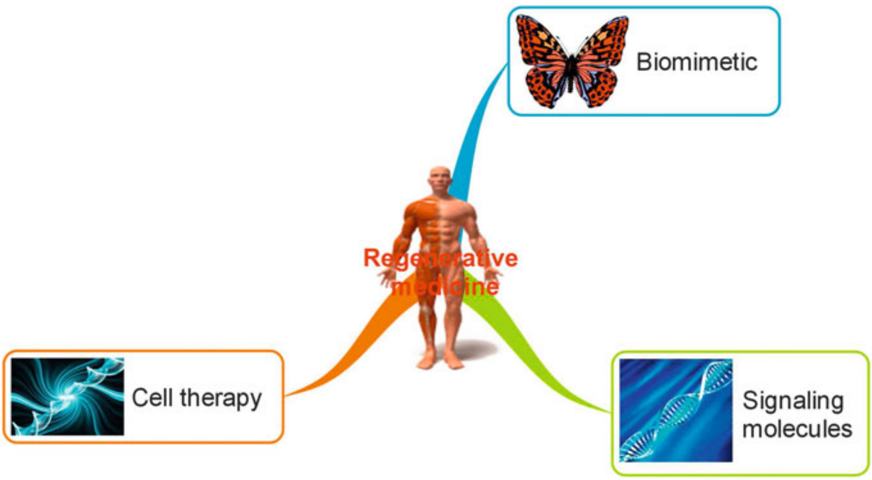


Fig. 12.9 Basic ingredients in regenerative medicine

goal is to prevent the adherence of biological material in the body. Using nanomaterials for implants is interesting because it can reduce their weight, make them stronger, and increase their lifetime compared with conventional implants.

Nanotechnology can be useful to improve cell adhesion and growth. In some situations, sensors located in the implant can monitor and control the tissues, allowing a better growth of cells around the implant and a better recovery. Sometimes, implants need energy to work. Nanotechnology can be used to develop very small batteries with associated control circuits.

As far as bones are concerned, also the case with dental implants, the important issue is to have good osseointegration. This requires a good match between the physical properties of the implant and the surrounding bone. It depends very much on the surface in contact between the artificial and natural bone: the larger the surface, the better the integration and the faster the healing will be. Nanotechnology, which has the ability to produce porous media with a large area and good mechanical properties, has several assets in this domain. For example, nanostructured titanium gives a better surface area and osseointegration in bone repairs. Growth factors and biomolecules grafted onto implants improve growth and integration inside the body of the patient.

Nanotechnology is also useful in cartilage repair, an ailment affecting many people. Cartilage tissues cannot repair themselves, which is an important drawback. It is possible to regenerate cartilage tissue *in vitro* using nanotechnology techniques and to transplant it in the damaged region of the body. Carbon nanotube composites are also being studied to grow cartilage cells.

The tissue engineering domain enjoys strong progress and could be useful in those cases where the mortality rate of the patients is high. Studies are in progress for tracheal, oesophageal, and bladder replacement by repairing damaged cells with new cells prepared *in vitro*.

Vascular implants and stents are often needed to treat cardiovascular diseases. Stents are thin tubular devices implanted into arteries. They restore blood flow but are subject to compatibility issues sometimes leading to a narrowing of arteries that then requires surgery. Tissue engineering can be helpful to solve this challenge. The aim is to manufacture a multilayer architecture of tubules. Three-dimensional structures can be produced using seed cells in scaffolds, cell sheet engineering, and hydrogels for cell growth. Nanocoatings are useful for improvement of the biocompatible properties of stents. Stents are also used in urinary or bile problems. In this case, a nanoscale sol-gel coating reduces sludge accumulation. Another interest for use of nanotechnology in stents is that drugs can be incorporated into the coating.

Developing neural implants is a difficult challenge. Because of their good electrical properties, carbon nanotubes are being investigated for the replacement of axons. Carbon nanotube fibers are being studied for the promotion of neuron cell growth, for reduction of scar tissue formation, etc. Biocompatible self-assembled monolayers formed on gold are also being studied. Electrical simulation is another aspect of neural implants where nanodevices have their place. The goal is to restore functionalities of a damaged brain, and could be useful in the treatment of neurodegerative diseases such as Parkinson's disease or Alzheimzer's.

Silicon nanowires are interesting because of their ability to detect multiple signals (several dozen times greater) from neurons compared to conventional electrodes.

Energy is an important issue for pacemakers. Even lithium batteries with a lifetime of between 7 and 10 years need to be replaced. Furthermore, pacemakers are sensitive to magnetic fields which are a problem if the patient requires magnetic resonance scans, for instance. One way to overcome the need for changing the battery is to have a rechargeable battery, using as an energy source the heat of the body, for example. Spintronics, a development described in Chap. 5, can be used in pacemakers, and in retinal and cochlear implants.

Vision and hearing

The human retina has photoreceptor cells (rods and cones) converting light signals received into the eye to electric signals that propagate through the optical nerve to the brain. Macular degeneration and retinitis pigmentosa are retinal diseases that destroy some of these cells.

Nanotechnologies are being developed for a new generation of smaller and potentially more powerful devices to restore lost vision. One approach uses a miniature video camera attached to a blind person's glasses to capture visual signals that are then processed by a microcomputer worn on the belt and transmitted to an array of electrodes placed in the eye. Another approach is to use a subretinal implant, designed to replace photoreceptors in the retina which uses a microelectrode array powered by up to 3,500 microscopic solar cells.

There are several projects around the world trying to build an artificial retina with increasing optical resolution. The principle of one of them is shown in the Fig. 12.10 taken from the US artificial retina project (http://artificialretina.energy.gov/). A small camera, mounted in eyeglasses, sends information by radiowave to a dedicated microprocessor worn on a belt. This chip sends signals to an array of microelectrodes through a small wire which transforms them into electric pulses injected directly to the cells of the retina which are still working. All these signals propagate through the optic nerve to the brain. Some time is needed for the patient to learn to interpret these data. The challenge is to get an increasing optical resolution with this artificial system. A 16-microelectrodes array was implanted in a patient in 2004 and an array with more than 60 microelectrodes in 2009. Arrays larger than 200 microelectrodes have been under development since 2007 and arrays larger than 1,000 pixels have been designed in 2010. At this stage, nanotechnologies are already present in this application.

Powerful nanodevices for hearing have also been developed: i.e., an implanted transducer is pressure-fitted onto a bone in the inner ear, causing the bones to vibrate and move the fluid in the inner ear, which stimulates the auditory nerve. An array at the tip of the device uses up to 128 electrodes, five times higher than current devices, to simulate a fuller range of sounds. The implant is connected to a small microprocessor and a microphone in a wearable device that clips on behind the ear. This captures and translates sounds into electric pulses transmitted by wire through a tiny hole made in the middle ear.

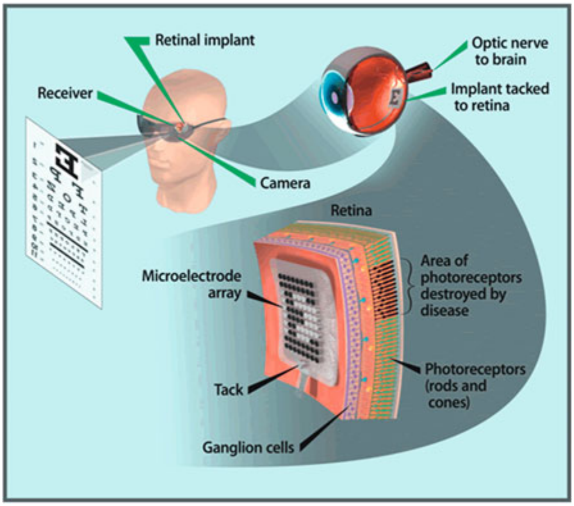


Fig. 12.10 Schematic principle of an artificial retina. Courtesy of http://artificialretina.energy.gov/

Tissue engineering for the human cornea is extremely difficult *in vivo* and studies are made *in vitro*. There are also attempts to make an artificial retina using active implants. Some examples are described in the frame box *Vision and Hearing*. It is not an easy thing to implant something in the eye. It takes more than 3 months for the nerves to recover after an implantation and one has to be sure that the artificial stimulation of the nerves does not damage the nerves.

12.2.5 Nanotechnology in Surgery

Nanotechnology is also present in surgery through many aspects.

Lasers are extensively used today, for example, in eye treatment. Femtosecond lasers are now available. They provide ultrashort pulses (1 fs $\approx 10^{-15}$ s) of high power ($\approx 10^{13}$ W/cm^2). The laser beam can be used to perform ablation at the nanoscale (to cut axons in the brain, for example). They can be used to reshape the cornea and correct the vision of patients. Femtosecond lasers can also be used to manipulate nano-objects, in particular biological molecules.

Nanosize surgery tools can be manufactured, for example surgical blades made out of crystalline or polycrystalline silicon, with cutting edges between 5 and 500 nm used in ophthalmic surgery.

Nanoneedles with a diameter of between 200 and 300 nm have the ability to penetrate inside cells without harming them. They can be used to perform cell surgery or to administer a drug directly into a cell.

Nanotweezers can grab and move biological molecules within cells. This allows measurement of their electrical properties, for example. Manipulation of DNA molecules can also be carried out with nanotweezers. They can be made of nanotubes attached to the ends of electrodes. They have a very small thickness (below 50 nm) and are controlled by electrostatic forces that are used to bend the nanotube in order that it can grab a molecule.

Catheters are often used in medicine. They are small tubes permitting the injection or the draining of fluid in or out the body, blood for example. The inner surface of a catheter may induce a blood clot (thrombus) formation. Coating the inner part of the catheter with nanomaterials such as carbon nanotubes reduces thrombus formation and gives the catheter better mechanical properties. Coating with silver particles gives antibacterial properties to the catheter. It is also possible to incorporate sensors to permit the measurement of different properties of the tissue and its environment.

12.2.6 Wound Dressing and Smart Textiles

The antibacterial properties of silver are used in wound dressings. Silver has been used in medicine for centuries, thanks to its antimicrobial properties. The new development is that nanoparticles can amplify the antimicrobacterial properties for textiles where they are incorporated. Nanosilver also has the property of increasing the speed of wound healing.

Smart textiles are designed to react to changes in the environment. In order to be able to do so, sensors are incorporated to monitor the environment. Sensors can, for example, measure the degree of inflammation in a wound, the local temperature, etc. A smart textile can also have communications nanodevices to inform doctors of the state of health of that person.

12.3 Nanotechnology in Dentistry

As medicine advances and people live longer, dentistry will become increasingly important in maintaining natural teeth and healthy oral tissues. The description of the tooth is schematically represented in Fig. 12.11.

Nanodentistry

Many applications of nanotechnologies are also possible in dentistry. Some composite resins already contain nanoparticles but other more elaborated technologies will be available in the future. For example, tooth renaturalization, using native biomaterials, may replace dental amalgams, crowns, etc. leading to repair outcomes indistinguishable from the original teeth. If required, the upper enamel of teeth could also be replaced by harder materials, like sapphire or diamond, especially tailored on the nanoscale in order to enhance their hardness, and covalently bonded to the lower surface of the teeth. In the long term, nanorobots could be designed to repair teeth locally, reposition them by manipulating periodontal tissues, and to reduce dentine hypersensititvity by occluding specific dentine tubules. Such operations could be done much more rapidly than with present technologies with the advantage of being painless for the patient.

Nanotechnologies will provide advances in the prevention of disease and decay in diagnostics and in the repair, restoration, and replacement of teeth; see Fig. 12.12.

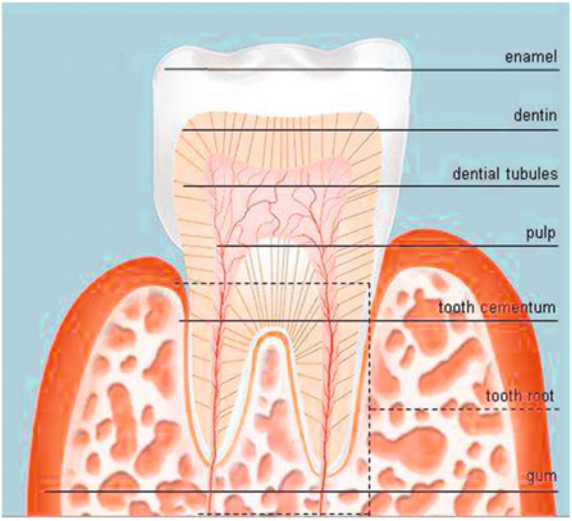


Fig. 12.11 Various elements of the tooth structure, Image courtesy of GSK, Dusseldorf

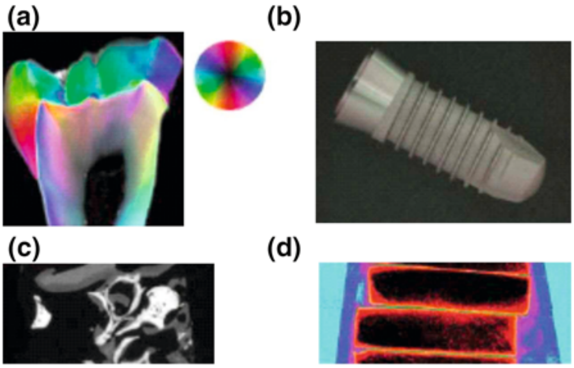


Fig. 12.12 Present applications of nanotechnology in dentistry with growing turnover. Image courtesy of B. Müller, Basel University. **a** Nature-analogue reconstruction, **b** Surface engineered dental implant, **c** Bone augmentation, **d** Re-mineralization with nanoparticles

12.3.1 Nanomaterials for Prevention of Caries

Dental caries—tooth decay—affects more than 80 % of the adult population by the age of 18 years in the developed world. It is caused by bacteria that "glue" themselves to the tooth surface, leading to a chemical reaction that dissolves the tooth enamel and dentine. Nanotechnology can be applied to the prevention of tooth decay by coating the tooth surface with an "easy-clean" layer with very low surface energy, and by using nanoparticles to block bacterial adhesion.

Fig. 12.13 Cavity repair: nanocomposites for esthetics, strength and longevity. Image courtesy of R.Sammons, Birmingham University

12.3.2 Materials for Tooth Repair and Restoration

At present, the “filling” of teeth to replace decayed areas uses dental composites that bond directly to dentine or enamel and can be almost invisible to the untrained eye. However, the slight reduction in volume that occurs when the filling is cured can result in tiny cracks that may permit infiltration of bacteria-laden saliva, leading to secondary decay. Fillings that incorporate nanoscale particles can prevent the problem of shrinkage, meaning that fillings can be more robust once in place. The materials being developed may also be suitable for applications such as orthodontic brackets where there is a requirement for high strength and flexibility (Fig. 12.13).

In future, high-precision powder jet blasting with nanoparticles of hydroxyapatite (a natural constituent of bone and teeth) may be used for the removal of decay, providing the simultaneous deposition of a layer of hydroxyapatite onto the tooth to initiate repair. Toothpastes and chewing gums containing nanophase hydroxyapatite particles or nanocomplexes of stabilized amorphous calcium phosphate are already marketed to arrest deterioration and prevent further attack. In future, products may incorporate natural molecules that more naturally promote hydroxyapatite nanorod self-assembly for dentine and enamel repair.

12.3.3 Engineering Dental Implants

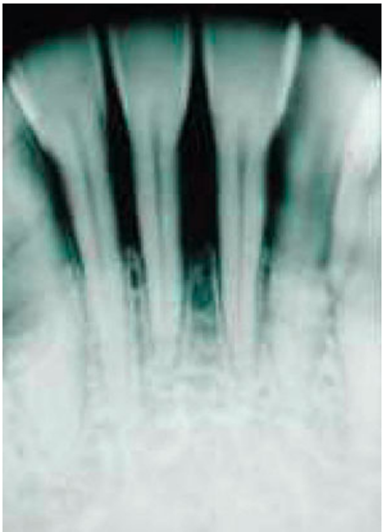
Dental implants (Fig. 12.14) are becoming increasingly popular for the replacement of lost teeth. Initial surgery to place the fixture in the bony socket is usually followed by a healing period of several months before adding the permanent crown, but there is now increasing demand to place the implant earlier, even immediately after extraction of an existing tooth in a single procedure. Implants that bond to bone or “osseointegrate” more quickly are required, and these could also benefit patients whose bone healing capacity is compromised. The solution lies in state-of-the-art laser nanopatterning techniques that modify the bone surface to act as a site where bone-forming cells will activate. The implant surface that interfaces with the gum tissue can also be engineered to promote tissue growth in this area, while resisting bacterial attachment, to make a better seal and prevent infection as a natural tooth does.

Fig. 12.14 Dental root implants: nanotextured surfaces and coatings for more rapid bone and soft tissue bonding. Image courtesy of R. Sammons, Birmingham University

12.3.4 Reconstruction of Hard and Soft Periodontal Tissues

One of the greatest challenges in dentistry is reconstruction following periodontal disease (Fig. 12.15).

Fig. 12.15 Enhanced photodisinfection of periodontal pathogens; injectable nanospheres for antibiotic delivery. Image courtesy of R. Sammons, Dental School Birmingham



Greater understanding of the interaction between bacterial and patient factors at a molecular level is leading to novel ways to halt disease and to repair damaged tissues. Three-dimensional biodegradable nanofibrous membranes that mimic the natural extracellular matrices of oral tissues can be used to segregate different cell populations in healing tissues to prevent epithelial cell overgrowth and promote bone formation. Nanopatterned surfaces may be used to guide periodontal ligament fibroblasts while nanospheres, -tubes, and -porous structures may function both as structural materials and for drug delivery. Meanwhile, nanotechnology is already leading to the development of materials for bone repair and augmentation with superior mechanical properties and controllable resorption rates.

12.3.5 Engineering Tooth Development

Novel nanohybrid synthetic nanocomposite matrices have been formulated that mimic the structure and properties of natural dentine and provide additional mechanical strength. They can also stimulate the natural dentine-forming cells of the body, so with further refinements, such structures could potentially be used in the future as scaffolds to pack into cavities in dentine to promote regeneration.

12.3.6 Salivary and Respiratory Diagnostics

The use of the oral cavity as a source of DNA is well known in forensic science, but saliva can also be used to detect usage of illegal drugs, alcohol, tobacco, etc., and to detect and measure hormones and markers associated with chronic disease. The presence of specific oral antibodies forms the basis of tests for viruses such as HIV, herpes and hepatitis B, and other infections. With the development of nanotechnology, microchips with sensors for specific molecules could be attached to cheek patches, floss, teeth, dentures or braces, as an aid to diagnosis and to monitor the progress of treatment regimes.

12.3.7 Conclusion

Dentistry has seen enormous advances from the application of technology over the last 100 years. Nanotechnologies can make the extremely rapid advances that will be needed to cope with the challenges of dental protection, repair, and reconstruction for an aging population. Within dentistry, the marriage of nanotechnologies with biological materials and molecules will give significant improvements in the biocompatibility of dental implants and will reduce the disruption and healing time associated with major dental surgery.

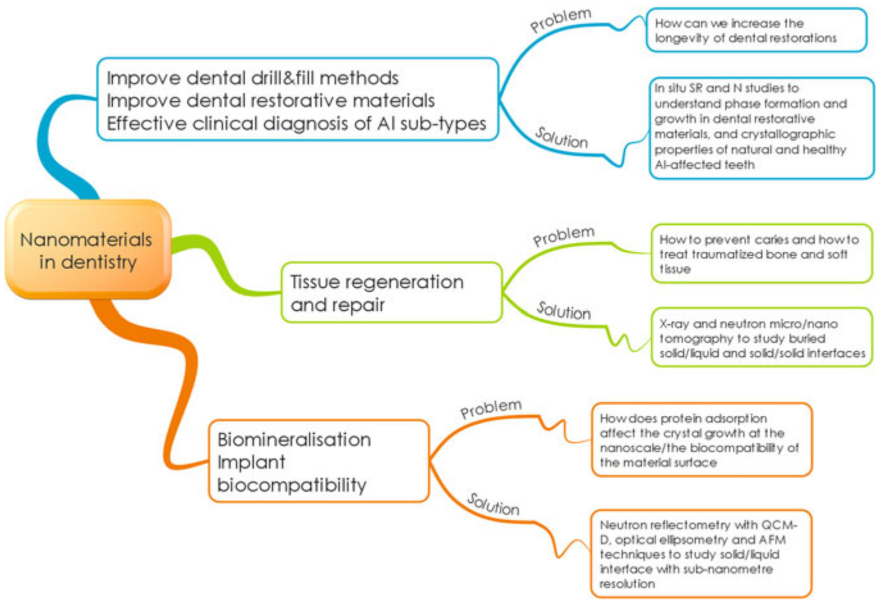


Fig. 12.16 Highlight the needs for further developments in this important field

Nanotechnology is facilitating exciting developments in dentistry, and will provide great benefits in replacing current technologies and in developing entirely new treatments and therapies.

The development of dental treatments with nanotechnology is revolutionary but the science and techniques needed are demanding (Fig. 12.16).

12.4 Nanopharmacology

The introduction of nanotechnology in pharmacology has revolutionized the delivery of drugs, allowing the emergence of new treatments with an improved specificity. Nanotechnology is now widely implanted in the move of revisiting drug delivery methods. These new nanosystems can be tailor-made according to the desired functions thanks to parallel progresses in the synthesis of colloidal systems with perfectly controlled characteristics. They can be administered by all existing routes for administration for systemic or local treatments. Their values are the control of the drug release and distribution, the enhancement of drug absorption (by mucosa or cells) and the protection of drugs from degradation. They offer so many advantages to improve the precision of the treatment that several reached market during the last decade. So far, there is still no universal platform suitable for the delivery of all types of drug. It is expected that in the future, several platforms will emerge, each being specific for

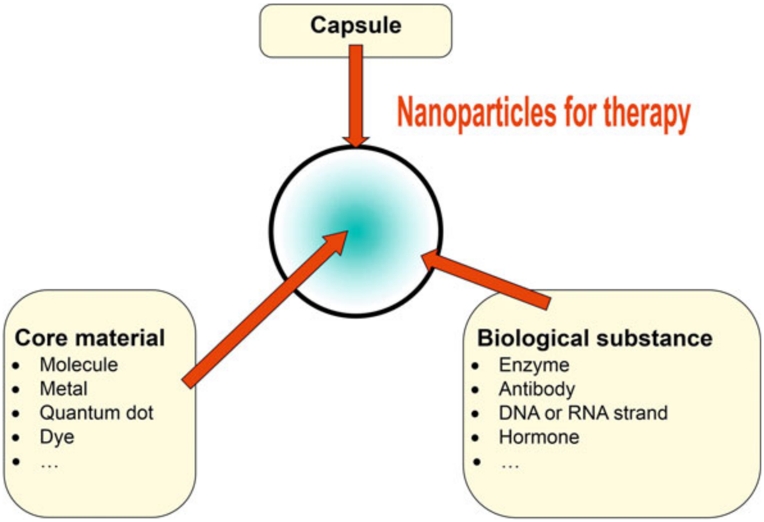


Fig. 12.17 Principle of nanoparticles for therapy

either a type of drug such as peptides or nucleic acids, or for a specific biodistribution mechanism. Additionally, some nanosystems may have special physical properties, like colloid metal-based systems that may be exploited to kill cells or to improve imaging techniques for diagnosis purpose.

The basic structure of nanoparticles used in therapy is shown in Fig. 12.17. A nanoparticle has to be understood here in the broad sense. It can be a spherical nanoparticle but also in the form of tubes, rods, etc.

As we go from inside to outside of the nanoparticle, there is first the core which can be either chemical species or a metal. This is followed by biological molecules grafted on the nanoparticle surface. Finally the capsule part, acting as a coating, is outside. Of course more complicated structures can be built.

The nice thing about new drug delivery methods based on nanoparticles is that the nanoparticle can find the specific cells, latch on and release the drug.

The various applications of nanotechnology proposed so far have already impacted thinking on the way we deliver drugs today. Comprehension of biological disorders causing disease will definitively help in making further progress to identify very precisely new targets and to enter the age of gene therapy. It may be expected that the major immediate scientific and technological block to overcome is the understanding of the functioning of the immune system in its whole. Because it seems to be involved in many of the physiopathological disorders, its resolution will boost the development of innovative treatments for numerous diseases and for controlling the biodistribution of drug nanocarriers. Another important lock is the identification of specific cell targets to allow more selective performance.

Although the introduction of nanotechnology has obviously permitted numerous milestones toward the development of the "Magic Bullet," a lot of work remains to be done. Future improvements will certainly come from the introduction of new

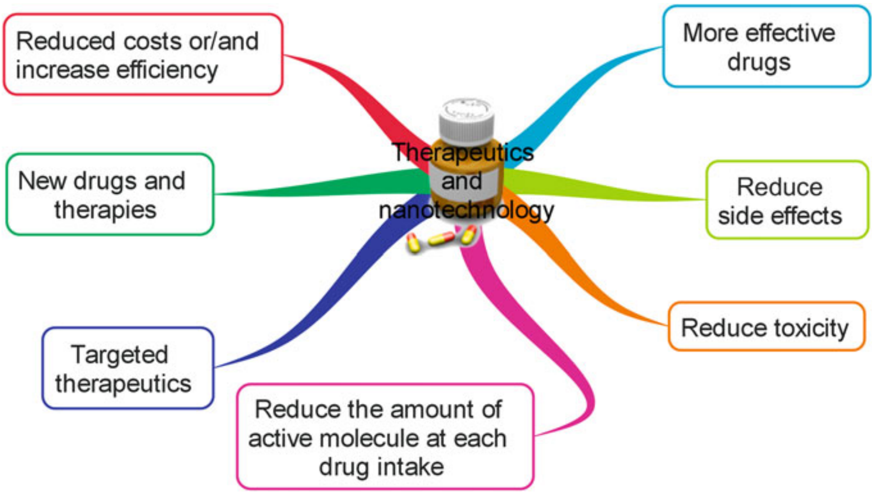


Fig. 12.18 Main benefits expected from nanotechnology

materials including stimuli responsive polymers to elicit the challenge of targeting the drug to its specific site of action, to retain it for the desired duration and to release it according to the correct time schedule. It may also be expected that more sophisticated and multifunctional systems will be conceived allowing a single system to perform *in vivo* diagnostics and to release a targeted drug on demand. Finally, the development of strategies aiming to develop entities existing in Mother Nature and based on biomimetism will also enable major progress in the next few years.

12.5 Conclusion

Great progress is expected at the therapeutic level as we move toward tailor-made therapeutic solutions. The main benefits expected from nanotechnology are summarized in Fig. 12.18.

Carrying active molecules to the right place and at the right time allows decreasing the amount of drug intake. It also decreases side effects and toxicity. With existing drugs this will reduce the cost. An interesting point is that drugs which are considered as too toxic to be used because of side effects could be used if the molecules are protected until they reach their target.

Nanotechnology is also expected to help in the development of new drugs that could be more efficient. They could eventually be more expensive but globally the cost of a treatment for the society may also be lower. Regenerative medicine will allow improved quality of life to live and may also go toward decreasing healthcare costs for society.

One example is the concept of "squalenoylation" consisting of the bioconjugation of anticancer, antiviral, or antibacterial compounds to a squalene lipid. When applied

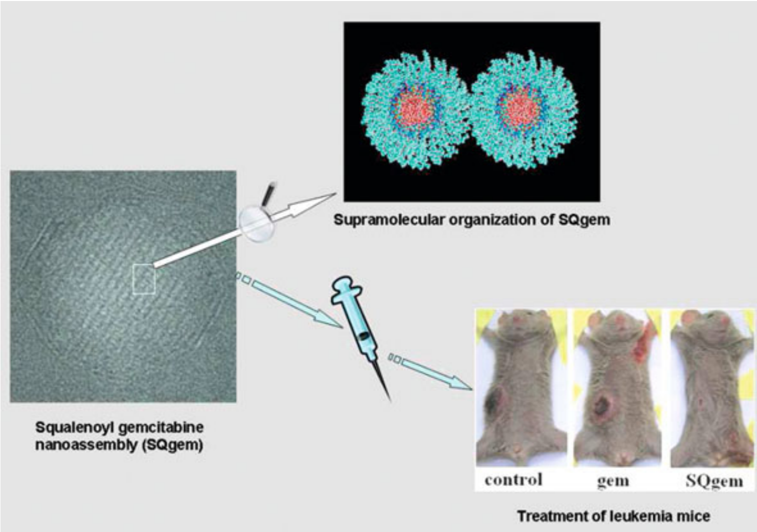


Fig. 12.19 Discovery of new hexagonal supramolecular nanostructures formed by squalenoylation of an anticancer nucleoside analog, Couvreur P., Harivardhan Reddy L., Mangenot S., Poupaert J.H., Desmaële D., Lepêtre-Mouelhi S., Pili B., Bourgaux C., Amenitsch H., Ollivon M., Small, 4, 247–253; 2008. *Copyright* Wiley-VCH Verlag GmbH and Co. KGaA

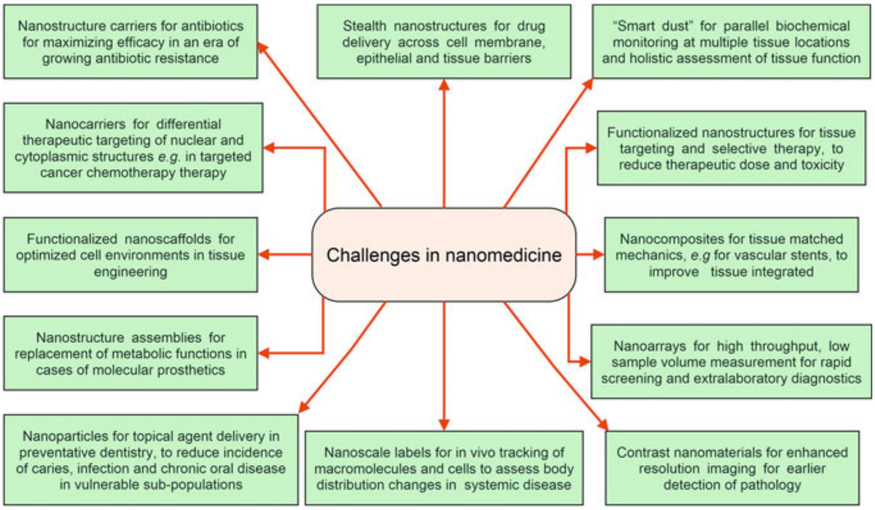


Fig. 12.20 Summary of challenges in nanomedicine

to the anticancer compound gemcitabine, dramatic improvement of the anticancer effect is obtained, Fig. 12.19.

A summary of the challenges in nanomedecine are shown in Fig. 12.20.

Chapter 13
Nanotechnologies in Agriculture and Food

The provision of food is a critical factor in ensuring good quality of life. The developing world struggles to produce sufficient food and to deliver it to a growing population, while for the developed world there is a need to provide safe foods over longer, and increasingly globalized, food chains. Europe is potentially vulnerable to the impact of global changes by reliance on food import from outside the European economic area (EEA).

The value of natural products for fuel, clothing, and pollution reduction, and the use of green spaces to improve quality of life in urban developments, means that the value of agriculture to global society will increase dramatically. Hence, as well as food production, arable land will be exploited for the production of biofuels, fibers for textiles and engineering applications, and chemical precursors; all of which will reduce the pollution associated with using oil-based resources as the starting point, and generate "at source" industries where a greater proportion of fundamental needs can be generated by a country using its arable land resources. Figure 13.1 shows the spectrum of biomaterials as a function of length scale.

Small particles can have very large effects on the properties of a foodstuff. There are consequently great possibilities in using nanoscale engineering for the development of synthetic foodstuffs to improve nutrition and conserve resources. However, the development of nanofoodstuffs is a sensitive topic in the food production industry.

Several areas of nanotechnology development are concerned with agriculture and food. They are shown in Fig. 13.2. Most of them are addressed in this chapter. Nanotechnology will arrive in products of mass consumption including foodstuffs; a very large market will develop from which Europe can profit enormously.

13.1 Agricultural Production

The application of nanoscience to agriculture can provide a wide range of technological benefits. Global warming has effects such as changing the needs for irrigation, and the increasing requirement to grow specialist plants outside their usual

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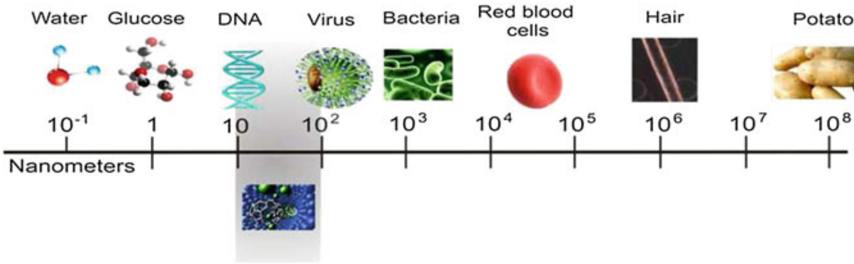


Fig. 13.1 Scaling of biomaterials

Fig. 13.2 Different topics relevant to agriculture and food

ecosystems. Novel sensing technologies can map changes in the environment so that land use can be planned and managed to produce the best yield of the most appropriate crops. Distributed nanosensors can provide real-time, localized monitoring of growing conditions throughout large agricultural areas. "Precision agriculture" will see a step change in the information available to farmers to help them maximize output sustainably.

New nanoanalytical techniques will provide better understanding of the interactions among soil types, nutrients, and plant cells. New synthetic techniques can then be developed, based on nanosynthesis, which provide increased soil fertility and improved crop quality and production. Soil can be assessed for its nutrient balance and crop suitability using chip-based sensors that can be deployed easily, with low power requirements that can be fulfilled by small solar panels with no need for grid electricity. Soil fertility can benefit from nanomaterial-based chemicals tailored to particular ecosystems to maximize productivity, for example in the efficient dosage of fertilizers and nutrients for plants, and the development of nutrient delivery systems that optimize resource usage and which can dose the soil optimally over the lifetime of the growing plant.

Nanosystems will be developed to enhance the availability to the body of "healthy" molecules in plants such as vitamins and antioxidants, as well as to improve the absorption of water in plants and crops. Nanoscale delivery systems can produce controlled release of fertilizers, nutrients, or pesticides, with dose rates dependent on external factors such as rainfall or temperature. Nanotechnology can be targeted toward reduced fat, sugar, and salt content in food and to increased fiber contents to give better food products (with improved texture and taste) for the consumer. Controlled release of fertilizers and pesticides means that less chemical product is used in the agriculture process which leads to a large reduction of the required raw product and the amount of chemicals applied to the soil, reducing groundwater pollution and therefore having a positive effect on the environment. Active nanoparticles remove microbial and chemical soil contaminants, and regenerate contaminated land for the future production of crops. There are potential hazards which must be addressed, however: for example, carbon nanotubes, which can assure an accelerated absorption of water, may arrive in the food chain with unknown consequences.

Nanopesticides cover a wide variety spectrum of products. Nanoformulations combine several surfactants, polymers, and metal nanoparticles in the nanometer size range. The aims of the nanoformulations are generally to increase the solubility of poorly active ingredients, to release the active ingredient in a targeted manner, and or to protect against premature degradation. Nanoparticles are expected to have an important impact on the fate of the active ingredients and provide the production of novel properties of (nano)pesticides.

Applications are not limited to arable farming. Nanosensors can also be used for the detection of plant pathogens, to monitor the health and location of farm animals, and to introduce controlled medication where medical treatments are required.

Nanochips for identity verification of nanocapsules to deliver vaccines, and nanoagricultural developments offer potential advantages: such as feeding chickens with bioactive polystyrene nanoparticles that bind with bacteria, as an alternative to chemical antibiotics in industrial chicken production.

The challenges for agriculture and the corresponding risk issues are summarized in Figs. 13.3 and 13.4.

However, it should not be forgotten that agriculture is not only a source of food but also of industrial products as shown in Fig. 13.5.

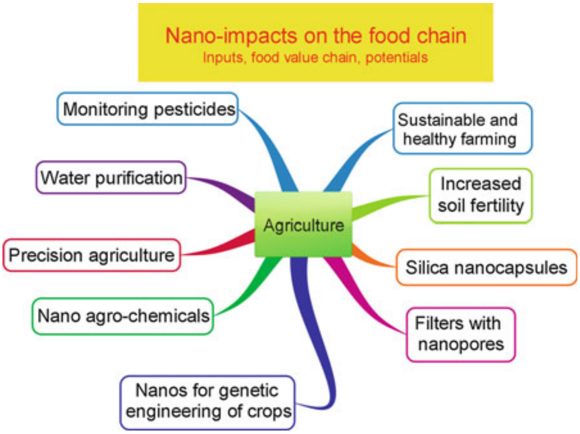


Fig. 13.3 Main challenges for nanoagriculture

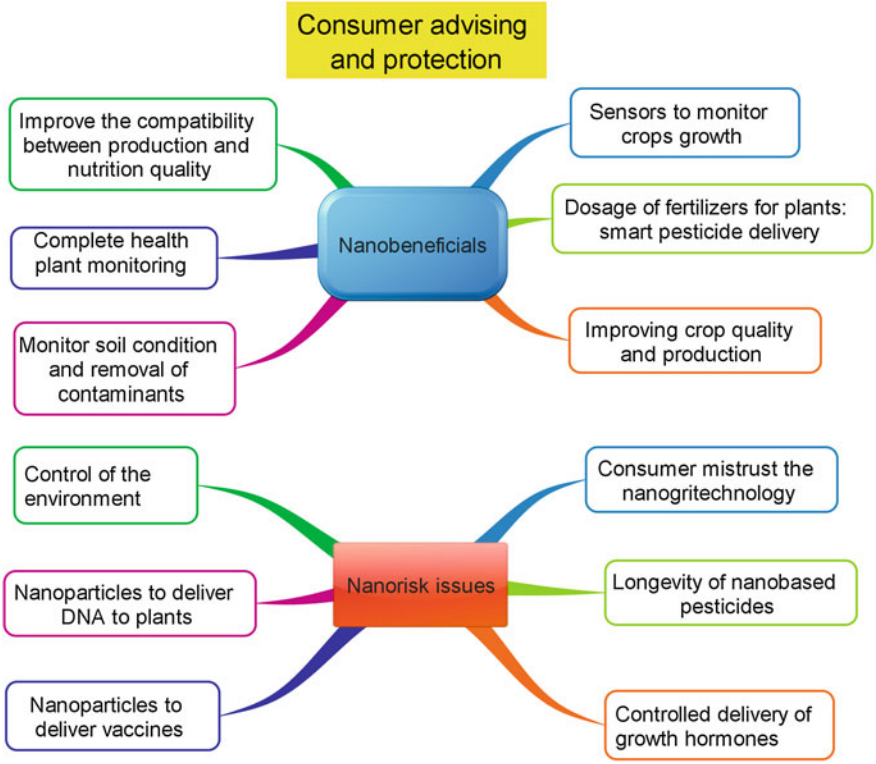
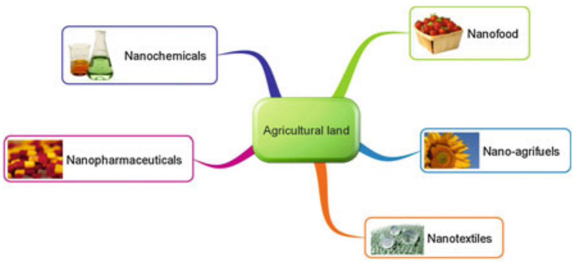


Fig. 13.4 Risks issues in agriculture nanotechnology

Fig. 13.5 Agriculture as a source of food and industrial products



13.2 Food Processing

In a few decades, healthcare will become a large financial burden for industrialized societies: demographic trends of an aging and increasing world population are combining with a growing prevalence of lifestyle diseases such as obesity, which in turn leads to health problems such as diabetes. Food, either as specific parts of a diet, or the diet more broadly, can be an important component of preventive healthcare. Modification of food and diet can be more effective with lower side effects than curative intervention by drugs. For example, a foodstuff with a low fat content can be tailored in taste and texture to mimic a high fat food, so making it valuable in the reduction of obesity. Processing many of these biopolymers into nanofibers and nanowhiskers or incorporating nanoadditives can augment barrier and mechanical properties of biopolymers.

Because a given food has ingredients that are good for you does not mean you receive the entire benefit: availability of the nutrients to the body is crucial, particularly of trace elements and minerals. There are many examples where nano-enabled ingredients can be better absorbed by the body. For example, many vitamins and other substances such as carotenoids are insoluble, but can easily be mixed with cold water when formulated as nanoparticles. Nanoencapsulation methods utilizing nanoemulsions or nanoparticles offer the potential for improving the uptake of nutrients in the human body, as well as reducing the sensitivity of nutrients to environmental conditions, so improving the shelf life and reducing the need for refrigeration. Nanotechnologies can make "bland" but nutritious food more attractive through enhancement of taste and texture.

Figures 13.6 and 13.7 show the challenges for food processing and production and the corresponding risk issues.

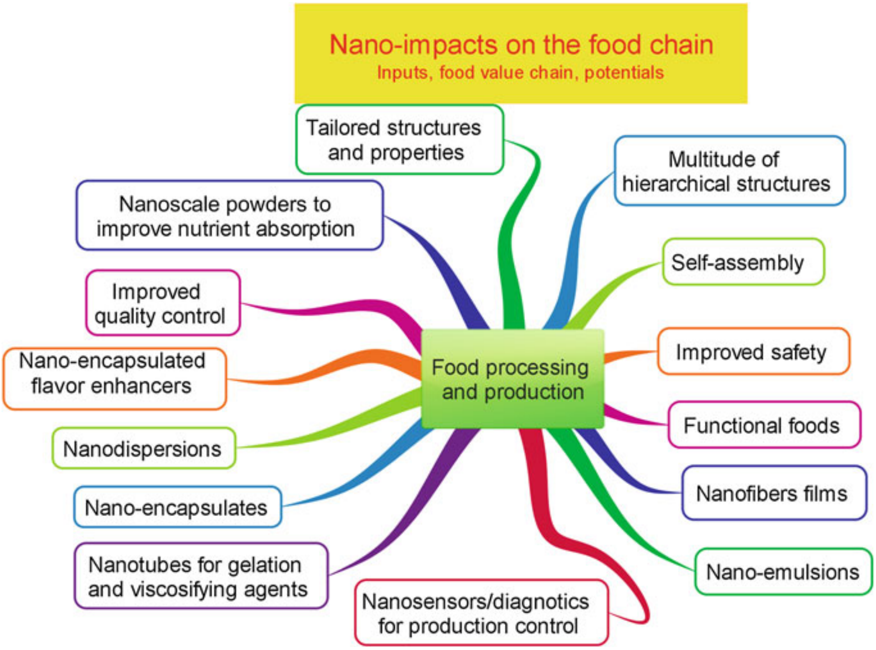


Fig. 13.6 Challenges for nanoagrifoods

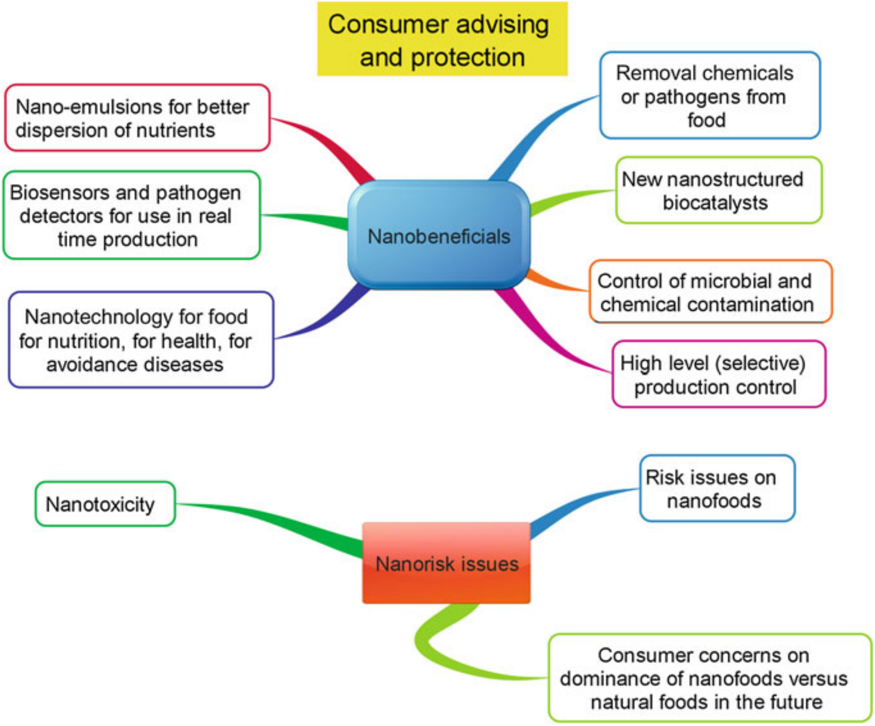


Fig. 13.7 Beneficials and risks issues in food processing and production nanotechnology

All foods ultimately have structure and chemical interactions at the nanolevel, and these structures are critical to the texture of the foods and therefore their acceptance by the consumer. Control of matter at the nanoscale level will enable a fine tuning of specific food characteristics like texture, taste, and viscosity to the demands of specific markets. However, much of the production and processing of foods has been empirical, and there needs to be much more emphasis on a serious study of the interplay between structure and texture, including modeling and simulation, and the impact of changing raw materials (due to many factors including climate change and the introduction of genetically modified crops). This is even truer of the interplay between structure and nutrition.

One very attractive area for nanotechnologies is in increasing our knowledge of our own *genetic heritage* and its implications for disease susceptibility. Faster, more accurate testing will be available to show disposition toward particular diseases and disorders, and what foods we should eat to mitigate this predisposition. Tailored foods will be available with enhanced levels of anticarcinogens, vitamins, etc., or alternatively with reduced allergens for susceptible individuals. Manufacturers will be able to target foods for different potential population groups and consumer demands.

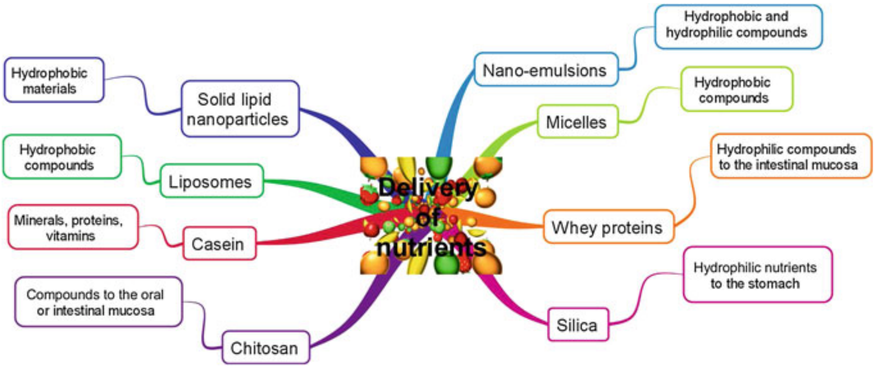


Fig. 13.8 Nanomaterials for nutrients delivery. Information taken from the ObservatoryNano project

In foodstuffs there are many applications for nanotechnology to deliberate on; for example, the nanoparticle-encapsulated taste-improvers, nanosize particles to increase absorption of nutrients and which assure a better viscosity, and nanoemulsions for improved absorption or distribution of color, taste, and ingredients, vitamin sprays dispersing active molecules into nanodroplets for better absorption.

In Fig. 13.8, we show nanomaterials which can be used to deliver nutrients and their potential applications.

Nanotechnology can devise novel routes to produce dry foods that can be reconstituted at the point of use to minimize transportation of water.

At the end of the food chain, the issue of waste must be addressed. Nanotechnologies should be developed to make better use of food waste—either for other products in the food chain or for novel products such as adhesives and packaging. This can include reuse of waste packaging as well as food waste itself. Landfill issues now put pressure on reducing such waste, and there should be increasing efforts directed toward finding alternative uses for waste products to encourage attainability throughout the food chain. Possibilities which offer opportunities for nanoscience applications include biofermentation and enzymatic routes to breakdown of organic material, for the production of new raw materials to be used by other industries.

13.3 Packaging

Nanotechnologies allow for improvements in food packaging. Preserving and protecting food is an important issue. Packaging has become one of the most important elements in the handling and commercialization of foodstuffs, to provide and assure the levels of quality and safety. Nanotechnology will become one of the most powerful forces for innovation in food packaging: giving longer shelf lives; safer and lighter packaging; better barrier properties; improved biodegradability; lower

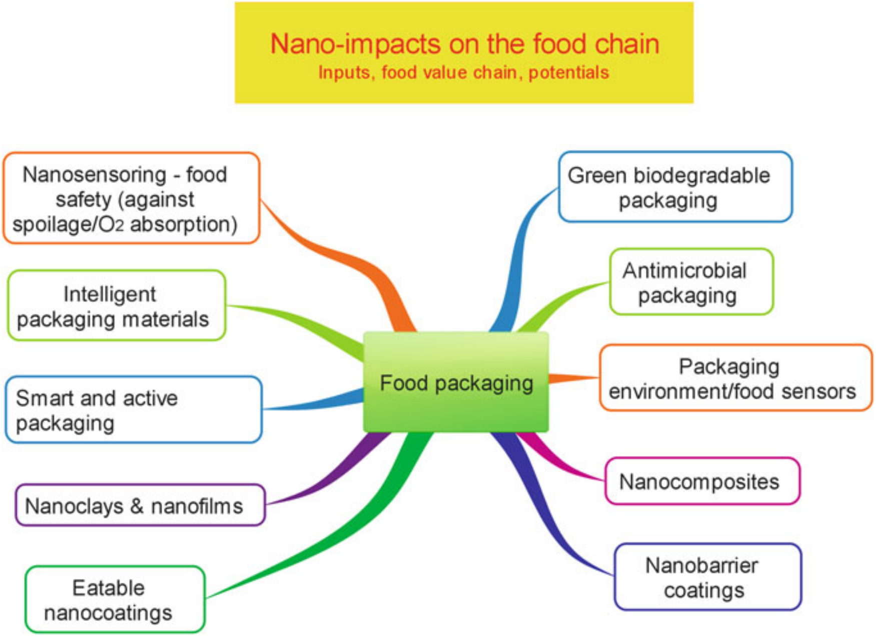


Fig. 13.9 Challenges for nanotechnology in food packaging nanotechnology

environmental impact; better traceability of products; and healthier food. Challenges for nanotechnology packaging are shown in Figs. 13.9 and 13.10.

In addition to food waste, food packaging waste is an increasingly serious problem because of the continuously growing demand for convenience foods, the individual wrapping of fresh produce such as fruit, and the use of packaging as a marketing tool. In many cases, existing plastics packaging materials are not safely disposed of or recycled effectively.

Nano-enabled natural polymers such as sugars or proteins combined with nanoclays and bio-based nanomaterials can result in "green packaging materials" that are nontoxic, biodegradable, and biocompatible. Such naturally based nanopackaging materials can be degraded, composted, or even eaten. This technology will reduce the amount of packaging waste generated by society and even agricultural waste may be used through recycled into natural nanopackaging materials.

Carbon nanotubes improve the strength of packaging materials, and nanocoatings will improve the barrier characteristics and reduce the microbial pressure on the food product inside. Nanosensors will signal oxygen leakage into packaging materials, which results in quality deterioration such as the ripeness of packaged fruits. Combined with printable RFID electronics sensors, this can provide direct information on the quality of a product, its origin, and the remaining shelf life.

In addition, natural nanopackaging materials may have additional benefits such as improved strength, water and gas impermeability, antimicrobial properties, and

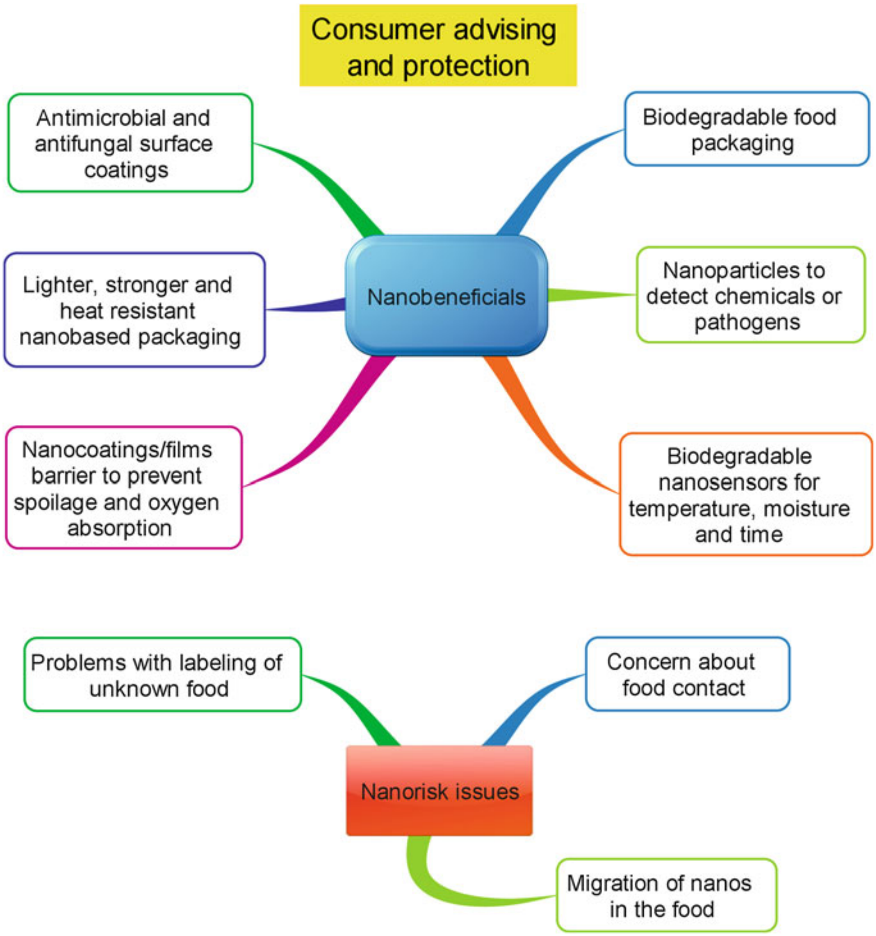


Fig. 13.10 Risk issues in food packaging nanotechnology

can have integrated biosensing capabilities to ensure longer shelf lives of foods and reduced food spoiling. In addition, the nano-enhanced packaging materials can protect the foodstuff from bacteria (or spoiling) but also can protect the foodstuffs for longer times without chemical additives.

Novel technologies can greatly reduce the volume and weight of packaging that has to be transported: for example, by using nanocoatings on food items that are edible and nontoxic, avoiding the need for polymer or card-based products. “Nanobarcoding” using edible inks directly onto food items themselves will provide information without the need for printed packets, and gives additional opportunities for direct identification of food by a home device for optimum cooking time. The future vision of smart food freshness labels is represented in the example shown in Fig. 13.11.

Fig. 13.11 Future vision of a smart food freshness labels. Courtesy of Hols Center (Netherland)

Integrated circuit technologies can be placed in packages that not only impose very low stress on the silicon, but also connect the device to a printed wiring board. Some materials in small concentration, such as nanoclays reduce moisture diffusion through polymers, so integration of nanomaterials with novel combinations of electrical and mechanical properties enable integrated circuit packages with high reliability.

Finally, thinner packaging materials for foodstuffs consume fewer resources in fabrication.

Packaging has low impact negligible on the consumer and generally goes unnoticed. It is an area where there can be rapid public acceptance: the packaging itself is not consumed, and thus technologies such as nano-based coatings and antibacterial nanocoatings offer clear advantages without hazards. Nanosilverparticles can be used in packaging for preserving foods and preventing bacterial growth and nanotechnology sensors can monitor the freshness of foods (Fig. 13.12).

Packaging should generate as little pollution as possible throughout its life cycle. Application of nanotechnology to the development of green packaging is an excellent opportunity to minimize the environmental burden of this important step in food distribution (Fig. 13.13).

13.4 Distribution and Transportation

The transport of food is a global problem where nanotechnologies can offer great benefits (Fig. 13.14). At present, many parts of the world are unable to generate sufficient food for the needs of their population, and this is as much an issue for European countries as it is for Africa and Asia. In poor countries, the gap between food production and food consumption leads to famine, while in the developed world there is heavy reliance on transport of foods between countries and even between continents. The twenty-first century will therefore see great emphasis on more local, sustainable production of food across the world.

Owing to the drive to reduce transport costs, carbon emissions, and environmental impact, we are likely to see an increased requirement not to transport foods when

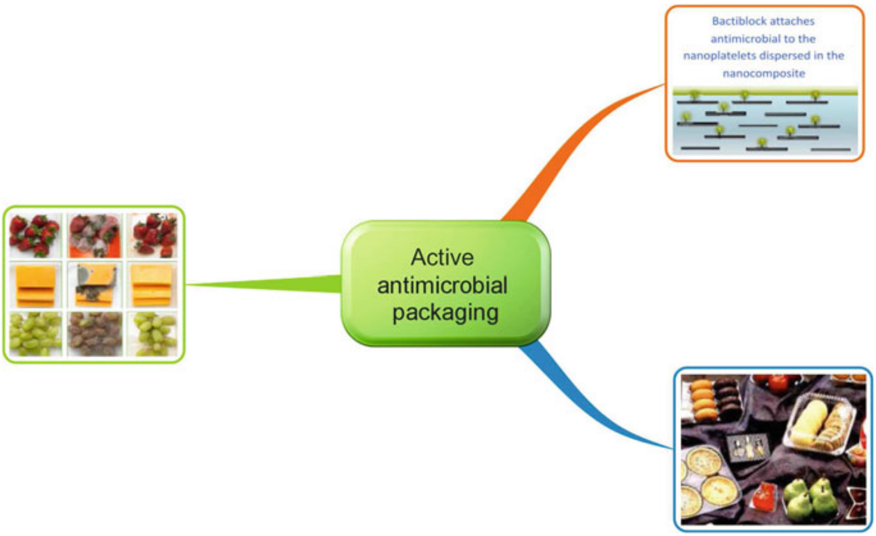
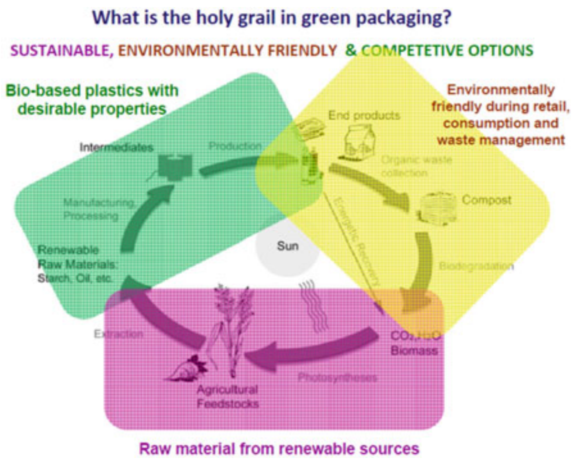


Fig. 13.12 Active antimicrobial packaging: nanosensing and diagnostics for food quality and food risk. Image courtesy of IoN, UK

Fig. 13.13 What is the holy grail in green packaging. Image courtesy of IoN, UK



they contain large quantities of water, and hence a drive toward the transportation of dry foods. This requires development of a better understanding of how to produce dry particulates of healthy foods that can be rapidly and easily rehydrated, either in local factories or in the home, to achieve the required texture and nutritional benefits. These requirements are likely to require appreciation of nanostructure production during drying, and of how the different nanostructures rehydrate to achieve an acceptable texture.

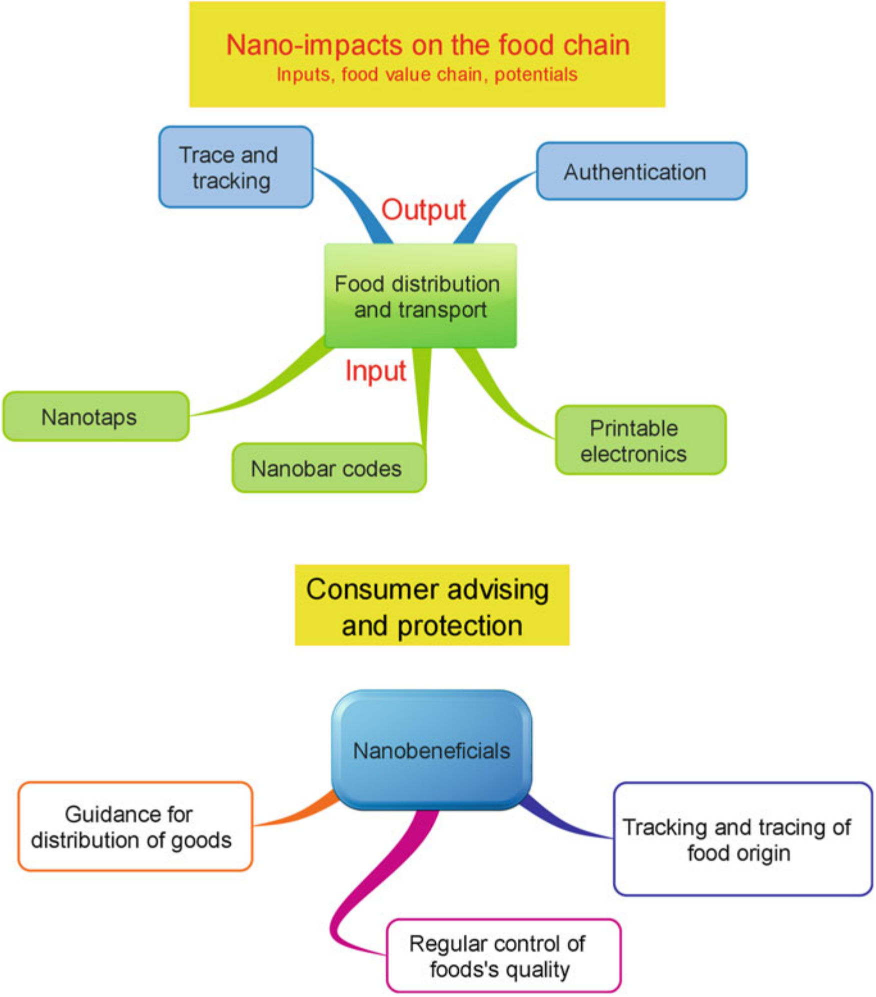


Fig. 13.14 Challenges for nanoagrifoods in food distribution and transport nanotechnology

13.5 Food Safety

Micro and nanotechnology will lead to sensors and diagnostic instruments, with improved sensitivity and selectivity that will enable monitoring of food production and assure food quality. Thousands of nanoparticles can potentially be placed on a single nanosensor to rapidly, accurately, and affordably detect the presence of any number of different bacteria and pathogens. Nanotechnology may reduce the time it takes to detect the presence of microbial pathogens from days down to hours and, ultimately, minutes or even seconds. These new instruments will enable much faster measurements on food production lines by nonexpert personnel.

Nanoparticles and related technologies offer great potentials in improving the efficiency with which we obtain nutritional benefit from novel (multifunctional) foodstuffs. However, to allay consumer fears, there must be the highest levels of scrutiny in applying new technologies to the human food chain, particularly given previous negative publicity around the development and application of nanotechnologies. A critical step is therefore in identifying societally acceptable procedures for testing the toxicity of nanotechnology-based packaging materials and products, so that consumers are assured that new products and processes are safe and offer immediate and long-term benefits. There must be stakeholder and consumer trust in risk assessment and management practices.

The risks associated with nanoparticles and nanomaterials are related to their special characteristics: their small dimensions make it possible that they can penetrate all parts of the human body. Particles that agglomerate when they enter the body, in contact with bodily fluids for example, tend not to be a cause for concern; nor are particles that dissolve and can be excreted. But particles that can pass into the bloodstream can cause significant problems, even in cases where they cause no apparent effects such as irritation or inflammation when initial contact is made. Fibrous nanomaterials are of particular concern, as fibers are well known to cause specific problems, such as in asbestosis.

Without sound research, a rigorous assessment of risk and advice on regulation is not possible. Regulation of nanotechnology in food and consumer products is urgently needed. For the time being, both industry and consumer have had to accept guidelines and self-regulation by industry!

The success of the application of nanomaterials in foodstuffs depends greatly on consumer confidence. In order to gain confidence, it is important and necessary to have clear and transparent characterization and testing, to make all information gained openly and available—which these days means on the web and to have early involvement of consumer organizations with a proactive attitude from the industry. In recent years, consumer confidence is growing but this is based on limited information and experience. This confidence could be lost quickly in the event of an incident in which a nanotechnology is claimed to be the reason or origin, whether or not that is correct. We live with "libertarian paternalism" meaning that the government tends to recommend precautions without restricting the freedom of choice. The food industry should opt for responsible innovation and self-regulation.

13.6 Conclusion

Nanotechnology offers promising new possibilities in the food industry but there is a lack of information about potential side effects. Nanotechnology therefore requires responsible innovation and thorough risk analysis if its benefits are to be exploited for both industry and consumers.

Many food companies are already investing in nanotechnologies and are on their way to commercializing products. Food companies are employing nanotechnologies to change the structure of food: creating "interactive" drinks containing nanocapsules that can change color and flavor, and spreads and ice creams with nanoparticle emulsions to improve texture. The present nanofood market value may be of the order of 15 billion euros.

Nanotechnologies can provide great benefits, from initial food production in agriculture and farming, through tailoring food for maximum nutrition and reduction in population disease, to reduction in waste products. There are beneficial impacts as widespread as the potential for reducing bowel cancer; to better absorption of vitamins, minerals, and trace elements; as well as in optimizing the profitability of crops used for textiles, fuels, and chemical production.

This vision will only be successful if all nanoscale processes are fully understood, within a framework of research and development which determines the role of nanomaterials in agriculture and food.

The application of nano-enhanced food additives in functional foods to improve taste or texture will have the highest potential exposure for consumers. There is also the potential for release from food packaging: during consumer handling if nanomaterials migrate to food, from the packaging; or exposure in the environment when nanomaterials are released in the waste phase from food processing procedures or use of nano-enabled technologies for disinfection, etc.

Lack of awareness and uncertainty about the potential benefits and risks is still dominant. Commercial release of foods should only be done when nanospecific safety laws and standard specifications are established and the public is involved in decision making.

Nanotechnologies in the food domain have a number of barriers to successful commercialization and marketing compared with existing conventional technologies despite the many benefits offered by nanotechnology in food products. Applications of nanotechnologies in food production or packaging raise sensitivities with the public compared to nanotechnologies used in energy of transport or electronics. The fears associated with health and safety have to be overcome to ensure successful exploitation. Applications of nano-enhanced food additives in functional foods or to improve taste or texture have the highest potential exposure for consumers of virtually all nanotechnology applications. Risks to the consumer can be posed by release of nanoparticles from food packaging during handling or after disposal, or if nanoparticles migrate into foodstuffs. There is also potential for nanomaterial residues to accumulate in agricultural production of meat, milk, and crops.

After the negative public response to genetically modified food in the recent past it is vital to establish a proper consumer strategy with respect to nanofoods, requiring the development and implementation of nanospecific standards and nanospecific safety guidelines and laws. There is a lack of awareness and uncertainty about the balance between potential benefits on one side and the potential risks on the other side.

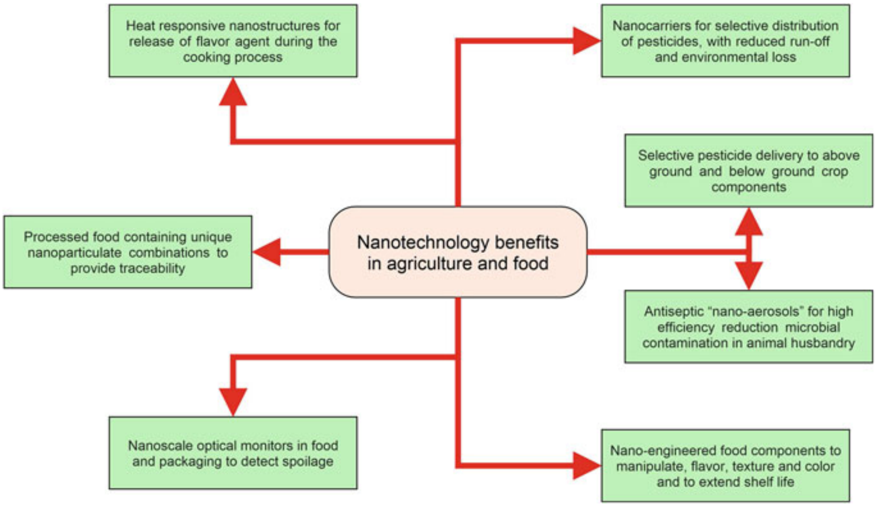


Fig. 13.15 Summary of benefits for nanotechnologies in agriculture and food

The success of nanotechnologies in food depends on various elements:

- *Manufacturing cost effectiveness*. Investment in new facilities, which makes it difficult for a nanotechnology to make a real breakthrough and be competitive with existing technologies.
- *Consumer perception of health and safety concerns*. Risk perception may play an important role in the uptake or rejection of this new technology. Acceptance is required from consumer organizations in the form of agreed standards and regulations.
- *Waste management*. Large-scale disposal sites will have to ensure the breakdown of nanoagents in foodstuffs and packaging.

It must be stressed that nanoprocessing and bionanocomposites hold great promise: frontally competitive and sustainable processing and more environment-friendly packaging solutions. Nanoencapsulation can greatly reduce the number of additives required during food production.

Figure 13.15 resumes the benefits of nanotechnology in Agriculture and Food.

Part IV
Healthcare

Conclusion

Medical domains can be more efficient with the help of nanotechnology. Some of them are summarized in Fig. IV.1. There is also a demand from clinicians for progress in the sectors indicated in Fig. IV.2.

Nanotechnology has potential to provide solutions to some of these problems. In oncology, it is important to have an individual detection of cancer cells and an appropriate treatment to destroy them selectively without side effect. A real-time measurement of glucose would be useful to monitor diabetic patients. A quantitative and real-time measurement of proteins and cellular interaction would be of great to treat infectious diseases. Cardiology would like to enhance biocompatibility of stents. Good targeting and elimination of malignant or abnormal cells in grafts is required in hematology. Finally, delivering drugs across the blood-brain barrier could be of great help in treating neurodegenerative diseases.

Thin nanofilms can have great benefits in foodstuff packaging materials, medical technology, etc. By coating artificial joints with a few nanometers thickness of a tailored material, stronger integration of the implants into bones can be achieved. In tooth technology, nanoscale ceramics can replace tooth fillings made of mercury compounds which have a toxic character. Nanomaterials can also be useful for food additives. Iron is a beneficial additive in foodstuffs, but most iron compounds are difficult to absorb by the human body. Iron sulfate, because of its metallic taste, is not acceptable. Nanoparticles consisting of a mixture of iron, zinc, and magnesium are however well absorbed by the human body.

Illnesses have their origin in the nanoworld. Nanomedicine assumes that illnesses can be cured more efficiently in this world. In this respect, nanotechnology offers additional possibilities for diagnostics and therapies. Present diagnostics can have some drawbacks. They are slow, can be imprecise, and misdiagnosis may occur. In addition, they are reagent intensive and demanding in time for doctors

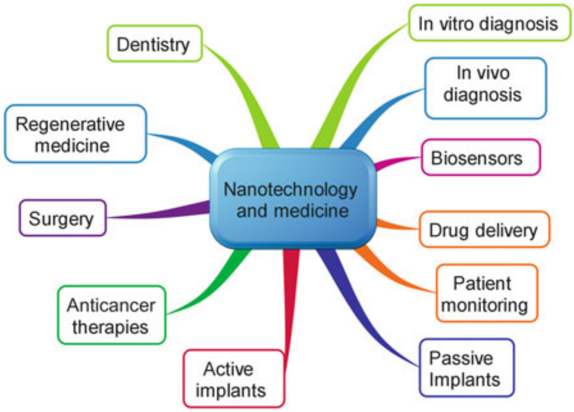


Fig. IV.1 Some domains of medicine where nanotechnology can be useful

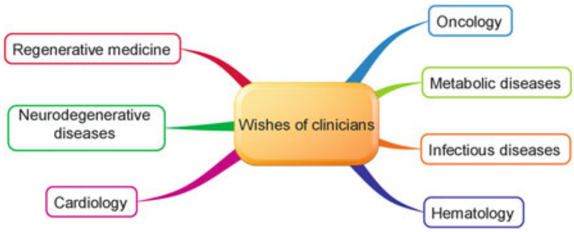


Fig. IV.2 Sectors where clinicians wait for progress using nanotechnology. Inspired from a LEEM report (www.leem.org)

and patients. Good diagnoses should be the opposite: quick, reliable, able to be used with confidence, resource friendly, and hygienic. Nanotechnology can satisfy these criteria with ultra-miniaturized diagnostic tests. The purpose is to detect with nanosensors individual molecules making an unambiguous diagnosis of an illness possible.

Nanotechnlogies can also be applied to existing therapies. Classical medicines are designed to be absorbed by the body. The body is not damaged but operates effectively against the target illness. Nanotechnology gives two functions to the medicines. The first is a nanocarrier containing and enclosing the active substance responsible for the undisturbed transport through the body. When it reaches the target, the nanocarrier releases the active substance which attacks and stops the illness in the most efficient way. The nanocarrier is structured in such a way that no side effects take place. Since the substance is only made available at the diseased location, and not on the way to the target, no active agent is lost. It is possible to induce healing with substantially less medication.

New nanotechnology treatments will only be applied when there is patient benefit with acceptable or no side effects. The interaction between nanomedicine and biological organs must be thoroughly investigated. Initial clinical studies are very promising and if success continues then a great future with new breakthroughs in nanomedicine can be expected.

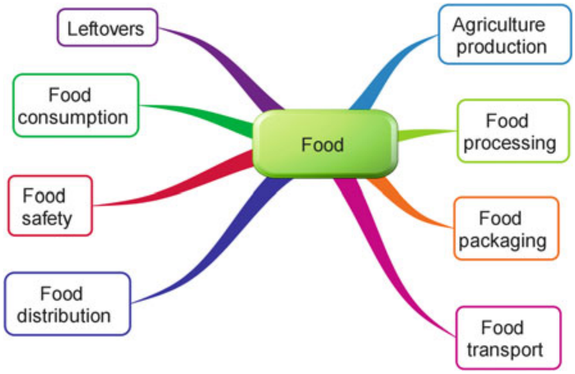


Fig. IV.3 Different sectors where nanotechnology can play a role

Everybody needs food to live. People in good health have several meals everyday. In the past, many people were starving and famines decimated entire populations. Nowadays, famines are rare and impact very poor countries or regions where a natural catastrophe occurred or war is present. However, the world population has enormously increased over the last two centuries (from 1 billion people in 1800 to 7 billion today). Feeding an increasing global population is a real issue. The world population has access to food because of chemical fertilizers, pesticides, and insecticides, and we can genetically modify plant species (by selection and modification). With a rapidly growing population, it is necessary to increase food production while producing it more efficiently. Furthermore, the modification of the climate may decrease the yield of farmland in some countries. Nanotechnology will certainly increase efficiency at all the steps from production to consumption of food. These steps are summarized in Fig. IV.3.

For example, it is necessary to reduce the quantity of pesticides and insecticides used in the agriculture. Nanotechnology can help to do that by releasing them at the right place and at the right time. This can also apply to chemical fertilizers. Better protection of food during transport and storage and preventing it from spoiling is also a domain where nanotechnology offers solutions. But even if advantages exist, one should be aware of the risks and possible long-term negative effects. Research should be carried to ensure the safety of all technologies that will be employed in this field.

Finally, it must be appreciated that nanotechnology is not a possible future addition to medical applications: it is here already and patients are benefitting from it. Silver nanoparticles are used in antimicrobial wound dressings, and nanofibers give improved design of textiles for vascular replacement with better mechanical properties. In diagnostics, enhanced imaging is obtained using paramagnetic nanoparticles of iron, which is not possible in traditional radiology. For *in vitro* diagnostics, detection of cell types in cancer is possible with antibodies labeled with nanoparticles. Nano-structured drug delivery systems provide targeted treatment not easy to do with conventional drug use.

The challenges for the future are manifold. We have indicated here some of the possible applications, and much research and development is now required in order to make them a reality. There are also generic issues to be addressed such as how to ensure that nanoparticles are eliminated safely from the body after use, how to design nano-textured surfaces with better, predictable biocompatibility, and how to avoid toxic effects with inorganic nanoparticles that otherwise have useful properties.

Part V
Nanotechnology for Environmental Engineering

Introduction

Nanotechnology can contribute solving the environmental problems of a rapidly increasing world population and the growing demands it places on the world's natural resources. Nanotechnology offers solutions to problems of resource usage, energy consumption, and waste generation. Fewer materials will be required for product fabrication; better reuse of waste materials will be possible; and there will be new and renewable energy sources. Environmental improvements will be enabled by smart devices for environmental monitoring, pollution detection and control, and purification and remediation of polluted water, contaminated air and soil (Fig. V.1).

Nanotechnologies can play a role in providing a secure drinking water supply by enhancing purification and decontamination. They can offer better crop fertilization and pest control, with more targeted and less concentrated chemical usage. They provide innovative solutions for keeping the environment clean through improving the efficiency of manufacturing systems, and reducing the amount of noxious emissions through nanocatalysts in the transport and chemical industries. Catalysts are also vital in the efficient conversion of greenhouse gases with high global warming potential, in particular N_2O and CH_4.

The ability to detect the presence of pathogens or toxic agents in air, water, and soil is of great importance for human health and the protection of the environment. Nanotechnology offers the potential for extremely sensitive and fast measurement with sensor equipment which is less bulky, simply to operate, and of low cost. Sensor technologies based on nanomaterials will have applications as widespread as environmental monitoring, healthcare diagnostics, and optimization of energy use.

Fig. V.1 Environmental protection address three main areas: air, water, and soil. Human activities can have an adverse impact on each of them

Fig. V.2 Schematic representation of the benefits of nanotechnology for the environment

As summarized in Fig. V.2, nanotechnology has applications in three time ranges:

- by helping to clean up damage done in the past where environmental concerns were not as high as today;
- by reducing the present human impact on the environment;
- by preventing or reducing future environmental impacts and reducing raw materials use.

This part will focus on the beneficial application of engineered nanoparticles and highlight the contribution of nanotechnology to an environment-friendly, sustainable, economy and society.

Chapter 14
Sensors for Measuring and Monitoring

Nanosensors can provide real-time data for a range of measurement applications in energy, transport, environment, health, security, and safety (Fig. 14.1). The much increased surface area of nanomaterials allows for a greater number of molecular interactions and, therefore, potentially much higher sensitivity, increased miniaturization, and faster detection times. They can be specifically targeted, are easy to operate, and are efficient in energy consumption: new sensors may even be able to operate autonomously without an external source of power.

With current technologies, in general, an individual has to collect a physical sample, which is analyzed at a different location (usually a central laboratory). This requires technical expertise, is labor-intensive, and can take a number of days, by which time the opportunity for optimal intervention could be missed.

14.1 NEMS Technology Development and Applications

A promising area of sensor developments is Nano-electro-mechanical Systems (NEMS). NEMS make use of electrically induced mechanical motion and, vice versa, can use induced motion to generate a detectable electrical response. NEMS devices can be the next generation of sensors in mobile phones and can be used as extremely sensitive detectors of force and mass down to the single molecule level. The continuous miniaturization of mechanical systems also enables the study of new phenomena: for example, tiny NEMS devices that can be used to test the basic principles of quantum mechanics in a mechanical system. NEMS will represent an increasingly diverse field of products owing to a continual increase in potential applications in a broad range of markets. An important area of convergence is between Nano, Bio, Information, and Cognition technologies (Fig. 14.2).

NEMS devices are fabricated with two approaches. The “top-down”, silicon-based method can be seen as a miniaturization of traditional technology, developed from surface micromachining. Freestanding structures are obtained using standard

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DOI: 10.2991/978-94-6239-012-6_14, © Atlantis Press and the authors 2014

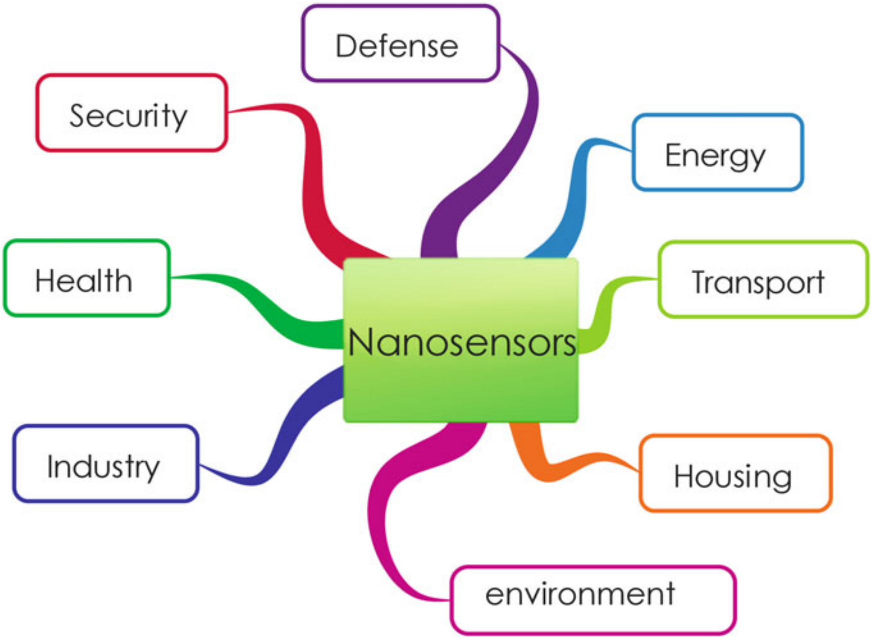


Fig. 14.1 Example of domains where nanosensors can play a role

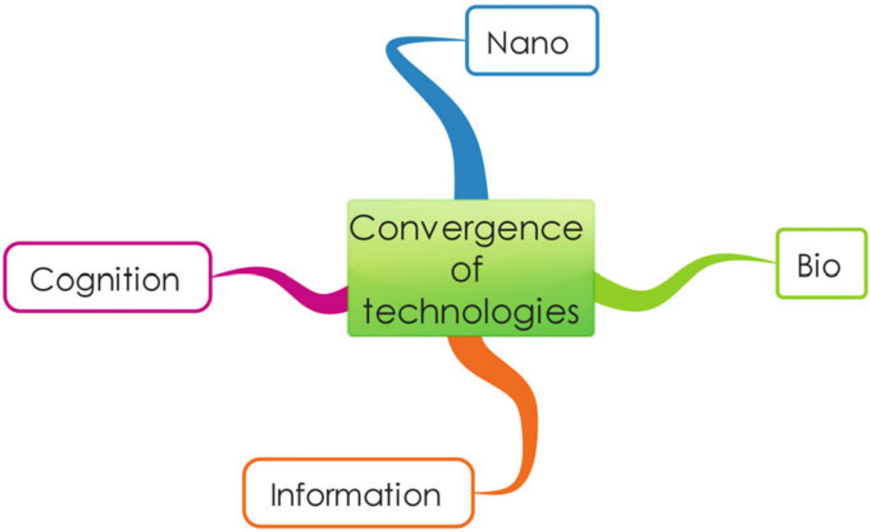


Fig. 14.2 Shows the interplay between the difference technologies: nano-, bio-, infotechnologies and cognition

electron beam lithographic techniques in combination with etching techniques to obtain the final structure.

Another trend is the “bottom-up” structuring of matter at the nanoscale level. Self-organized matter can provide new, unforeseen functions, or the realization of previously existing functions at dramatically decreased cost. In the bottom-up approach, NEMS devices with carbon nanotubes have acquired a central role. Singly clamped nanotubes (cantilevers) have recently shown at room temperature a switching behavior and their bending modes have been excited and visualized in a transmission electron microscope. Doubly clamped suspended nanotubes have been used to study their thermal motion at room temperature, and to probe vibrational modes. These modes can be used to provide highly accurate information in motion sensing.

Nanomaterials of many different types are being explored for their potential application in new nanosensors: carbon nanotubes, nanowires, nanofibers, and nanoparticles. Molecular and polymeric conductors and semiconductors have recently been developed driven by a number of properties exhibited by organic materials: structural flexibility, low weight, potential low cost, and low temperature processing. They can be fabricated on large areas using nanoscale methods, such as with inkjet printing.

Nanostructured materials for sensor applications have advantages in sensitivity and selectivity of detection from minute sample quantities. The ability to analyze and detect multiple species (inorganic or organic) in one sensor will be hugely advantageous. Fabrication techniques for the sensors must be able to provide the correct material composition to achieve the desired sensitivity and selectivity, requiring the lowest number of processing steps. Vapor-based processes including atomic layer deposition are a promising approach, using new precursor chemicals. Future trends in sensor miniaturization and integration with electronics will be developed ensuring processing compatibility with silicon-based technologies and so minimizing cost.

Miniaturization of functional devices brings new advantages in terms of manufacturing: robots can be smaller, thus reducing the production plant footprint and therefore radically modifying business processes. Commercialization will ultimately require measurement electronics to be integrated on the same chip as the NEMS device to reduce or eliminate interface connections. Integration and packaging will play an extremely important role, ensuring not only that the required functions are available, but also that devices are usable with optimized sensor placement, human-device interfacing, and simple methods for deployment.

14.2 Nanotechnologies for Detection and Monitoring

Nanotechnologies offer unique capabilities contributing to security, safety and maintenance, human health, and the environment.

It is far better to prevent a criminal or terrorist attack than to have to deal with the consequences. Current security technologies rely on relatively discrete installations requiring high human effort: closed-circuit television (CCTV) monitoring, security patrols, sniffer dogs, and X-ray examination of baggage at transport terminals and critical buildings. As well as their role in detection, the presence of patrols and monitoring installations act as a deterrent.

The use of widely distributed nanosensors, which are not localized and which can provide in-depth monitoring, being both selective and sensitive (at the single molecule level), with fast autonomous response, can be used to identify a range of threats with far greater efficiency at a reduced cost. They have great advantages as a deterrent in that they are not as obviously visible as a police patrol, so they cannot be avoided and when the likelihood of detection becomes a near-certainty, there is a very strong disincentive to plan or implement an attack.

A particular example where fast response is important is in the detection of explosives by nano-enabled technologies in security applications. At present, sniffer dogs are still employed because they offer one of the best methods of sensing with a fast response time! Thus, there is a goal of replacing the sniffer dog with a nanosensor that responds equally quickly, but which is even more sensitive and can provide detailed and accurate chemical information within a short time from an initial warning (Fig. 14.3).

The high sensitivity and fast rapid response of nanosensors can be crucial, as the time to detect the first molecule/particle/pathogen is vital in determining as quickly as possible the nature of the alarm, so that prevention or protection measures can be deployed in a timely fashion. Selectivity and discrimination are of prime importance to avoid false alarms, and to choose technologies to be deployed that can capture toxic substances and reduce contamination. Topics which are associated with the "electronic nose" concept are shown in Fig. 14.3.

Some nanodevices will offer the possibility of reconfiguring themselves in response to a detection event: from a rapid "broad" sensing mode to a "narrow" identification of the specific agent that triggered the initial detection alert (Fig. 14.4). A successful nanosensing device requires not only the nanoscale sensor system, but also miniaturized computing, communications and power, all integrated into the smallest possible device volume.

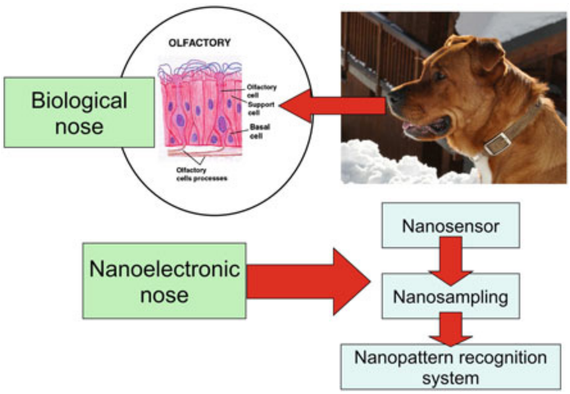


Fig. 14.3 Nanoelectronic nose where nanoelectronics is used to mimic the sniffer dog

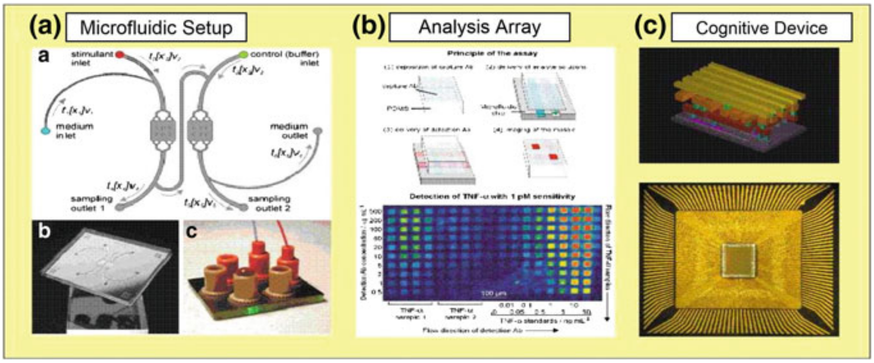


Fig. 14.4 Research topics which are associated to the artificial nose concept. **a** Microfluidic setup; **b** a highly sensitive chemical analysis array; **c** chip ultimately targeting cognitive-type operations. Image courtesy of IBM Research-Zurich

Using devices with small volumes allows large-scale deployment of very large numbers of individual sensors. This allows for multiple redundancy of the sensor system, leading to high overall reliability. A high level of redundancy also gives extremely good robustness to the monitoring network, whether or not individual sensor elements are robust in themselves, as elements can fail without compromising the overall function.

In the broader environmental context, the ability to "seed" nano-based devices over wide areas for monitoring allows for much improved data acquisition that can enhance agricultural production or provide new information for environmental scientists. Sensors built into clothing or mobile telephones can provide "crowd-sourced" data with high accuracy and multiple redundancy, with information available immediately from readings in local areas. A key feature of nanodevices is their robustness and versatility to be used in a range of applications, and the ability to be implemented by people who do not have specific nanotechnology knowledge. Following Fukushima, there was significant concern over potential exposure to the public, with uncertainty and mistrust of measurements and estimated radiation doses. The use of personal sensor networks can provide a high level of public reassurance.

14.3 Overview of the Possibilities for Nanosensors

In this section, we briefly review applications of nanosensors in different sectors. Some are already at a commercial stage, others at the laboratory stage, and some are just potential opportunities. In most cases, sensor systems will incorporate both nano- and microtechnologies (Fig. 14.5) and use the best of the two worlds.

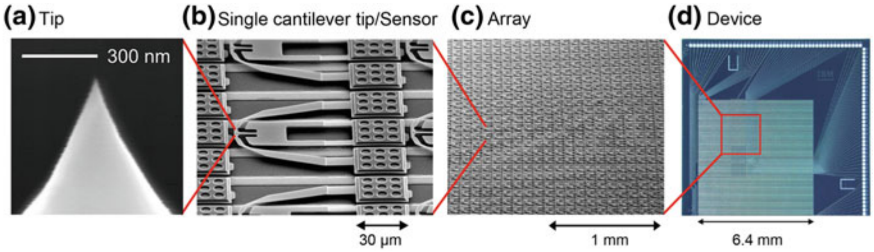


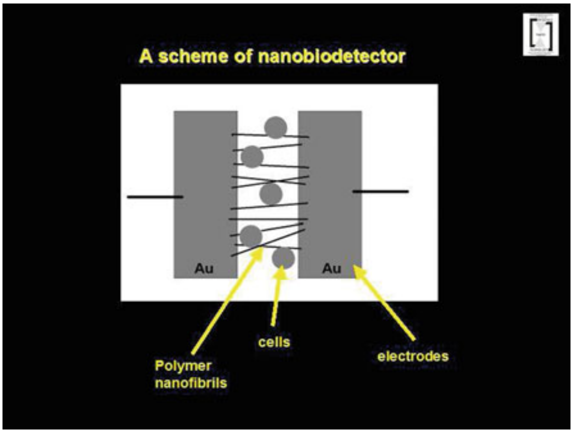
Fig. 14.5 Example of the integration of massive parallelized nanosensors (*left-hand side*), here probe-microscopy tips, into a silicon-based prototype microdevice for storage purposes (*right-hand side*). Image courtesy of IBM Research, Zurich

14.3.1 Health Care

Nanosensors will have great impact in the health care sector, especially in targeted diagnostics which require quick results, and which must be cheap, reliable, and simple to use. A local doctor will have access to detection and analysis facilities currently found only in major national and international centers, aiding diagnosis and leading to earlier, more accurate detection and treatment of disease. The principle of a nanobiodetector is shown in Fig. 14.6.

Single and multi-wall carbon nanotubes have potential to be used as chemical and biological nanosensors for applications as diverse as glucose detection, cholesterol measurements, and breathing monitoring. Semiconducting nanowires can be used for virus detection at very low concentrations. Nanoparticles may also find applications as biological markers for *in vivo* imaging. Nanobiosensors can be incorporated into wound dressing to monitor the healing process.

Fig. 14.6 Scheme of a nanobiodetector



14.3.2 Clothing Industry

Nanosensors incorporated in textiles have the possibility to monitor breathing and heart functions: important for athletes, and for people with respiratory or cardiac illness. For people with particular medical conditions, textile-based sensors can provide continuous monitoring, and can even communicate directly to a medical center for advice on treatment or to summon emergency help if required. Functional clothing can automatically adjust airflow and permeability depending on skin temperature, humidity, and outside environment.

14.3.3 Sensors in the Automotive Industry

This industry is probably at the forefront of the development of nanosensors. As an example to illustrate their importance, Fig. 14.7 shows present and future sensor needs in diesel multijets. Sensors will have an extensive use in vehicles—initially "high end" luxury cars but increasingly becoming standard for all possible parameters: interior and exterior temperature and air quality; tire pressure; engine control to maximize fuel efficiency; electronic stability controls; exhaust gas optimization including catalyst function; filters; fuel quality; and even monitoring of the driver for alcohol, in which case the engine will be disabled. The interior environment can be adjusted automatically to reduce fatigue and maintain driver alertness.

14.3.4 Oil and Gas Exploitation

Nanosensors have potential in pinpointing the large quantities of remaining oil and gas in existing reservoirs, and to discover new oil or gas fields which are difficult or impossible to locate with conventional macro-measuring techniques. Nanosensors can provide a 3D distribution map of oil and gas reserves; and in new fields can enter the pores of hard rocks and provide detailed mapping data on not only the location of reserves, but also their quality via rapid physical and chemical analysis without the need for large-scale bore holes and sample extraction.

14.3.5 Security

The high sensitivity of nanosensors means that they are able to detect biological and chemical traces in very small quantities, giving great improvements in defending against the transport or use of chemical and biological weapons. Because of their small size, they can be distributed widely at critical locations, providing multiple

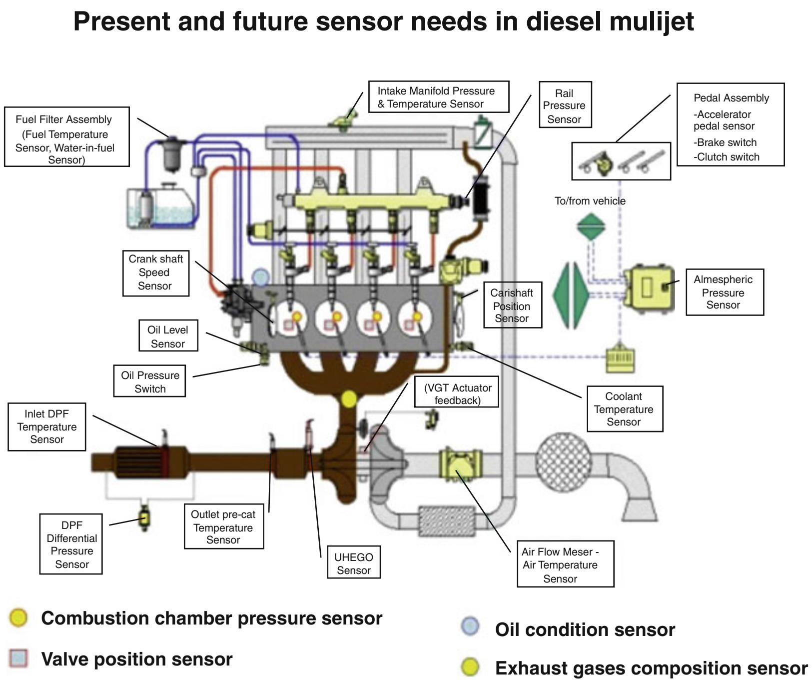


Fig. 14.7 Application of sensors in cars. Image courtesy of P. Perlo Torino e-district, IFEVS

and redundant coverage and greatly improving the chances of successful detection at lower concentrations than is currently achievable.

14.3.6 Smart Structures

For safety and security, it is increasingly desired that structures are real-time monitored. This can only be done with sensors containing nano or microsystem as well as processing circuits allowing treatment and transmission of information in real-time. The sensor should not perturb significantly the structure and this is one reason why nanotechnology is ideal. A second reason is of course to achieve costs that are as low as possible.

Fig. 14.8 Strength monitoring of a bridge with nanosensors. Image courtesy of IoN, UK

Control of structures

The Confederation Bridge is the world's longest bridge over water, spanning 12.9 km from Prince Edward Island to New Brunswick, Canada (Fig. 14.8). The bridge sees very low temperatures and regular icing. It has columns of fiber optic sensors wrapped in advanced composite materials. These wraps help hold the structure together and the embedded sensors can precisely measure potential corrosion that may be occurring underneath owing to the long-term effects of wind, ice, and traffic loads on the bridge. This helps maintenance in general and ensures fewer closures of the bridge.

14.3.7 Sensors for Environmental Monitoring

Nano-enabled biosensors are able to provide detailed information on their local environment. This allows for greatly improved control of the environment in homes and offices: temperature, humidity, and airflow, for example. In large buildings, individual workers will be able to customize their workspace, and a high level of sensing will ensure that it is maintained to their desires with optimal airflow and air quality to aid concentration.

In the home environment, sensor arrays will assure correct ventilation, and adjust heating and cooling depending on the occupation of different rooms in the house, so that energy usage is optimized and reduced. Control of air extraction from bathroom environment can be altered depending on humidity levels, for example.

14.3.8 Food Science

Nanotechnologies can provide improved monitoring of foodstuffs throughout the production and distribution chain: for example, in the detection of bacterial contamination, food-borne pathogens and other contaminants that can lead to illness and death. At present, sampling for contamination by bacteria or chemical products is expensive and requires intensive intervention, while nanotechnologies can provide automated sampling and real-time (on the spot) detection, and discrimination between numerous toxins with advantages in speed, cost, and flexibility.

Nanosensors can revolutionize food packaging materials; for example, a sensor can change color to indicate that food is no longer edible, based on detection of bacterial action in the food rather than a conservative assessment of a "use-by" date that means fresh food may be discarded unnecessarily. Nanomaterials can also provide antimicrobial properties directly within the packaging to reduce contamination and extend product life. This leads to an overall reduction of food waste. Bio-based nanocomposites and nanofiber materials can be used to develop biodegradable packaging and can even produce edible packaging materials.

Radio frequency identification data tags (RFIDs) can be used to give quality assurance in the supply chain.

14.3.9 Environmental Pollution

The ability to detect the presence of pathogens or toxic agents in our environment is the first step in being able to take early action for remediation and clean-up. Nanotechnology will help in monitoring environmental pollution and assessing the environmental risks of toxicity of chemicals, biochemicals, and bacteria.

The regional, continental, or even the global use of many nanotechnological air quality and climate gas measuring devices will greatly improve the current data limited verification and improvement of regional and global climate- and chemistry-transport models, and therefore improve air quality and climate forecast systems of the future.

As well as artificial pollution, nanosensors can be used in agriculture to detect mycotoxins and bacterial action indicating the early stages of spoilage.

14.3.10 Farming Industry

Nanosensors can, in future, be used in farming technology to perform real-time crop monitoring, leading to targeting the intervention a farmer must take for better quality and higher yields of food, so ensuring food security and reduced food price inflation (Fig. 14.9).

Networks of individual sensor nodes can be dispersed over a landscape to measure local variables and report to a central processing unit, so that all aspects of crop and livestock can be monitored for precision farming. Biosensors, such as unimolecular sensors or bioarrays, utilize biomolecules to detect the action of pests or disease, or gases relevant to agricultural growth. A range of natural bioactive molecules, such as antibodies, enzymes, cells receptors, and nucleic acids can be integrated as the sensing receptors in biosensors. Nanotechnology will augment biosensors by enabling improvements in speed, sensitivity, portability, and the possibility for crop/livestock sensor networks. Nanosensor technologies can provide information to farmers concerning environmental conditions, plant and animal health, and growth parameters; allowing for optimal, targeted, tailored, and controlled application of fertilizers, pesticides, and irrigation. The key challenges are cost reduction for widespread use, and an unclear regulatory environment for the use of nanoparticles.

Carbon nanotubes and nanoparticles are sufficiently small to trap and to measure on individual proteins or other molecules and provide real-time information on ripening, irrigation effectiveness, and the action of both pests and pesticides. Nano-enabled materials will also ensure better nutrient uptake by optimizing the transport of beneficial agents from application to soil penetration to absorption by the crop, resulting in reduced use of agrichemicals and so reducing their impact on the ecosystem. Nanofertilizers can have multiple functions that can be activated at different points in the growing cycle, for example, by magnetic fields, moisture (by controlled irrigation or by rainfall), heat, or ultrasound.

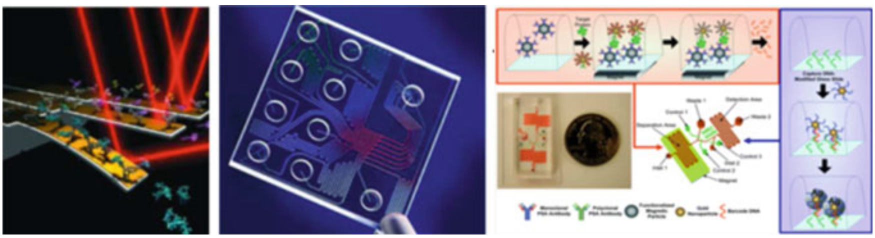


Fig. 14.9 Sensors and diagnostics in precise agriculture. Image courtesy of IoN, UK

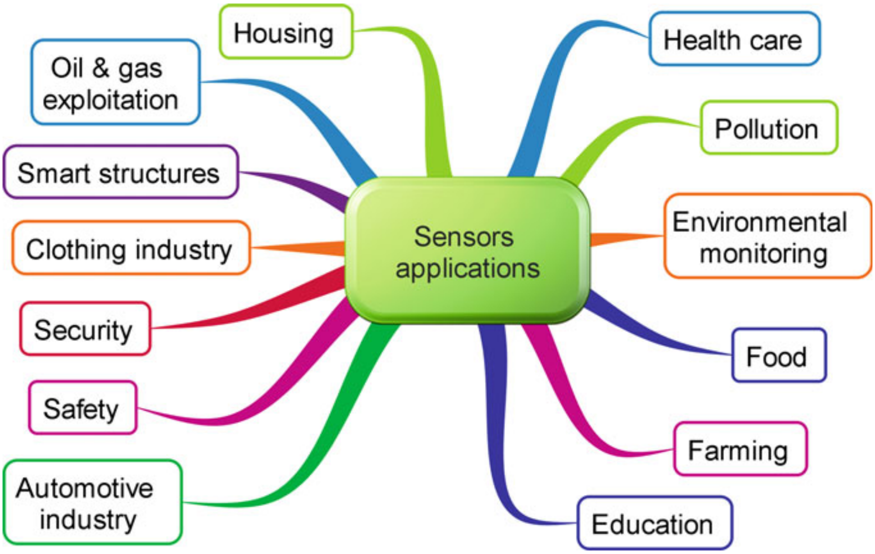


Fig. 14.10 Sensors can be used in many fields

14.4 Conclusion

Most technological devices rely on sensing in some form, and the number of sensors in our ambient environment is increasing exponentially. They can be used in many fields (Fig. 14.10). Nanosensors offer the possibility of taking this trend to the next level, with highly sensitive, highly discriminating, widely distributed sensor arrays that fulfill requirements in applications from farming to health to security. For successful widespread deployment, it is important that nanosensors can be produced in large quantities so that they can become cheap and easily available in different variants for different industrial sectors. The development of nanosensors should be directed to genuinely cover applications for which micro and macro devices are not suitable. So, for example, as the rules criteria and severity rules for security screening are likely to become stricter, we should be prepared for these future applications by having nanosensors at hand. It is also important that nanosensors should integrate with existing and newly developed systems, and therefore standardization is important for their interfacing and data formats. The market opportunities in this field are very great, with the right level of investment and development to ensure success.

Chapter 15
Nanotechnology Applications for Air and Soil

Everyday a person breathes an average of 15 kg of air, and consumes nearly 1 kg of oxygen, drinks several liters or kilograms of water, and eat about a kilogram of food. This means that there can be severe impact on us from pollution of air, water, and soil. In each of these areas, nanotechnology has and will have an important contribution in the future.

15.1 Nanotechnology for Air Purification

(Artificial Environment Hazards)

The total mass of the atmosphere is equal to 52×10^{14} tons. The troposphere is the layer of the atmosphere in which we live. It goes from the Earth's surface up to about 11 km in the average. It is higher at the equator than at the poles. Most of the air is contained in the troposphere (about 82 %) and its volume is equal to 5,600 million km^3. Ensuring that the air that we breathe is of good quality is therefore an important issue.

Cities and their suburbs are confronted with serious environmental problems associated with air pollution and smog. The hazardous compounds present in the air as a consequence of artificial pollution include particulate matter (especially nanoparticles less than 1 millionth of meter in size (1 μm)) and aerosols, CO_2, NO_x, soot, ozone, CO, and organic, toxic and biological substances; Fig. 15.1. This is particularly dangerous for vulnerable groups such as children and the elderly, and persons with respiratory disorders.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_15,

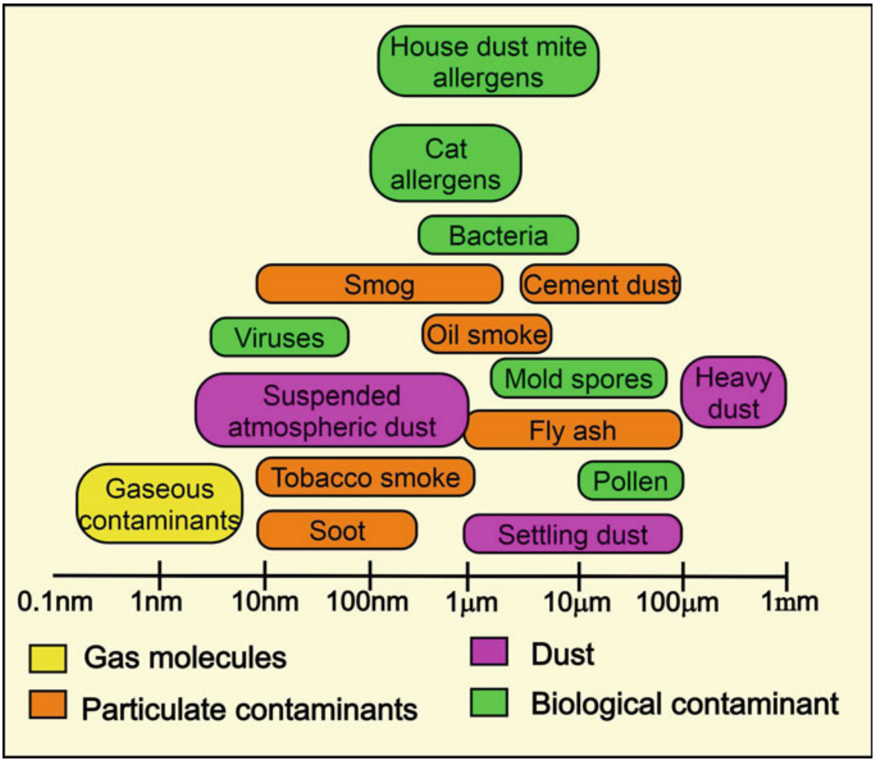


Fig. 15.1 Air particulate distribution. Data from wikipedia (particulates)

15.2 Aerosols Nanoparticles

The aerosol particles can be effectively deposited throughout the human respiratory system, particularly deep in the lung alveoli at the air/blood interface. Therefore, these particles may be harmful by their pure existence, even if the substance is nontoxic. The effect of pollution on mortality is schematically given in Fig. 15.2.

Particle matter is either of natural origin—sea salt, dust, pollen, or volcanic ash—or from human sources mainly from fuel combustion in thermal power generation, incineration, domestic heating, and vehicles. In cities vehicle exhaust, road dust, and burning of wood, fuel, or coal for domestic heating are the main local sources. The change in the composition of the troposphere is connected with the increasing world population and its growing demand for energy, food, and living space. These demands are associated with growing industrialization and urbanization, developing megacities, increasing traffic, and general landuse change. Increasing and changing emissions of primary trace gases and particles into the troposphere impact atmospheric chemical processes which control the removal of greenhouse gases and pollutants from the atmosphere (atmospheric self-cleaning), but also the chemical formation

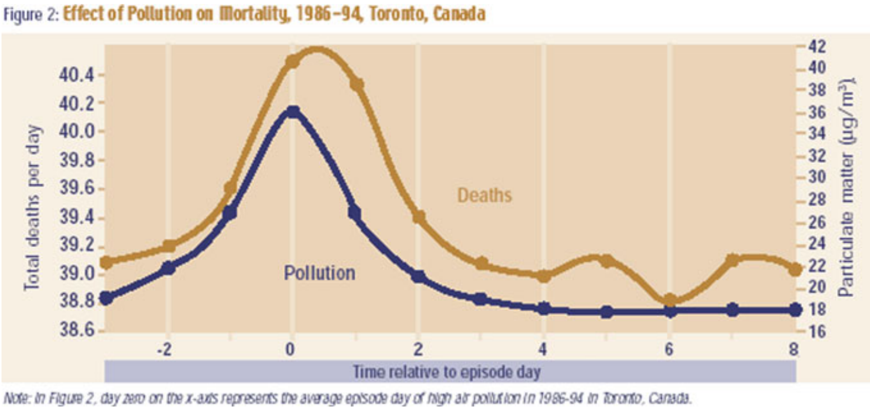


Fig. 15.2 Particle loading in pollution related to mortally. Courtesy of A. Wahner, Forschungszentrum Jülich, GmbH, Institut für Chemie und Dynamik der Geosphaere, Jülich Germany

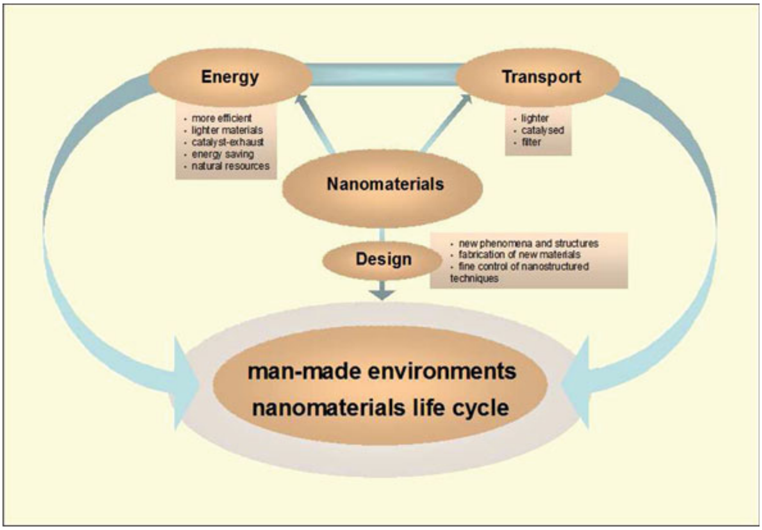


Fig. 15.3 Nanoparticles are generated by human activities

of new pollutants in the atmosphere like ozone and secondary organic aerosols. It is expected that the trend in atmospheric composition change will lead to significant climate changes with detrimental effects on large parts of the world population.

Figure 15.3 schematically represents the nanomaterials substances generated by energy production processes and transportation.

Air pollution can be tackled by nanoscale photocatalysis that degrades pollutants and provides a gaseous cleaning effect. Nanostructured filters designed at the molecular level remove the most minuscule contaminants from the air. Both of these effects result in the reduction of greenhouse gas concentrations and in better air quality. So nanotechnology opens up new possibilities in the solution of environmental problems.

CO_2 capture has so far mainly been achieved through a large-scale approach: attempting to capture CO_2 directly in the atmosphere. Nanotechnologies can be effective for CO_2 capture and storage via solvents and sorbents such as ionic liquids. A decentralized approach is to capture CO_2 at the exhaust output of power plant chimneys, home heaters, and car engines. Nanomaterials are robust in the presence of impurities (particulate matter, sulfur dioxide, nitrogen oxides) in the exhaust gas that can reduce the effectiveness of certain existing CO_2 capture processes. Dense (polymer) nanomembranes are more efficient future alternatives to reduce CO_2 emissions. Nanostructured membranes improve the efficiency and robustness of CO_2 capture. Nanomaterials can play a major role in biocatalysts for CO_2 binding and as substrates for long-term storage of CO_2.

To safeguard the environment from hazardous and toxic substances, including waste products, and to comply with more stringent future legislation, nanotechnology offers a lot of opportunities. Catalysts for example, can convert or degrade ambient air pollutants such as benzene, formaldehyde, and naphthalene to carbon dioxide; to the extent that some modern vehicle exhaust systems output air that is cleaner than in the surrounding city streets! Nanomembranes are now playing a vital role in diesel exhausts. Adsorbents like iron oxides, dendrimers, or carbon nanotubes can be used to remove polycyclic aromatic hydrocarbons (PAHs) from waste streams; and photocatalysis by TiO_2 or ZnO doped with noble metals like Pt, Au, Ag can be applied for degradation of pollutants such as NO_x and PAHs.

The final goal in ensuring sustainable optimal use of raw materials is to see the outputs of one technology or production process become the inputs for another technology in the industrial process chain. What this means in essence is the use of waste (whether that is gases, substances, or whole products) for the production of new materials or compounds resulting in a worldwide "industrial ecosystem." Figure 15.4 represents a demonstration plant that highlights the reuse, recycle, repair, refurbish, and remanufacture steps in an industrial materials life cycle system. This cyclical approach means that raw materials used in products never reach end-of-life and disposal.

Nanotechnology offers great challenges in this world of environmental concern and climate change. The application of nanotechnology presents the possibility of disassembling existing and future waste to the molecular level, and then reassembling it into new resources and products. Similar to nature, bioengineered mechanisms will be the blueprint for the assembly and operation of products at this scale. As an example, nanotechnology-based remediation techniques not only break down toxins but can actually lead to the production of valuable by-products and completely new substances.

In the case of CO_2, climate change concerns can be addressed by capturing CO_2 such that it can be reused as an input product for new chemical processes. CO_2-based processes can also be used in multiple production systems, such as for cement and engineering alloys.

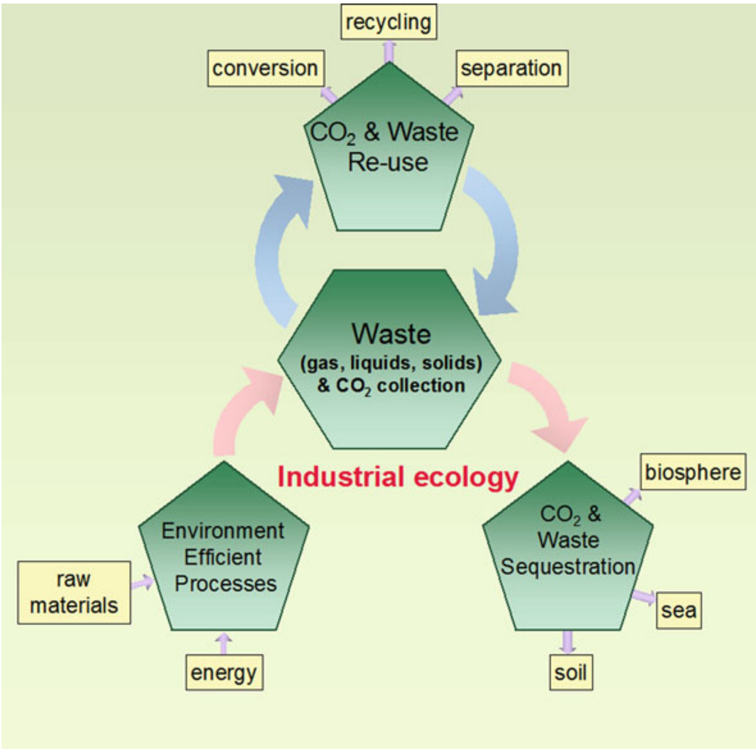


Fig. 15.4 Overview of the end-of-life cycle approach

Industrial Ecology promotes changes from a wasteful "once-through-and dispose" economy, to a closed loop system of production, consumption, recycle, and reuse.

An example of this is shown in Fig. 15.5: a cement factory that produces nitrates that can be used by agriculture which will produce bio-organic waste used to power a thermal power station.

15.3 Aerosols Nanoparticles and Climate Change

The consequences of unsustainable development since the Industrial Revolution up to the twentieth century, specifically climate change, will have substantial human, economic, biodiversity, and geopolitical consequences. Human activities have been responsible for observed trends in the chemical composition of the atmosphere since the preindustrial era (Fig. 15.6 with impact on climate).

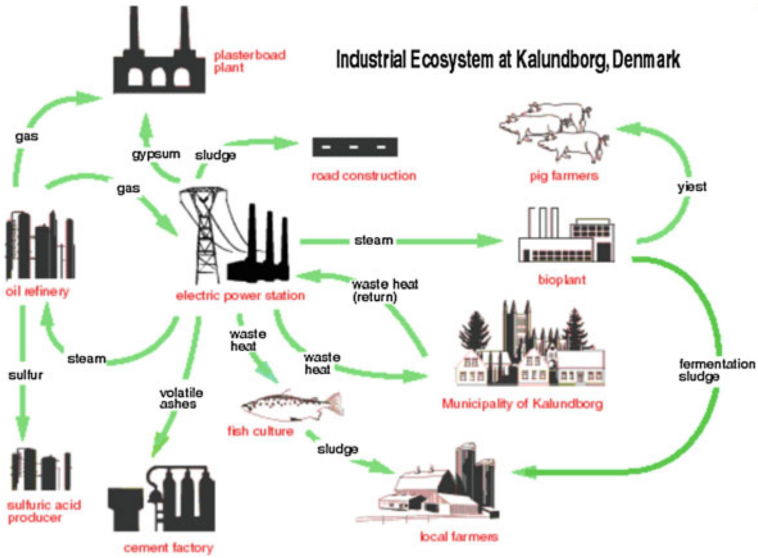


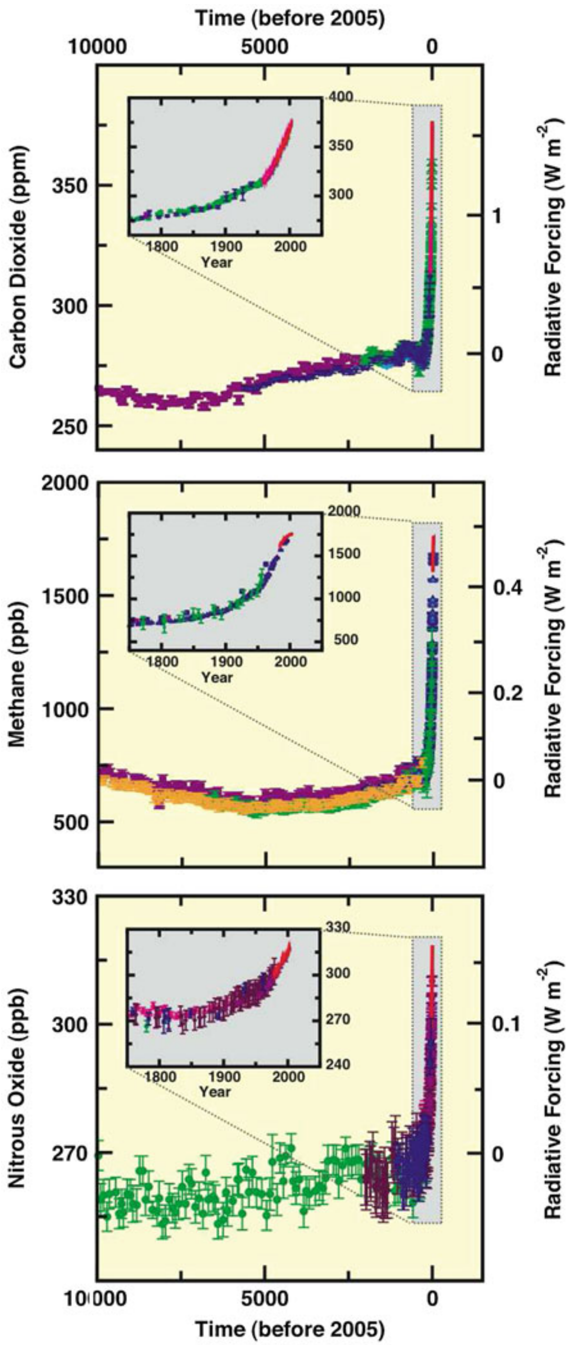
Fig. 15.5 Synergy in an industrial pilot plant in operation Industrial Ecosystem at Kalundborg, Denmark, from http://newcity.ca/Pages/industrial_ecology.html

Greenhouse effect

If there were no atmosphere on the Earth, the average temperature at the surface of our planet would be −18 °C. Water would be in the form of ice and life could not have developed as we know it. Fortunately, the atmosphere contains a small quantity of gases that are able to trap the infrared radiation emitted by terrestrial system and hence to warm the Earth's surface. The average surface temperature (+15 °C) is therefore 33 °C higher than it would be without the presence of these radiatively active gases.

The Earth's temperature results from an equilibrium between solar energy captured by the Earth system (incoming solar visible and near-infrared energy minus reflected solar energy) and the terrestrial energy escaping to space. Part of the terrestrial (infrared) radiation emitted by the surface and the lower atmosphere is absorbed by atmospheric greenhouse gases, and some of it is radiated back toward the surface. This trapping of radiative energy by radiatively active molecules (H_2O, CO_2, CH_4, N_2O, O_3, etc.) is referred to as the greenhouse effect. It leads to an average surface temperature of +15 °C.

Fig. 15.6 Human activities have changed the composition of the atmosphere since the preindustrial era. IPCC 2005. www.ipcc.ch



Greenhouse effect

The greenhouse phenomenon is sometimes described by an analogy with the situation of a car parked in the sun with the windows closed. The windows are transparent to visible solar radiation but opaque to infrared radiation. Visible light energy passes through the glass, and is absorbed by the objects located inside the car. They emit part of that energy as infrared radiation, which cannot pass through glass and is then absorbed by the objects and the air inside the car leading to an increased temperature. The same phenomenon occurs in the Earth's atmosphere. Some gases, present in small quantities, absorb some of the infrared radiation emitted by the Earth, but they are largely transparent to direct sunlight. After absorbing the energy, they reradiate it evenly and a portion of it warms the surface of the planet. The problem with which we are faced today is that the human activities release large quantities of greenhouse gases into the atmosphere. The most important one, as far as anthropic activities are concerned, is carbon dioxide (CO_2) *coming mostly from burning fossils fuels. Each year, human activities release in the atmosphere twice as much* CO_2 *that the ocean and the biosphere can absorb. As a result, the atmospheric concentration of* CO_2 *is gradually increasing and so does the greenhouse effect. Climate change is a consequence expected from this increase. Scientists are actively trying to understand and model this response of the Earth system to increasing atmospheric concentrations of greenhouse gases.*

Radiatively active gases such as water vapor, carbon dioxide, methane, nitrous oxide, halocarbons, etc., contribute to the greenhouse effect of the atmosphere. The atmospheric concentration of these gases has increased considerably as a result of human activities (industrial, agricultural, etc.). Anthropogenic greenhouse gases add to radiative forcing produced by greenhouse gases of natural origin. Their contribution is shown in Fig. 15.7. The largest contribution comes from carbon dioxide (CO_2). The atmospheric concentration of water vapor is only directly affected by human activities through a positive feedback mechanism: the warming produced by anthropogenic greenhouse gases such as CO_2 enhances the evaporation of water, which leads to substantial amplification of the greenhouse effect.

Global climate change is also affected by changes in the atmospheric aerosol content resulting from human activities. Aerosols are small liquid or solid particles suspended in the air. Their size (radius) varies from less than 10 nm to typically 100 μm. A population of aerosols is characterized by its size distribution, chemical composition, mixing state, and atmospheric concentration. One generally distinguishes between primary aerosols (i.e., particles such as dust and sea salt particles released to the atmosphere) and secondary aerosols (i.e., such as sulfate or organic particles formed in the atmosphere by gas-to-particle conversion). Aerosol particles such as sulfate particles scatter solar radiation back to space, and so tend to cool the Earth's surface; they partially reduce the warming produced by greenhouse gases. Other particles such as black carbon are absorbing terrestrial radiation and hence tend to warm the Earth's surface. The processes are responsible for the formation (e.g., nucleation) and transformation (e.g., coagulation) of aerosol particles are complex

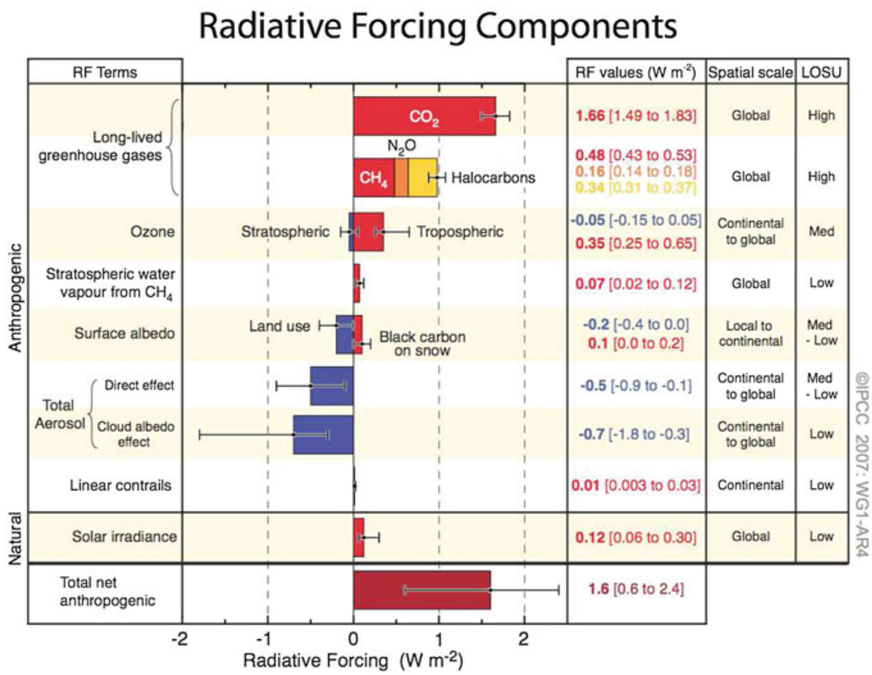


Fig. 15.7 Global-average radiative forcing estimated changes and ranges between 1,750 and 2,005. IPCC 2005. www.ipcc.ch

(see Fig. 15.8). Aerosol particles can be coated by water (activation) and form cloud droplets. They are removed from the atmosphere by wet and dry deposition on the Earth's surface (see Figs. 15.8 and 15.9).

Nanotechnologies have great potential for reducing the impact of climate change in various ways. A more efficient use of natural resources, enabled by nanotechnologies, will result in reduced material consumption in product fabrication and the minimizing of waste in industrial processes. These and other factors will contribute to a reduction in CO_2 emissions. A mechanistic understanding of the role of nanoparticles in global warming will lead to a better prediction of climate change and provide means to react against the causes and effects of the increase of the greenhouse effect.

The atmosphere around us is filled with microscopic particles. When reading this sentence you are likely to breath in anything from 10,000 to more than 10,000,000 of these tiny particles. Atmospheric aerosols are composed of many different materials, including soil, smoke, sea salt, sulfuric acid, and organic compounds (Fig. 15.10).

Natural sources of primary aerosols include such phenomena as dust storms and volcanoes (Fig. 15.11). The human contribution of aerosols to the atmosphere is equal to the quantity emitted by natural sources and has increased considerably during the last decades.

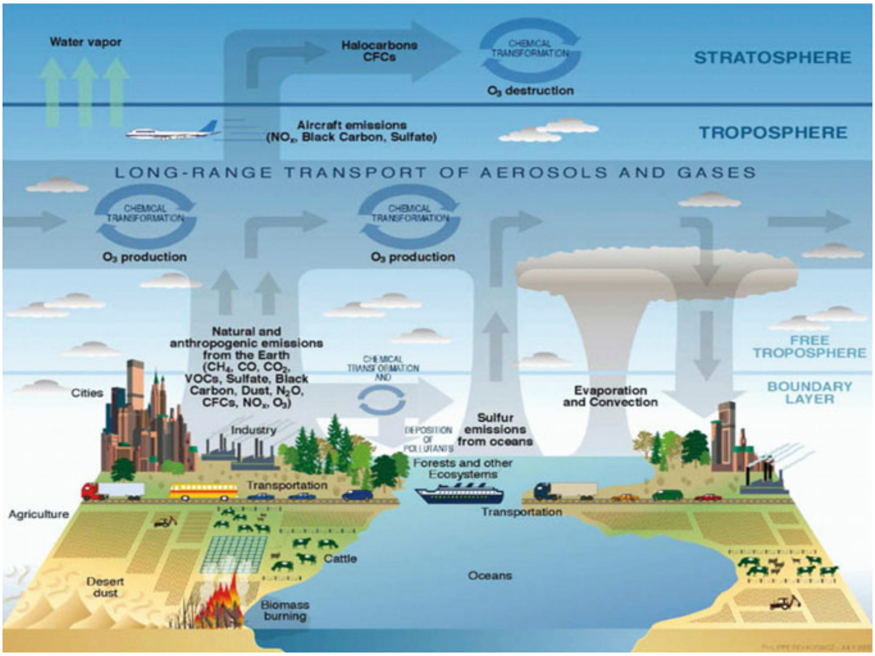


Fig. 15.8 Long-range transport of aerosols and gases. *Source* University Corporation for Atmospheric Research (UCAR)

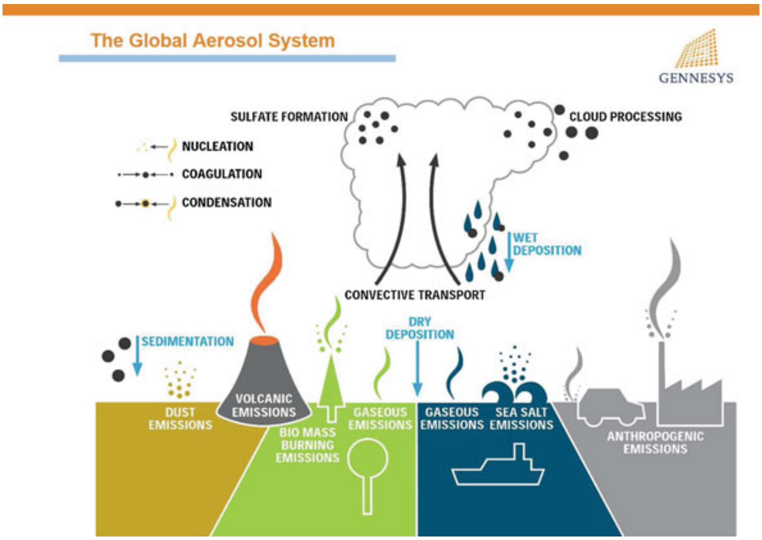


Fig. 15.9 Overview of the aerosols cycle and key-related processes includes emission of primary particles and gas-phase precursors, nucleation, coagulation, condensation, evaporation, cloud processing, sedimentation dry deposition, and wet scavenging

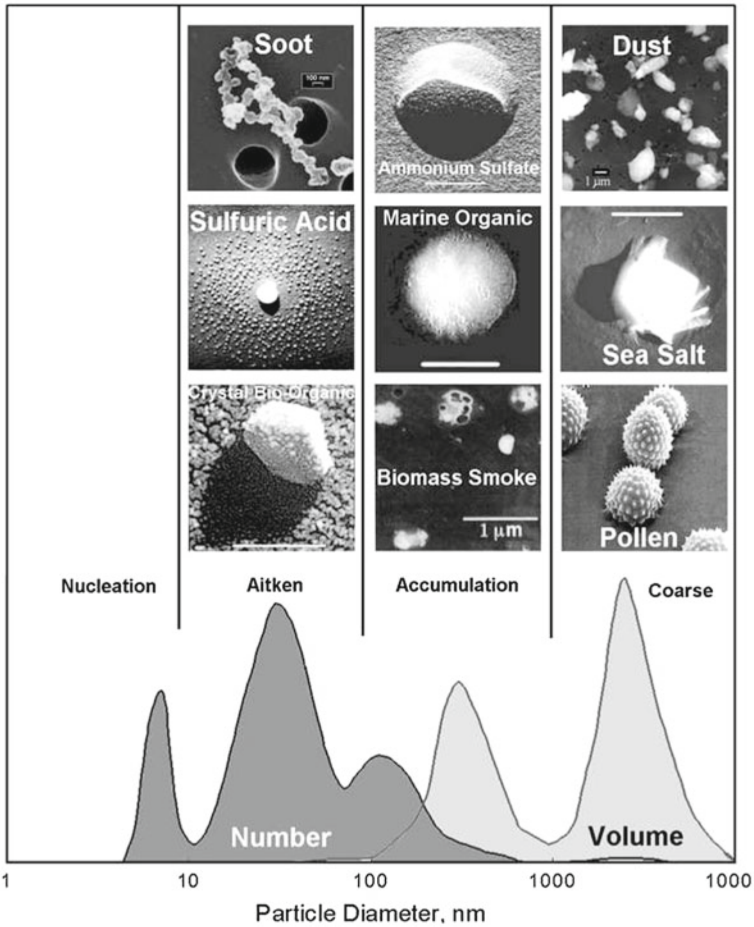


Fig. 15.10 Different types of aerosol particles in the air and their size distribution with different modes: (nucleation (<10 nm), Aitken (10–100 nm), accumulation (100–1000 nm), and coarse(>1000 nm))

Fig. 15.11 Natural and industrial sources of aerosols

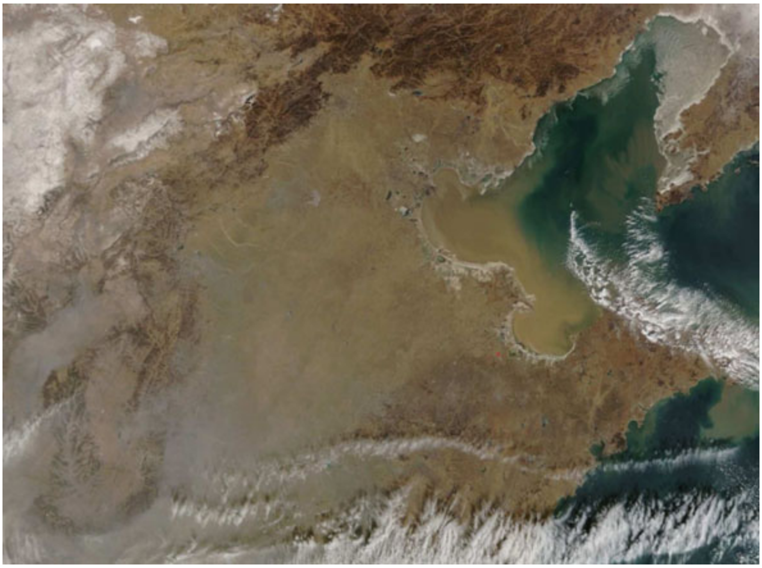


Fig. 15.12 Satellite view of North China on a clear day. The Atmosphere, F.K. Lutgens and E.J. Tarbuck, Prentice Hall, 9th ed. 2004

Most human-generated aerosols come from the sulfur dioxide, soot, and organic gases emitted during the combustion of fossil fuels and as a consequence of burning vegetation to clear agricultural land. Chemical reactions in the atmosphere convert the sulfur dioxide into sulfate aerosols. Secondary organic aerosols result from the gas-to-particle conversion of organic compounds (mostly of biogenic origin) in the presence of oxidants whose atmospheric concentrations are affected by human activity (Figs. 15.12 and 15.13).

Aerosols affect the climate directly by reflecting sunlight back to space and indirectly by making clouds "brighter" reflectors. Many aerosols attract water and thus are especially effective as cloud condensation nuclei. The large quantity of aerosols produced by human activities (especially industrial emissions) triggers an increase in the number of droplets that form within a cloud. A greater number of small droplets increase the cloud's brightness: so more sunlight is reflected back to space (Fig. 15.14, ship tracks over the ocean).

By reducing the amount of solar energy being converted to heat at the Earth's surface, aerosols have a net cooling effect. Studies indicate that the cooling effect of human-generated aerosols could offset a portion of the global warming caused by the growing quantities of greenhouse gases in the atmosphere. Unfortunately, the magnitude and extent of the cooling effect of aerosols remain highly uncertain. This uncertainty is a significant hurdle in advancing our understanding of how we, humans, alter Earth's climate.

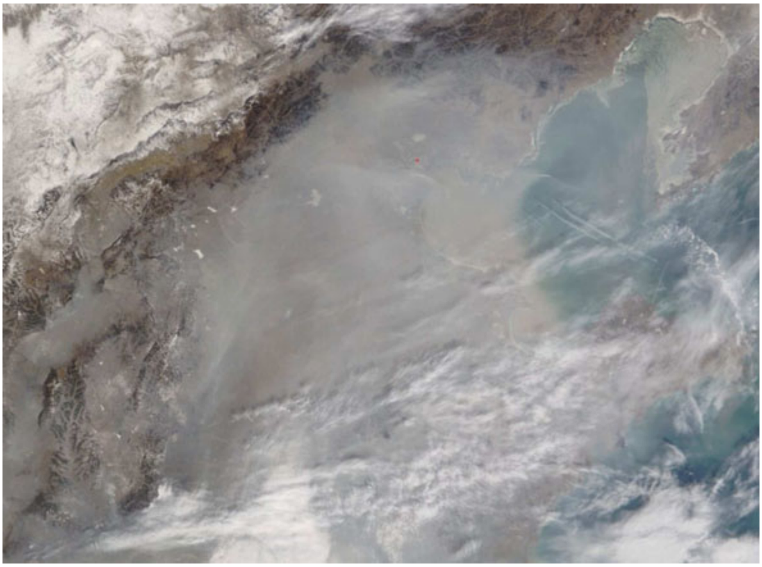


Fig. 15.13 Satellite view of North China on a polluted day, *gray colors* are due to aerosols formed by atmospheric chemical processes from anthropogenic emissions. Brighter reflection to space induces less heating of the atmosphere (*right*). The Atmosphere, F.K. Lutgens and E.J. Tarbuck, Printice Hall, 9th ed. 2004

Fig. 15.14 Nanoparticles emitted from ship emissions produce more droplets in marine clouds, which are brighter than natural clouds. Brighter reflection to space induces less heating of the atmosphere. Images courtesy of Jacques Descloitres, MODIS Land Rapid Response Team, and Mark Gray, MODIS Atmosphere Science Team, both at NASA GSFC

There are significant differences in the effects of greenhouse gases and aerosols. After being emitted, greenhouse gases such as carbon dioxide remain in the atmosphere for many decades. By contrast, aerosols released into the troposphere remain there for only a few days or, at most, a few weeks before they are "washed out" by rain. Because of their short lifetime in the troposphere, aerosols are distributed unevenly over the globe. Human-generated aerosols are concentrated near the industrialized regions that burn fossil fuels and land areas where vegetation is burned. Because their lifetime in the atmosphere is short, the effect of aerosols on today's climate is determined by the amount emitted during the preceding couple of weeks. By contrast, the carbon dioxide released into the atmosphere remains for much longer spans and thus influences climate for many decades.

15.4 Soil Remediation

The pedosphere is the outermost layer of the Earth where we are living. It is composed of the soil and has an average thickness of about 5 m and an average density of 2.5 g/cm^3. It corresponds to an area of 130 million km^2 and a mass 16×10^{14} tons.

Soil is therefore the top layer of the Earth's crust. Compared to air and water, soil is an inhomogeneous medium making any analysis more difficult to be representative of a whole volume. It does not move except very slowly, apart from extreme events such as earthquakes or landslides. However, pollutants present in the soil may be extracted by water streams or into air.

In many areas, soil is contaminated by previous industrial activities that were conducted without any caution concerning environment. Carcinogenic organic substances and heavy metal can be found in many places over the world. The challenge is to clean up these sites at low cost and with good efficiency. Conventional technologies operate either *ex situ* using soil washing techniques or *in situ* by filling the soil with scrap iron. As far as nanotechnology is concerned, little research is done so far in this area compared to what is done for water remediation.

Metal nanoparticles for soil remediation

Metals can be used as a remediation agent. The mechanism is based on a reduction–oxidation reaction (redox reaction). The metal is the electron donor which reduces an electron acceptor contaminant. Iron is often used in this respect because of its abundance, low cost and ease of preparation. Iron was first used at the macroscale without any special preparation. Now, nanotechnology offers the production of iron-based compounds at the nanoscale with specific properties of remediation. For example, iron particles can be coated with noble metals to make bimetal nanoparticles. Using iron only, the corresponding nanoparticles are called nano zero-valent iron (nZVI) in the literature. Studies show that nZVI are more effective and less costly than macroscale ZVI.

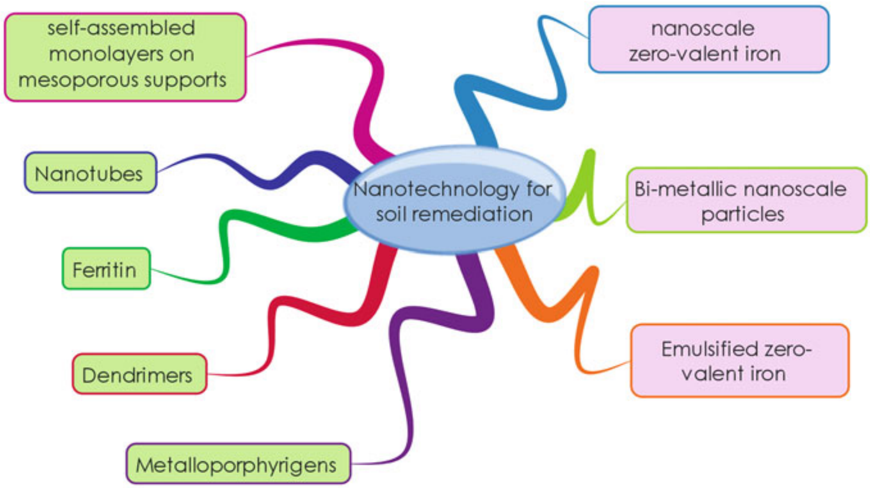


Fig. 15.15 Nanotechnology for soil remediation

> ***Metal nanoparticles for soil remediation***
>
> If the chemical properties of the metal are important for the redox process, the physical properties of the nanoparticles play an important role in the remediation process as well. For example nZVI can be used within a permeable reactive barrier or in a reactive medium in the form of slurry. In this later case, the slurry is injected directly into the subsurface through injection wells. These technologies have different domain of application. Permeable reactive barriers are efficient for well-defined contaminant zones. Slurry injection is quite efficient to treat large source areas.

Sorption methods are another route for soil remediation. Several nanomaterials are able to absorb or destroy contaminants by means of *ex situ* or *in situ* processes. Nanoparticles able to do the job are self-assembled monolayers on mesoporous supports (SAMMS, a registered trademark), ferritin, dendrimers, and metalloporphyrinogens. SAMMS are adsorbents made using molecular engineering.

In Fig. 15.15 we show some of the techniques used for soil remediation.

15.5 Conclusion

Air and soil are two extreme as far as pollution is concerned. In the case of air, pollution spreads quickly and can cover large distances from its origin. In the case of greenhouse gas emissions, the effect is shared across the world's atmosphere. They are other pollutants that are dangerous at short distance from their emission point but, at large distances, the dilution are such that they become harmless. Nanotechnology

Fig. 15.16 Potential air freshener sensor. Image courtesy of Holst Center (Netherland)

can help in reducing pollution. This is especially needed indoors because air can be far more polluted inside than outside. Furniture, carpets, paintings, and electronics equipment are all potential sources of pollution from chemical treatments, and nanotechnology can be used to decrease it. A future vision of personal air freshener indicator is shown in Fig. 15.16.

Pollutants present in dry soil can eventually migrate but at very small speed. This is accelerated if a water flow is present. In this case water can carry pollution to other places. Crops growing on a polluted soil can be dangerous to the health. Nanotechnology can help both by remediation of the contaminants and with sensors for measuring the intensity of the pollution in the environment, particularly in the food chain. Some heavy metals[1] can be of benefit for health at trace concentrations but they can be toxic at larger concentrations. On average, a man weighing 70 kg has less than 10 g of essential metals in his body. The main problem of metals is that they can be transported unchanged over a large distance by air or water. The main toxic heavy metals are mercury, lead, and cadmium. They are the most dangerous if they are in a soluble chemical form. In an insoluble form they are usually harmless.

[1] A metal is called a heavy metal if its density is greater than 5 g/cm^3.

Chapter 16
Water Demands for Nanotechnology

Water covers 71 % of the Earth's surface. It is essential for life and has the power to clean surfaces. It is often used to transport pollution away from a source, especially to the sea, and to dilute it. Water is essential in the photosynthesis mechanism and in the regulation of the Earth's climate. Water vapor is responsible for a large part of the natural greenhouse effect . However, anthropic activities do not affect the greenhouse effect by their water vapor emission because they are negligible compared to natural evaporation. Indeed, 0.5 million of km^3 of water are evaporated each year and 85 % of this amount comes from the oceans. The amount of water on the Earth is equal to 1.4 billion km^3. Most of the water is found in the seas (1.37 billion km^3). Lakes and rivers contain 0.13 million of km^3 and water tables 9.5 million of km^3. Water is a vital resource wealth for humans and must be protected.

Secure, pure, and safe drinking water is a critical resource for public health. Clean water is also required for a wide range of high-technology industrial processes. Water is abundantly available on Earth but mostly with high levels of salt in the form of seawater and thus not useful or even tolerable for drinking purposes. Today, Europeans do not have concern of not having clean drinking water readily available. However, the impacts of global climate change are predicted to substantially increase water stress, and in Southern Europe, water purification is becoming crucial. Population growth and increasing industrialization lead to a rise in water consumption but also to more polluted aquifers, rendering the water quality unsuitable for drinking without excessive treatment. Additionally, the lack of clean drinking water in developing countries is a major cause of disease and early death. Rivers in Europe are becoming more and more polluted and for example, the Danube water quality, despite improving, is mainly used for agricultural purposes.

Nanotechnology has here great potential to make a significant difference.

The sources for drinking water depend on the geographic region: in Industrialized countries, groundwater is the main source; sometimes seawater in regions with water scarcity (e.g., Saudi Arabia); and in developing countries often surface water from lakes and rivers; and sometimes rain collection where microbial contamination is the

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DOI: 10.2991/978-94-6239-012-6_16, © Atlantis Press and the authors 2014

major problem. In some countries contamination with harmful substances such as arsenic is a danger, and for reasons of convenience the removal of calcium is often desired.

Groundwater is subsurface water located in soil pores, spaces in the soil/rock formation and aquifers. Polluted groundwater needs intensive purification, or may never be suitable for drinking. It may also affect the soil ecology and/or other water compartments such as lakes and rivers. Groundwater sources are frequently contaminated with pesticides and fertilizers, and sometimes with heavy metals or halogenated compounds. Landfill leakage, agriculture, and chemical accidents are the main sources of groundwater pollutants.

Traditional filtering techniques used in drinking water production and for the treatment of wastewater may not remove micropollutants such as pesticides and pharmaceuticals and they are not able to desalinate seawater. As groundwater becomes more and more polluted and as industrial wastewater increasingly loads the environment with toxic substances, nanotreatments may, in future, become necessary in Europe and their usage should soon be encouraged in developing countries.

Reactive iron barriers can be installed based on iron grains of nanometer size. When the polluted groundwater permeates this barrier in the ground, the iron particles are oxidized which results in reducing the contaminants into harmless immobile products that afterwards can be easily removed.

16.1 Nanotechnology Opportunities

Filtration on the nanoscale using novel innovative nanotechnologies offers great benefits. The new generation of grafted nanomembranes has an extraordinary high permeability due to their high surface areas and thus a strongly improved throughput. They are energy efficient in operation and have antibacterial properties. In addition, these new membranes are thermally stable and have excellent mechanical properties so guaranteeing long lifetime with minimal maintenance.

Innovative solutions such as nanopurification will help secure the supply of clear, transparent, and tasteful drinking water, which needs to be free from biological contaminants, and free from micropollutants including heavy metals, organic and inorganic substances, fertilizers or run-off from farms, hormone-containing chemicals, cosmetic products, pharmaceuticals, and industrial pollutants and suspended impurities.

In many industrial countries, soil is often contaminated with organic substances, carcinogens, or heavy metals. Conventional techniques are not very successful at remediation of this pollution and are extremely expensive; therefore, new methods with nano-based techniques may offer notable advantages.

Nanotechnology can produce adsorbents with very high surface areas and tunable adsorptive properties. Nanoscale photocatalysis can be applied for degrading environmental pollutants, filtering out solid contaminants, and in the desalination and softening of water.

Fig. 16.1 There are two categories of nanomembranes (see text)

16.2 Nanofiltration and Membrane Processes

Nanomembranes can be subdivided into two categories (Fig. 16.1): nanostructured membranes, where the term "nano" refers to the internal pore structure of the membrane; and nano-enhanced membranes where membranes are functionalized with discrete nanoparticles or nanotubes and are used to reject suspended particles.

Membrane-filtration processes are classified according to the membrane pore sizes, which dictate the size of the particles they are able to remove. In the case of nanomembranes, the filtration range for particle/molecule filtration is between 1 and 100 nm. Such particles include viruses, bacteria, pesticides, pharmaceuticals, and heavy metals. In addition, this is also an ideal technique for the removal of pigments and coloring matter from water and for desalination and softening.

The membranes are made from materials such as thin organic polymer films, metals, or ceramics, depending on the application. They are manufactured in different forms such as hollow fibers or flat sheets, which are incorporated into housing modules optimized for the most efficient separation conditions. This technique gives improvements of separation properties in terms of efficiency, retention, permeability, and chemical and mechanical stability, compared to conventional techniques. There are several possible nanomaterials and methods for the functionalization of membranes. The most frequently used nanoparticles are titanium dioxide (TiO_2), silver, and CNT. In the case of thin film composites, nanoparticles can be integrated in the polyamide top layer of the membrane or applied on the surface of the membrane material. Surface deposition of nanoparticles can be carried out by vapor deposition, electrophoretic coating, or dip coating.

A number of pollutants can be removed in one single filtration step using these technologies. Figure 16.2 shows a plastic filter membrane with tiny pores measuring around 20 nm and Fig. 16.3 shows a nanomembrane system that can trap harmful viruses, bacteria, and germs. Such extremely fine filtration techniques can be harnessed to microbiologically clean drinking water, process water, wastewater, and seawater.

16.3 Nanostructured Ceramic Membranes

Nanoceramic filters offer new possibilities in the treatment of drinking water. They are very expensive to manufacture but have a high efficiency. Purification procedures with a high throughput can be executed under high pressure conditions, which is not the case for polymer membranes that are more easily damaged.

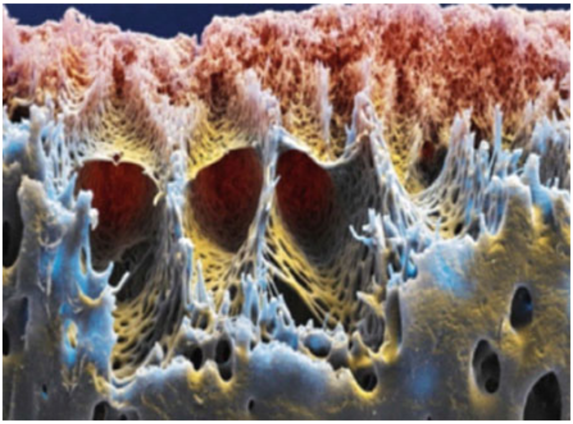


Fig. 16.2 Plastic membrane with nanoscale pores for water purification. Image courtesy of BASF SA, Ludwigshafen

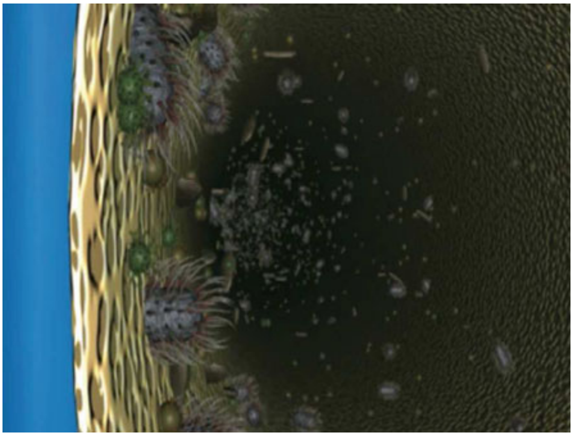


Fig. 16.3 Nanopores within the membrane are able to successfully trap bacteria, viruses, and germs successfully out. Image courtesy of BASF SA, Ludwigshafen

Nanoparticles can be used for the preparation of a new generation of ceramic membranes, giving excellent control of the distribution of the pore sizes, which result in membranes with a selective separation ability (Fig. 16.4). Ceramic membranes have the advantage of being resistant to mechanical forces, chemicals, and temperature (so they can be sterilized), but are significantly more expensive to manufacture. The membranes generally have a lifetime of about 10 years depending on their application. Their mechanical, thermal, and chemical properties are crucial to ensure the stability of the membrane under pressure and to allow for cleaning and regeneration.

A conservative water industry might be reluctant to instigate the use of novel nanotechnologies, owing to higher costs and ongoing debates about health and safety concerns where toxicity studies have proved inconclusive. The integration of such systems will have to be driven by the introduction of new legislation and the demand for higher quality standards and cost efficiency.

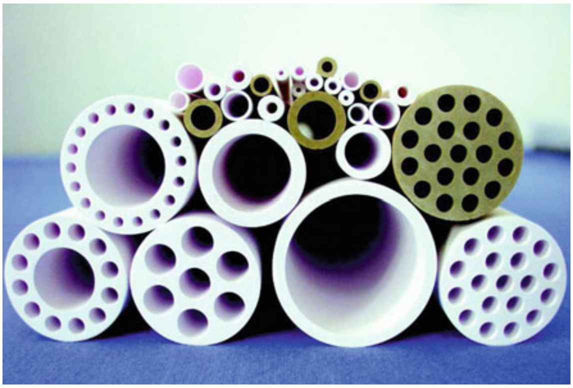


Fig. 16.4 Ceramic membrane modules. *Source* EU FP7 Project CeraWater, http://www.cerawater.eu

16.4 Photocatalysis: Organic/Inorganic Hybrid Membranes

Photocatalysis is a promising technique for the treatment of contaminated water, with the possibility of providing a step-change breakthrough. The principle of photocatalysis is very simple, with a catalyst harnessing radiation from sunlight or an artificial source and using the energy to break down contaminant substances. Polymers with nano-TiO_2 adsorbed or coated can exploit photocatalytic disinfection to kill bacteria and microorganisms, and break down organic pollutants such as herbicides and pesticides. The nanoscale activity also prevents biofouling and pollution of the membranes themselves, and thereby extends their operating lifetime.

Modification of the TiO_2 with noble metals such as gold can give it improved activity for a variety of catalytic processes. Silver can provide antimicrobial properties, metal oxides such as alumina and zirconia can remove chlorinated solvents, and carbon nanotubes (CNT) can remove various metal contaminants.

16.5 Adsorption Mechanism

Nanosorbants remove contaminants such as arsenic from drinking water. The surface properties of nanoparticles have a very selective adsorption spectrum, so particular impurities will be adsorbed while neutral or beneficial substances will not. Use is often made of nanoparticles with magnetic properties in order to separate phases after the adsorption process. Various carbon-based materials, metal oxides, and nanoclays are under investigation to tackle a variety of low concentration contaminants.

Remediation of groundwater following pollution incidents can be undertaken by a range of nanosorbents, depending on the compound to be targeted: nanoscale iron can be used for heavy metals and nanoclays target organic compounds. Nano iron oxides can remove pharmaceuticals from wastewater and drinking water.

Much attention is given to the removal of arsenic from water by making use of metal oxides embedded in a polymer matrix. Arsenic is carcinogenic on exposure for long times and at high concentrations. Chrome, nickel, mercury, and cadmium are also potential targets for removal by an adsorbing system. Palladium, rhodium, and platinum, widely used as catalysts, can find their way into effluent water streams in which precious metals are soluble. In this case, it is important to recover and reuse these valuable metals.

A particular advantage of nanotreatments is that different pollutants can be removed in one filtration step. The use of chemicals is minimal. In addition, in wastewater treatment, filtration methods are ideal for plants with space restrictions since the filtration elements are relatively small thanks to their modular structure.

16.6 Nanosensors in Water Analysis

The increasing constraints on water supply have led to the implementation of recycling plants for both potable water and industrial applications, thus increasing the demand for low-cost and rapid contaminant detection technologies. Nanotechnology and nanoparticles are an important element in the development of new sensors which can be used in controlling the treatment of drinking water and in the monitoring of water quality. Miniaturized multiarray sensors will provide real-time online monitoring of biocontamination. The current demand from water utilities is particularly in the detection of viruses, micropollutants and bacteriological indicators, and detection of membrane fouling.

By specifying and adjusting the specific functioning of the nanoparticles it is possible to make sensors that can detect biological structures such as proteins, nucleic acids, and viruses. Nanoparticles have potential to be used for the quantitative analysis of heavy metals present in only a few parts per billion.

By using easily detectable nanoparticles in the disinfection streams of water, "on-line" monitoring of the membrane-filtration and adsorption system efficiency and integrity is possible. The ability to detect leaks and thus to assure the integrity of the membranes and/or the absorbers is of great importance in assuring that there is no drop in water quality because of undetected damage to the membrane or absorber.

16.7 Removal of Nanoparticles Used in the Purification Process

There are no concerns regarding the environmental impact of nanostructured membranes, with nanosized structures like pores but without integrated nanoparticles; indeed nanomembranes can used for the removal of nanoparticles. By contrast, all materials in contact with water that are functionalized with nanoparticles (including nano-enhanced membranes) must be subject to leaching tests and strict regulation.

It should be assured that no particles are released and that they are nontoxic during production as well as during handling and use.

Experience of the removal of nanoparticles after water treatment shows that the removal efficiency is highly dependent on water characteristics such as pH, the presence of natural organic matter, and salt concentration. The removal of free nanoparticles from the purification process can be achieved by special sand filtration techniques or coagulation, where the nanoparticles are destabilized via polymers and agglomerate into larger flocculent particles that are easy to eliminate. Titanium dioxide, the most common photocatalyst, is for example inert when used in bulk form, and nanoscale TiO_2 is also expected to have little negative impact, since it is usually immobilized in or on a substrate material. From silver-enhanced membranes, silver can be washed out in ionic form; however, silver nanoparticles very quickly change to silver sulfide that has low water solubility and no antimicrobial activity in wastewater-treatment facilities. They also bind to other solid particles and are transported away. The wastewater system acts as a multibarrier system and toxic release of particles can therefore be effectively dismissed.

Nanosorbents in the form of free nanosized objects present environmental and human health concerns, and should be carefully selected and studied in order to comply with stringent water regulations. No metals with known toxicity should be used, but rather compounds already applied in water treatment like iron, titanium, and carbon.

16.8 Conclusion

In Europe, great efforts are being given to extend and upgrade the sewage water treatment processes to reduce micropollutants, chemical residues, and pharmaceuticals. Nanotechnology has great potential for the purification of drinking water: nanomaterials can be used to control pollution and detect toxins, bacteria, and other contaminants in water. They are also efficient in removing water-soluble drugs or carcinogenic contaminants which cannot be separated by activated carbon. There are few active applications at present owing to technical challenges, complex risk assessment processes, and high costs.

Nanopurification techniques will find a place on the market unless photocatalytic systems prove to be cheaper or yield a significant improvement in water quality. Nanotechnologies have the potential to be extremely beneficial for future water purification needs in Europe. The introduction of nanotechnologies in water purification is currently hampered by the need for new and costly infrastructure and new maintenance expertise.

Unintentional release of nanoparticles causes concern; however, nanoparticles used in drinking water production can be easily removed, at the final stage of the purification process, to prevent toxic side-effects from their use. In any case, if the nanoparticles are immobilized in membranes or ion-exchangers the chance that nanoparticles leach into the water stream is very small.

Part V
Nanotechnology for Environmental Engineering

Conclusion

Nanotechnology will not be able to solve all the problems faced by humanity in the coming decades, but it can potentially offer solutions in a number of the challenges being faced.

Nanotechnology can help in maintaining and restoring the quality of the environment whether this be for air, water, or soil. Preventing pollution is a great concern but remediation of polluted natural media is also of tremendous importance. We summarize, in Fig. V.1, some of the applications of nanoparticles to purify the environment.

Nanotechnology can have application in fields as diverse as carbon capture and storage, fuel and energy efficiency, and purification methods to improve drinking water quality. Nanotechnologies can help in having more efficient product life cycles to reduce waste. All of these contribute to a sustainable economy for the future.

One of the great challenges today is the global warming phenomenon; nanotechnology may contribute to minimize this effect. A key focus is to reduce exhaust gases such as CO_2 in automobile exhausts, and nanotechnology can help here in various ways. New construction materials, especially nanocomposite materials, will drastically reduce the weight of vehicles, so reducing energy consumption and thus reducing the CO_2 emissions.

Care must be taken that unintentional release of nanoparticles from any material used in, for example, water purification, do not occur. However, the benefits and

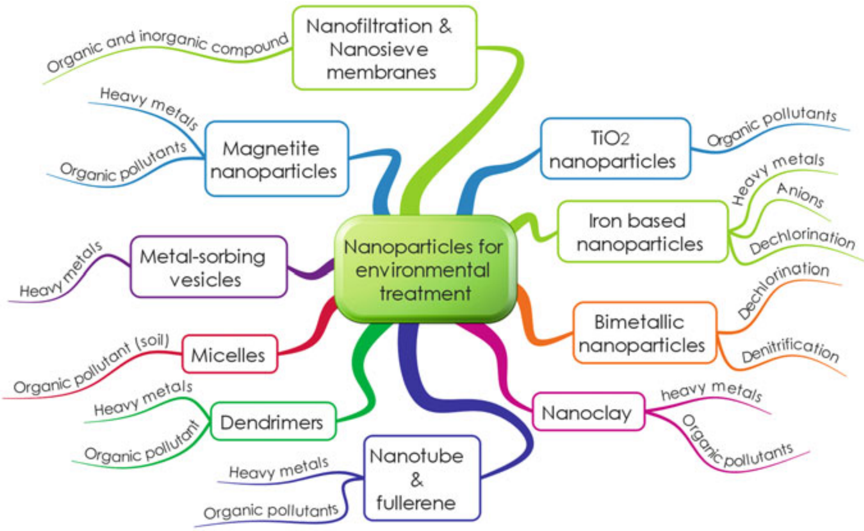


Fig. V.1 Overview of environmental treatments using nanoparticles. Fig. V.1 is built from the results obtained by G. A. Mansoori, T. Rohani.Bastami, A. Ahmadpour, and Z. Eshaghi, AnnualReview of nano Reseach, Vol. 2, Chap. 2, 2008

risks of nanotechnologies must be properly understood; not all nanotechnologies will be toxic, and some will only have benefits for health and the environment. Carbon monoxide is a deadly poison but the smallest computer circuit is made from 500 carbon monoxide molecules! This exemplifies the application of nanotechnology, where appropriate use of materials is safe and justified.

Part VI
Nanotechnology and Daily Life

Introduction

Nanotechnology will not only find application in high-technology industry, manufacturing processes, and novel medicines. It is already to be found in consumer products such as sunscreens and other cosmetics. Some of the high-value markets for nanotechnology in the future will be in day-to-day applications such as clothing and household products. Nanotechnology will provide great benefits in food, textiles, and cleaning, making life more efficient and comfortable. It will improve the sustainability of our modern lifestyle through the use of fewer resources, consumption of less energy, and the reduction of emissions from our homes and from the manufacture of consumer products.

Nanotechnology will arrive in mass-produced goods, resulting in large markets from which consumers will profit enormously. It will be present in all domains of activity, from textiles to paints, and from electronics to cosmetics. Nanotechnology will become increasingly integrated in new materials and new applications. At present, nanotechnology is present as nanomaterials in cosmetics, sports, textiles, electronics and informatics, and self-cleaning white goods. The future will be in medical sciences with advanced diagnostics, in energy with high-performance solar cells, and in the environment with water purification technologies. Following the estimates of the OECD, the global nanomarket in 2015 may reach a figure of trillion dollars.

At present, the use of nanotechnology by industry is subject to confidentiality and proprietary restrictions, and the scope of its industrialization is difficult to measure. As long as the public is not fully accepting of the applications of nanotechnology in consumer products, large-scale marketing will have to wait. Nanoscientists are conscientious of the toxicological risks and many studies are undertaken to understand the interaction between nanoparticles and human health; however, this research has still much to do. We know that some materials can have inflammatory and even toxic responses under certain conditions, while others appear benign.

A rapid growth in the use of nanotechnologies must be accompanied by rigorous safety and toxicity guidelines. Natural nanoparticles permeate our environment, but the effects of artificial nanoparticles, whether released deliberately or accidentally into the environment, must be evaluated if their use is to enjoy full public acceptance.

One must take into account that many products used today are potentially dangerous, but their use is accepted because precautions necessary to use them safely have been taken. For example, gasoline is a toxic product, volatile and easily inflammable, containing dangerous additives such as benzene. Despite this nobody hesitates to fill their car at a petrol station. The use of nanotechnologies is not more dangerous; it is a question of using them responsibly with all necessary precautions. This is also valid for nuclear power and genetic manipulations.

Chapter 17
Products for the Home of the Future

The nanotechnologies of the future will find applications in daily life, and the house of the future will contain numerous examples in different areas of application (Fig. 17.1).

Cleaning products, health and personal care, energy efficiency, and clothing will all be improved by new advances in nanotechnology.

17.1 Household Innovation

Nanoparticles are used for their functionality as additives in many household products or substances. They can provide abrasion resistance, anti-condensation properties, self-cleaning behavior, and corrosion protection. In the home, many innovations are possible where new nanomaterials and nanotechnologies can play a role ranging from an improvement in the efficiency of laundry processes by using new formulations or catalysts, to the implementation of activated surfaces in paints, or wall decorations to combat odors generated by cooking or household waste.

17.1.1 Cleaning and Cleanliness

Nanoparticles can be applied to form a very thin "self-cleaning" film on household surfaces which protects from dust or grease accumulation, corrosion attack, and the deposition of scale. Such nanofilms are safe for skin contact. Areas of application range from computer equipment to kitchen surfaces to shower screens. In wet bathroom areas, the films can prevent misting over from steam. Such self-cleaning surfaces will reduce the amount of detergents used and time spent on cleaning: possibly even removing the need for cleaning by making use of multifunctional and unique properties.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_17,

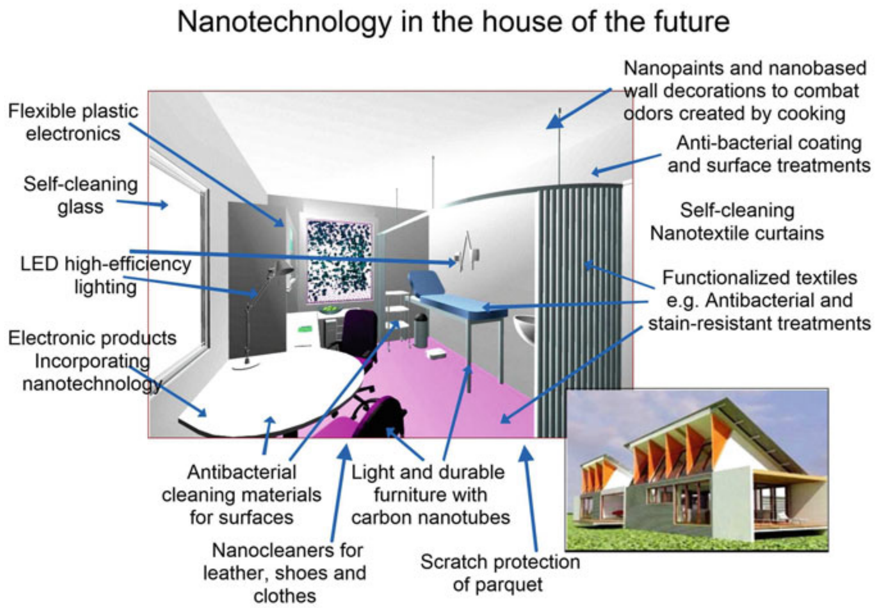


Fig. 17.1 Nanotechnology in the house of the future. Image courtesy of IoN, UK

Fig. 17.2 Application of nanotechnology-based paints. Image courtesy of IoN Bioni company (D) and Fraunhofer Chemical technology Institute (D)

Nanoparticles can provide very effective cleaning through a range of mechanisms, for more environmentally friendly degreasers for ovens and cookers, to gentle cleaning for jewelry and decorative metalwork, to cleaners for leather, shoes, and clothes. The use of silver in nanoparticle form can provide antibacterial properties to internal surfaces of refrigerators and microwave ovens. Nanoencapsulation of fragrance can provide freshening of clothes through slow release in wardrobes, as well as in personal hygiene products and laundry detergents.

Nanofiller combinations have been developed which, when used in interior and exterior paints, permanently prevent the formation of mould, bacteria, and algae. These new coatings neither negatively affect the health of the residents nor pose a threat to the environment (Fig. 17.2).

The coatings use a combination of nanoparticle zinc that acts as a photocatalyst, and nanoparticle titanium dioxide. Together in the presence of light and water

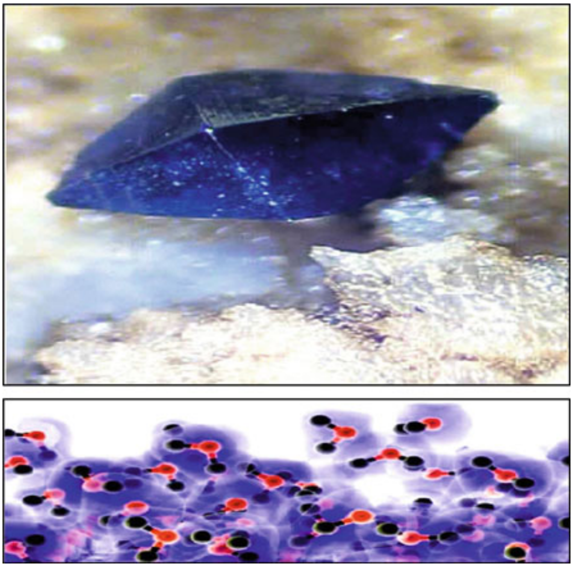


Fig. 17.3 Importance of antimicrobial coatings. Image courtesy of Ion, UK. Image EcoActive Surfaces Inc—OxititanTM coating manufactured by EcoActive Surfaces Inc of Florida

vapor, two highly reactive substances: hydroxyl radicals (OH) and an oxide anion (O_2^- or 'singlet oxygen') are produced. They act as extremely powerful microbial killing agents by damaging critical molecular structures resulting in the death of the microorganism (Fig. 17.3).

Even a new and shiny parquet floor can become lusterless very quickly because of the accumulation of dust and scratches. Nanoparticle coatings can improve the scratch and wear resistance considerably. A binder mixed with hard nanoparticles is applied, and UV light hardens the varnish within seconds. Thereby the nanoparticles get connected tightly with the binder via linker molecules, leading to a tough coating that, owing to its nanoscale properties is transparent.

A self-healing effect can be achieved by embedding liquid filled capsules or layers of active healing agents that rupture when a scratched, to release agents into damaged areas of coatings or paints. As well as internal domestic uses, the paint can be applied to car chassis, bumpers, door mirrors, and so on (Fig. 17.4).

These self-repairing materials will have great advantages across the domestic and transport industries, lengthening product lifetimes, improving weathering resistance, increasing safety, and lowering product costs by reducing maintenance requirements.

A cleaner environment is one way in which nanotechnologies benefit health. They can also develop new and unique solutions for personal healthcare.

17.1.2 An Energy-Efficient Home

Nanotechnologies enable cost-competitive, sustainable, and effective energy generation and storage in the home environment. Superior photovoltaics will be developed

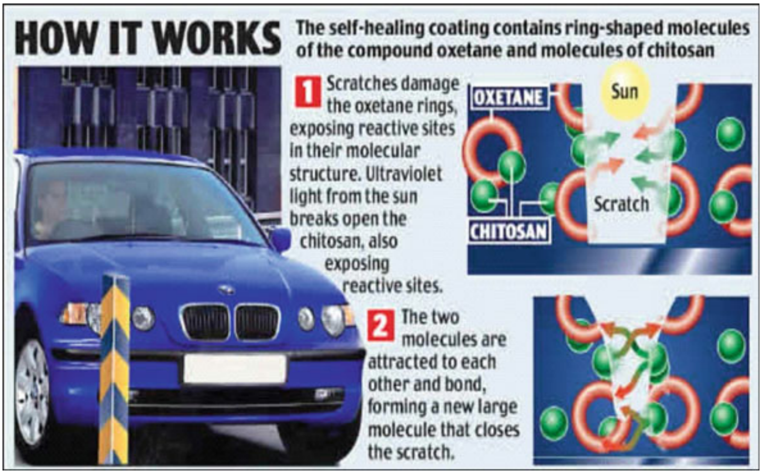


Fig. 17.4 Self-healing application of nanocoating for automotive parts. Image courtesy of IoN, UK

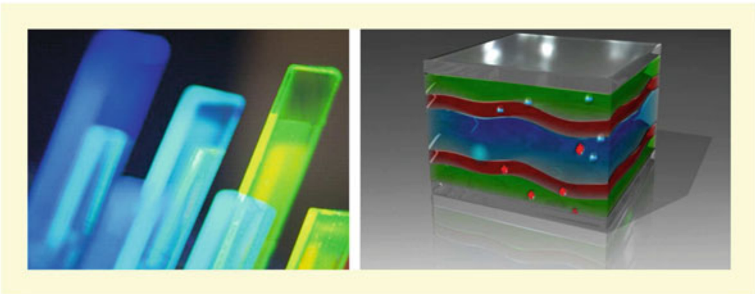


Fig. 17.5 Some layouts of light-emitting diodes. Images courtesy of BASF, Ludwigshafen

for application to surfaces in houses using silicon and conjugated polymer alternatives combined to form new solar panels. Superior domestic batteries and fuel cells will be available. For example, lithium batteries for energy storage using nanostructured electrode materials: mesoporous carbon electrodes or electronically conducting polymer electrodes fabricated to have the required properties by nanotechnology.

Nanotechnology brings benefits to the lighting and electronics industries: organic light-emitting diodes (OLEDs) with nanometer thin semiconductor layers allow tailor-made physical properties, most notably in the color of the light emitted. The thickness of the organic semiconducting layers determines the efficiency of the OLED with the optimum being 20–30 nanometers.

OLEDs' increased energy efficiency will dramatically reduce the electricity bill for home lighting. They also enable new properties such as area light sources and transparent light sources: they open up a new range of design possibilities for lighting applications. Figure 17.5 shows layouts of light-emitting diodes.

In order to reduce energy use and to create eco-efficient products that are attractive to consumers, breakthroughs are required in building materials, such as high-performance insulating materials made from aerogel nanofoams. Photochromic films and coatings for glass can help to optimize internal temperature and reduce heating or cooling bills. Other developments of new materials to improve the eco-efficiency of the home include: functional textiles for lightweight nanoporous construction materials, self-healing and self-cleaning inorganic and composite nanocoatings, and innovative cement compositions based on industrial scrap and recycled materials.

Active systems can assure pleasant and cost-effective indoor air quality in buildings and can bring health benefits such as detoxification by products that use nanoscale catalysts to decompose substances such as tobacco smoke and volatile organic compounds. The increase in comfort and convenience brought about by new nanoproducts for the home environment will have significant impact on creating a "healthy home."

17.1.3 Sport and Nanotechnology

Nanotechnology is increasingly present in sport applications providing high-end sporting equipment. For example, composite materials that include carbon nanotubes (CNTs) provide 20 times higher tensile strength compared to carbon fibers composites. In addition, professional athletics are protected from medical accidents (see Fig. 17.6 showing a control device for cardiac accidents).

17.2 Personal Hygiene

Nanotechnologies will have great benefits in advanced medical treatments and new drugs. They will also be used in everyday healthcare products in the home. One example is new toothpastes with unique functionality. In sensitive teeth, the gums pull back and expose the dentine below the enamel cap of the tooth. This causes pain because the microscopic dentinal tubules convey unaccustomed stimuli such as heat, cold, or contact through the inner parts of the teeth to the dental nerves.

This natural tooth dentine can be protected by nanoscale calcium phosphate. This nanotechnological substance in a dental cream formulation cleans the teeth thoroughly while simultaneously depositing a bio-analogous layer on the surface to form a protective film on the tooth neck and seal the dentinal tubules, so they no longer convey stimuli to the nerves. The artificial film effectively undergoes the same processes of formation and wear as the natural surface of the tooth. Also, because of the nanosize of the particles, they can penetrate into the thin tubules and deposit there, so insulating the nerves beneath. This new nanodental cream has superior properties and behavior to the most sensitive toothpastes on the market. Mechanisms in healing tooth problems are shown in Fig. 17.7.

Fig. 17.6 Necklace for long-term and robust cardiac monitoring in sports life. Image courtesy Holst Centre (Netherlands)

The light-absorbing properties of tiny gold particles can be applied in home pregnancy testing. Nanoscale gold particles are bound to antibodies, which specifically bind to the hormone hCG, that indicates pregnancy at a very early stage. The particles are transported by capillary forces to control windows on a tester and lead to formation of a colored line.

Nanotechnologies also find extensive use in cosmetics, as covered in the following chapter.

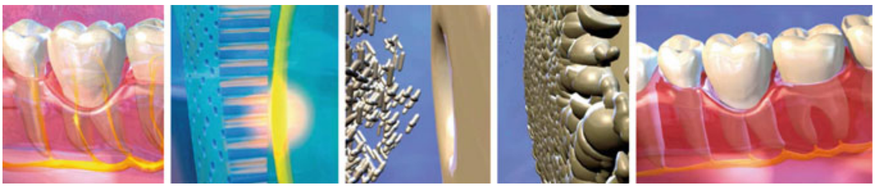


Fig. 17.7 Mechanism in healing tooth problems. Image courtesy of GSK, Düsseldorf

17.2.1 *Nanotechnology and Textiles*

Silver reacts with atmospheric oxygen to produce silver ions which are toxic to bacteria. As bacteria are the main cause of body odors, this effect is now being used in many textiles such as socks, underwear, sports clothes, bed linen, and seams in shoes. In such cases, the textiles are covered or impregnated with nanosilver layers. There is, however, some causes for concern as washing such nanosilver-treated textiles releases silver in the wastewater, and it is still uncertain how this may accumulate in the environment and effect ecosystems.

17.3 Healthcare

Healthcare has already been discussed in part IV, Chaps. 11 and 12. We shall just briefly recall here a few items and introduce some new subjects. A typical example is the protection from cardiac incidents during daily working conditions or at home (Fig. 17.8).

17.3.1 *Vaccination and Drug Delivery*

Nanocarriers can be used as a tool for skin delivery of pharmaceuticals.

This has not yet been fully explored, although there is great interest from the pharmaceutical industry. In the next decade major breakthroughs can be envisaged, and the most important one is the replacement of conventional injections by direct transfer through the skin or through the hair follicles. This is "vaccination without a syringe."

The delivery of vaccines across the skin can be achieved using nanoparticulate carriers, delivered through an area of skin the size of a postage stamp. Nowadays, most vaccines are delivered by injection. However, there is an urgent need for noninvasive delivery routes: the number of vaccines is increasing, and in pediatric vaccination programs only limited injections per year are permitted. This technique avoids pain and bleeding, and removes the risks of infection.

Targeted delivery of nanoparticles can be used to stimulate immune response using proteins (generally known as biologics) that cannot be administered orally. Nanoparticulate carriers also protect these drugs during administration. DNA can also be delivered in such a way across the skin, for vaccination purposes, and for the treatment of skin diseases (including hereditary conditions).

One novel drug delivery system is the microneedle array. Such arrays pierce very small conduits in the skin, thereby facilitating the transport of especially high-molecular weight drugs across the skin. Microneedles are very short and therefore do not reach the nerves located in the deeper layers in the skin that signal pain. One of

Fig. 17.8 Necklace for long-term and robust cardiac monitoring in daily life. Image courtesy of Holst Centre (Netherlands)

the most elegant delivery systems will be a combined approach of microneedles and nanoparticulate carriers. Microneedles facilitate the transport across the skin, while nanocarriers will be used to protect the drug against degradation and to facilitate uptake in the target cells.

It is expected that skin delivery treatments will, in the future, be easily applied at home.

17.3.2 Sunscreens and Skin Protection

The role of a sunscreen is to prevent ultraviolet (UV) light from the sun from penetrating the skin and causing damage such as sunburns, prematurely aging of the skin or the origin of skin cancer (Fig. 17.9). UV filter substances perform many different functions: They reduce the amount of UV light penetrating into the skin by reflecting

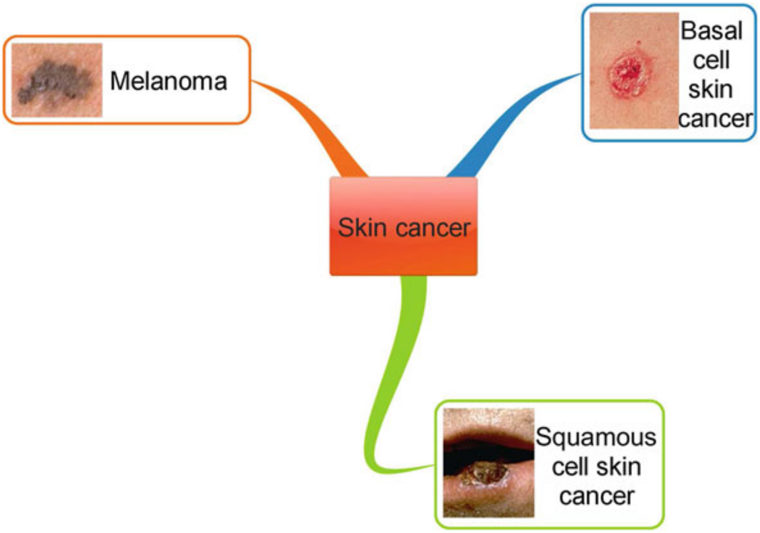


Fig. 17.9 Three main families of skin cancer. Images are from www.skincancer.org

or dispersing it, or converting it into harmless heat. Usually, several different filters are now combined in one sunscreen product to filter out the entire spectrum of UV radiation from sunlight.

Skin cancer

Different cells of the skin can become malignant. Skin cancers can be classified in three main families depending on the nature of the cells involved (Fig. 17.9). Basal cell skin cancer is the most common type of skin cancer. It can be triggered by a too large sun exposure without protection. People with fair skin are especially vulnerable. Squamous cell skin cancer begins in squamous cells. People with dark skin can develop it on the parts of the skin protected from sun exposure (legs or feet) but people with fair skin can also develop it in exposed parts (head, face, ears, and neck). Melanoma is the most dangerous skin cancer. It starts in the melanocytes which are pigment cells. Skin cancer cells can spread over the body (metastasis) through the blood vessels and/or the lymph vessels. Basal cell skin cancer rarely spreads. Squamous cell skin cancer spreads sometimes but melanoma has a much greater probability to spread.

A necessary feature of a UV filter substance is that the molecules must absorb the energy without reacting with other molecules or being destroyed, which would make them ineffective very quickly. Substances have been developed where, when UV radiation is absorbed, there is a change in the arrangement of atoms inside the molecule. The atoms then return to their original positions, and a tiny amount of heat

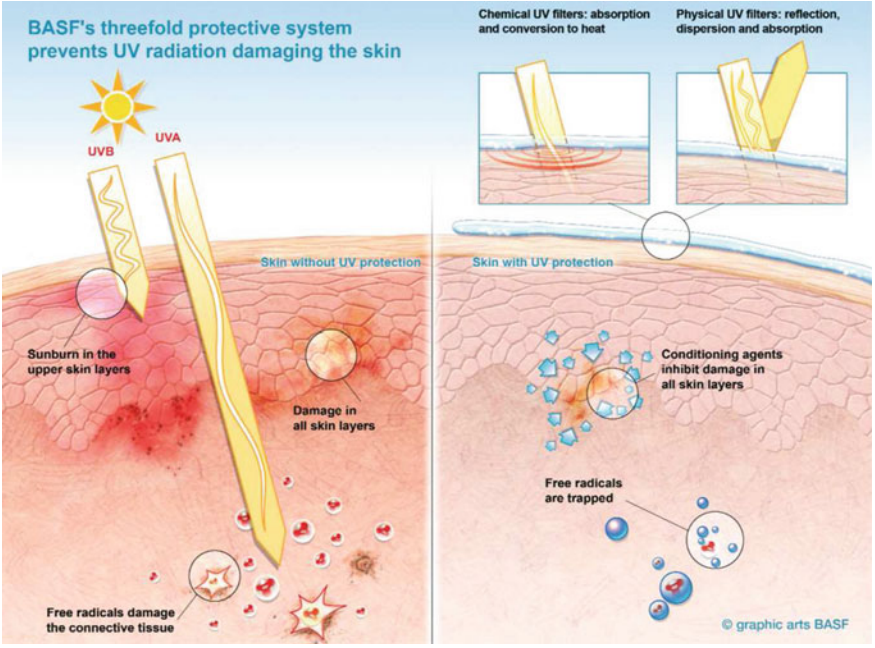


Fig. 17.10 New generation of UV filters provide reliable all-round protection for the whole day-protecting and caring for the skin. Image courtesy of BASF, Ludwigshafen

is released. This "photo-stable filter" mechanism ensures effective and long-lasting protection.

Physical UV filters are based on microfine particles of titanium dioxide or zinc oxide. Incident UV radiation is not only reflected, but also dispersed and absorbed by them. Since these particles are white, they can cause an undesired whitening effect on the skin at high concentrations. This is prevented by reducing the size of the pigment particles to about 200 nm which makes them transparent on the skin. Physical UV filters are used mainly in sunscreens with high sun protection factors (above 25). They are also suitable for the sensitive skin of children and people with allergies. The new generation of UV filters provides a better and longer lasting protection than in the past (Fig. 17.10).

It is worth noting that even half-shade sun exposure needs protection (Fig. 17.11). Similarly, UV radiation from sun can pass through fabric. For example a white T-shirt which is wet, because you have taken it for a swim, has smaller UV protection than a dry T-shirt. You can be burned by UV radiation without warning since you do not feel the heat from infrared radiation because the clothing is wet.

Fig. 17.11 Even in the half-shade, we are exposed to UV rays. The UV filter absorbs the remaining radiation and converts it into harmless heat. Image courtesy of BASF, Ludwigshafen

17.3.3 Nanoatomizer

The use of cosmetics has an important psychological impact and helps keep people healthy. One of the main aims of beauty products is to have simple application and maintain skin that is hydrated and supple for the entire day; this condition will keep make-up intact. Devices that provide a spray of hydrating mist are already available, but have to be used repeatedly throughout the day. Using ultrasonic vibrators, a mist of tiny nanosized droplets can be made that will penetrate make-up layers and the skin below, ensuring hydration for the entire day with a single application in the morning. This process will also keep the make-ups in perfect conditions: a fine homogeneous look, stable color, resistant to hand and/or other touching. The device will, in future, be a revolutionary consumer product in the field of cosmetics. This “Mobil beauty nanodevice” will not have to be carried in the pocket during the day.

17.4 Nanofoodstuffs

Food is a nanocomposite material containing many different components including proteins, polysaccharides, fats, water, vitamins, antioxidants, microorganisms, colorants, and salt; see Fig. 17.12. All foods, whether natural or processed, contain nanoparticles. For example, milk contains caseins, a globular nanoscale protein, and meat is made up of protein filaments that are much thinner than 100 nm. These structures and how they are changed by processing and cooking affect the texture and properties of the food. Examples of products that contain nanoparticles resulting from manufacturing processes include margarines, chocolate, and cheese. For example, toffee is made up of fat droplets surrounded by a thin nanoscale protein membrane in a matrix of sugar containing milk protein. The stability of the interface is important as it controls the fat droplet size and hence the sensory properties, such as texture and creaminess. Understanding how the properties of food change with the size of the constituents, and the manufacturing of foods with controlled size and structure, should allow improvements to properties that are of benefit to the consumer.

Food nutrients

There are essentially six nutrients in food: carbohydrates, lipids, proteins, vitamins, minerals and water (Fig. 17.12). Carbohydrates are a family of organic compounds that are the most important source of energy for the body. They can be simple or complex with a few examples indicated in Fig. 17.12. Simple carbohydrates, such as sugar, provide energy quickly while complex carbohydrates, such as rice, provide energy on a longer time scale. Lipids, or fats, provide insulation for the body. In addition to providing fatty acids necessary for life, fat food has also often vitamins. Fats can be saturated or unsaturated. Saturated fats can induce heart diseases and increase the level of cholesterol in the blood. Unsaturated fats, found for example in olive or sunflower oils, are better for health. Proteins are essential in the development of muscle tissues, to make hair, skin, blood cells, bones, antibodies, etc. They are found in animal and plant foods. Vitamins are complex organic compounds necessary for human metabolism and for the organs to function properly. Vitamins in variable concentrations, usually small amount, are present in most foods. There are two families of vitamins: fat soluble and water-soluble vitamins. An excess of water soluble vitamins is removed in urine while an excess of fat soluble vitamins can reach toxic concentrations in the body. Minerals are also essentials to many bodily functions. Major minerals such as sodium or calcium, for example, are to be found small amounts while trace minerals exist in extremely small concentrations. A delicate balance of concentration between the different minerals is needed. An excess of one mineral may have negative effects on the others. Water is of course needed for life. We can live a few weeks without food but only a few days without water. Water is present in many foods.

17.4.1 Food and Nanotechnology

The various constituents of foodstuffs are schematically represented in Fig. 17.13 and lead to all possible foodstuff compositions.

Some food additives are naturally structured at the nanoscale. For example, the permitted additive silicon dioxide can be used in nanosize particles; in tomato ketchups in order to reduce thickening in kitchen-salt to prevent clumping and to absorb humidity; and to prevent meat or sausage parts sticking together.

Using nanoparticles can have real health benefits. There is a strong drive from governments to lower the amount of salt in the diet as the current intake is considered too high and dangerous for the health. It has been shown that smaller salt particles provide a more intense flavor than standard size table salt. This is due to the increase in surface area giving a change in properties. By using smaller, and potentially nanosized salt particles, the level of salt in products such as crisps and snacks could

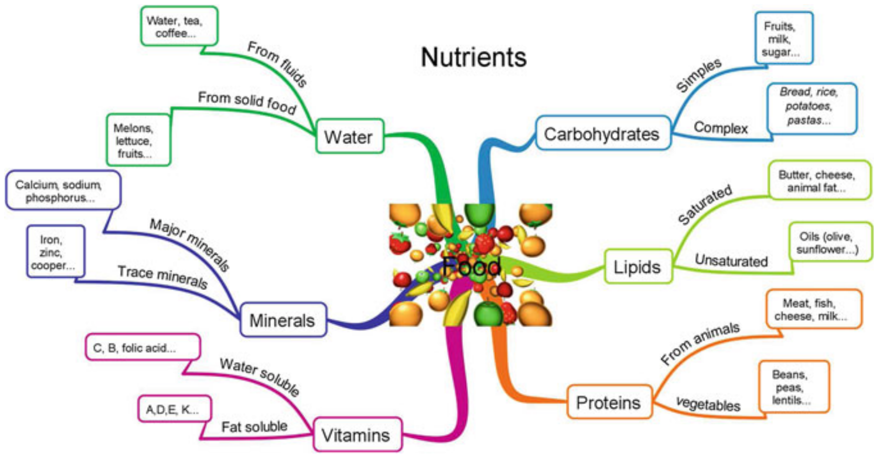


Fig. 17.12 Different families of nutrient which can be found in food and some examples of food containing them

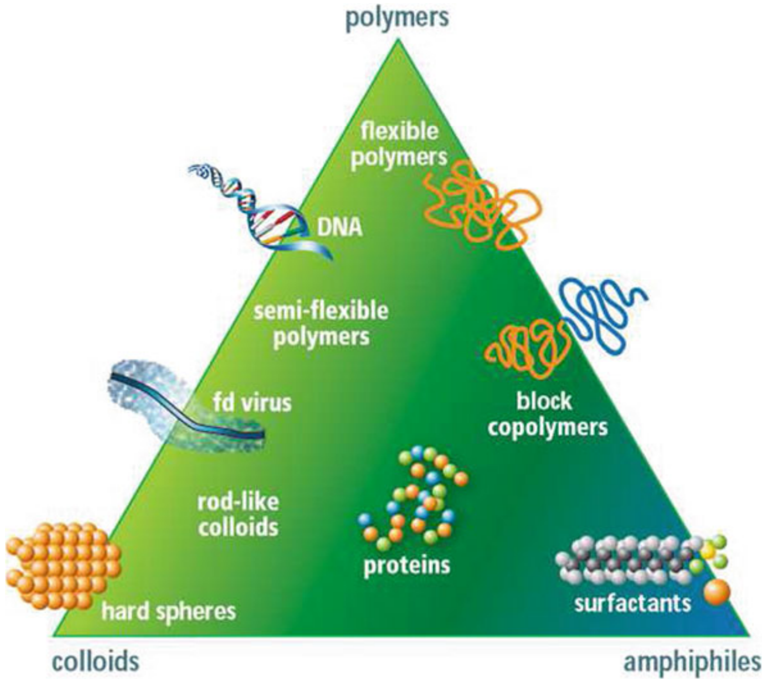


Fig. 17.13 Base elements for food constructions. From G. Gompper, J.K.G. Dhont, D. Richter, The European Physical Journal E: Soft Matter and Biological Physics, Volume 26, Numbers 1-2, 10328-1, 2008

be reduced, giving a healthier product. Silica nanoparticles can be used to make chocolate slimming shakes, where the silica nanoparticles are coated with cocoa to give a creamy chocolate taste with reduced fat content. Using technology to put nanosized water droplets inside fat droplets can produce mayonnaise that is much lower in fat but is indistinguishable in taste from the high fat product.

Vitamins, enzymes, and flavorings can be packed in nanocapsules of 5–100 nm size. These can mask unpleasant flavors or smells, while still delivering full nutritional.

During recent years, consumer skepticism has developed for the application of nanotechnologies in foodstuffs. However, the application of nanotechnologies to standard ingredients such as salt, fat, and biopolymers to produce foods with improved properties should not pose any danger as it is thought that they will be broken down in the body in the usual way. This needs to be emphasized to the media and consumers, so that the development of new foods benefiting from nanotechnologies can proceed. Inorganic nanoparticles that could be a risk include silver, titanium, and silica, and the main concern is that these are not normally eaten and metabolized. Thus, it is certainly sensible for the food and drink industry to look at the use and safety of these inorganic nanoparticles. The use of silica nanoparticles in diet products has raised the question as to whether and how these products should be regulated. Without careful communication and research, the future vision for nanofoodstuffs will not be realized.

17.4.2 Packaging

Nanotechnology can also have an impact on the materials used to package food and drink (Fig. 17.14). Here, the situation is quite different as there is not necessary direct contact with the food, and so little risk of human consumption. Advances include: smart sensors incorporated into packaging that provide a visual indication of food freshness or ripeness in case of fruit (through color changes in respond to changes in gas composition within the package); nanoscale coatings which can be applied to plastic (PET) bottles to prevent oxygen penetration and avoid foodstuff damage and degeneration; and the inclusion of nanoscale clay particles within the plastic to achieve the same. Each of these have been tried and tested without any negative reaction from the consumer.

17.4.3 Drinks

Nanotechnologies can have applications in "functional foods" with a positive effect on health such as improving nutrition of drinks, and increasing flavor with minimal addition of artificial ingredients. Vitamins, enzymes, and flavorings can be packed in nanocapsules of 5–100 nm size. So, for example, products are already on the market

Fig. 17.14 Nanovisions for bottled products. Image courtesy of IoN, UK. Source Lux Research reference study. The Nanotech Report 5th Edition, 2007

where nanocapsules are filled with fish-oils, that have unpleasant taste, but where the consumer can benefit from the Omega-3-fatty acids without experiencing this. Nanocapsules can give increased stimulation of taste buds by having a very large number of nanoscale flavor particles dispersed into a drink.

The nanotransport carriers of these enriched foodstuffs or medicines are broken down by the body and/or excreted, which makes them acceptable to consumers.

17.5 Conclusion

There are now many applications of nanotechnology in daily life and many more will arrive soon. We have quoted a few of them in this chapter. Others have been addressed in previous chapters or will be treated in subsequent ones. Before closing this chapter we would like to give examples of applications of nanotechnology in a few fields which impact our daily life.

Nanoelectronics. In April 2012, the first deliveries of microprocessors made using a 22 nm process have been made (the Intel Core i7 and i5 processors based on Ivy Bridge technology). Flash memories with a 24 nm process were made by Toshiba in 2010.

Health. Brain tumors are difficult to detect and it is not preferred to do a biopsy to determine whether a tumor is benign or malignant. A nano-patterned pen has been developed at the CEA (France) allowing collection of floating cells and biomolecules without removing brain tissue. The position of the tip of the pen has to be precisely known and guided to perform this operation without harm to the surrounding tissues.

Energy. Using a gel-based nanoscale catalyst, a Chinese company has shown that it is possible to liquefy coal and transform it into gas with an improved efficiency and a lower cost compared to present technologies. This could pave the way to synthesize diesel fuel or gasoline from coal at a competitive cost.

Environment. An American company has made a filter based on nanosized alumina fiber, attracting and retaining micro and nanosize particles. It could retain 99.9999 % of viruses present in water at a flow rate which is hundred times greater than dedicated ultraporous membranes.

Materials. An American company has made a tungsten-carbide-cobalt composite powder with a grain size less than 15 nm which can be used to make a sintered alloy as hard as diamond. This can be used to make drill bits or cutting tools, for example.

Home. Coating each fiber of fabric with nanowhiskers produces a stain-repellent surface. This technology can be used to make ties, suits, and other clothes stain-repellent.

Sport. A nanocomposite coating for tennis balls keeps them bouncing longer than ordinary tennis balls. In the future, such a technology could be applied to tyres which would last longer.

Chapter 18
Nanomaterials and Cosmetics

The cosmetics industry covers a very wide spectrum of products: body lotions, shower gels, hand creams, shampoos and conditioners, after shave balsams, shaving foams, foot gels, antiperspirants, moisturizing creams, lip balms, eye care creams, and so on. Then there is the whole range of make-up products: eye shadows, skin foundations and concealers, micellar lotions, lipsticks and gels, mineral powders, brow pencils, nail conditioners, nail lacquers and removers, cuticle softeners, and so on. As we can see in Fig. 18.1, just for the face there are numerous products giving different results.

From the Egyptian era onward, nanomaterials have been used in the preparation of make-up and skin care products, initially with craft skills but today with the careful development and application of technology. The cosmetics industry has seen a huge impact of nanotechnology in recent decades. In 1985, the cosmetics industry introduced nanotechnology-based products that used the self-assembling properties of phospholipids to adjust the biocompatibility of active ingredients. This was the birth of liposomes in the cosmetics industry, which have now become common ingredients in topical lotions.

There are two main fields of applications of nanotechnology in cosmetics (Fig. 18.2). The first is the use of nanoparticles as UV filters; the second is the use of nanodelivery agents to carry and release cosmetic products at the right place and at the right time. Nanoparticles used as UV filters are mostly titanium dioxide (TiO_2) and zinc oxide (ZnO) but there are also studies on organic alternatives. Liposomes and niosomes are the most frequent nanovehicles used to deliver cosmetics.

There are common features between drug delivery for healthcare and delivery of cosmetic products. Therefore, we shall not repeat here what we have said in part 4 but rather focus on new points.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_18,

Fig. 18.1 Applications of nanotechnology in cosmetics and a picture of zinc oxide nanoparticles picture in cosmetics. Image courtesy of IoN, UK

Fig. 18.2 Two main fields in cosmetics where nanotechnology applies

18.1 Sunscreens

Sunscreens contain nanoscale titanium dioxide or zinc oxide particles. These compounds provide improved UVA and UVB protection due to the formation of thickly condensed layers of nanoparticles which reflect like small mirrors. They are transparent for the human eye because of their nanosize, are easily applicable on the skin and do not cause visible whitening on application of the lotion; they are also finding extensive use in foundations for people with sensitive skin profiles that need UV protection, for antiaging and antiacne.

Nanotechnology has led to the production of highly sophisticated sunscreen formulations that provide photostable broad spectrum UV protection and thus better and safer sunscreens. Traditionally, UV absorbers were organic molecules, many of which break down in the presence of UV light. Today, the majority of high-performance sunscreens use a combination of both organic and inorganic absorbers, and many formulations are composed of inorganic nanoparticulate absorbers alone. The science involved spans physics and materials science for optical properties such as UV absorption, through organic and physical chemistry for controlled release of molecules into the skin, to biology for bio-inspired (biomimetic) materials.

Different physical properties for a cosmetic-color, UV protection, texture, and ease of application—can be obtained with only small variations in the composition of its chemical constituents, which allows the tuning of some target properties through appropriate formulations, particularly when nanoscale effects are being exploited. A recent development is the use of a dopant in a common inorganic compound. For example, insertion and/or substitution of iron atoms in the crystallographic structure of titanium dioxide microsize particles induces an interesting effect called photochromism, where a product is able to change its color when the lighting changes. Additionally, interferential effects have great use in make-up products, based on the difference of optical index between material layers. Controlling the layer thickness and the optical index gives materials that change their colors according to the observation angle.

The stability of the ingredients is an important factor: organic UV absorbers can destabilize in a number of ways including through interaction with other molecules and by undergoing photo-induced decomposition, resulting in reduced protection. TiO_2, the major protection agent of many sunscreens, provides the desired protection, but reactions may generate harmful chemical species at the surface that can affect the stability of other ingredients in the formulation. The surface area of nanoparticulate TiO_2 is very high so this effect is amplified. Problems in the use of TiO_2 in sunscreens can be addressed through the production of hybrid materials. Formulations commonly add actives such as vitamin A, vitamin E, and vitamin C, which act as antioxidants and solve the unpleasant surface effects. Furthermore, the crystal structure of TiO_2 is critical in reducing the free-radical generation process. In the past, both the anatase and rutile crystal forms of TiO_2 were manufactured for use in personal care formulations. Experience has shown that the rutile phase material is less photoactive than the anatase, and 100 % rutile material is now the preferred option in sunscreen formulations.

Another way of minimizing free-radical generation from inorganic materials in sunscreens is to coat the TiO_2 or ZnO nanoparticles with another material, for example alumina–silica. The most recent solution to minimize free-radical generation by inorganic nanoparticle UV absorbers is by the incorporation of manganate-ions into the TiO_2 crystal lattice, a genuine hybrid nanomaterial.

18.2 Cosmetics Delivery

We have seen, in part 4, that nanoparticles can be used in drug delivery systems. Such a function is also valuable in the cosmetics field. Nanovehicles can carry appropriate products while protecting them before they reach their target.

There are numbers of delivery systems that can be used in cosmetics. Figure 18.3 shows the most important ones and we shall elaborate a little bit on the diverse routes

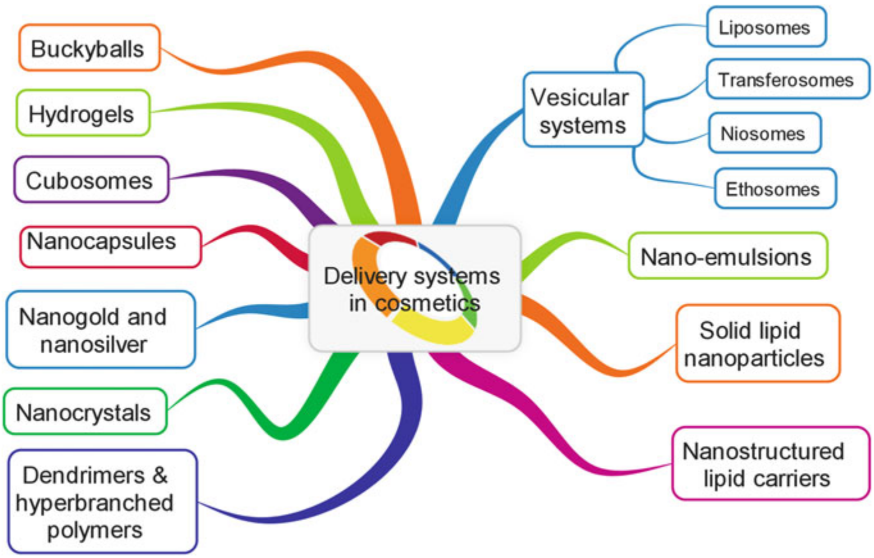


Fig. 18.3 Different delivery systems which can be used in cosmetics. Classification partly coming from the Observatorynano project

of cosmetic product delivery. Some of them could be used for drug delivery as well. More details about these systems can be found in the Observatorynano project.

Vesicular structures are often used as delivery systems in cosmetics. Liposomes belong to a subcategory which is the most widely used. Liposomes are vesicular structures with an aqueous core surrounded by a hydrophobic lipid bilayer. Products soluble in water are trapped in the core because they cannot pass through the hydrophobic bilayer. Liposomes can be manufactured in such a way that hydrophobic molecules can be kept in the lipid bilayer. *Liposomes* have a size ranging between 15 nm and a few microns. If their size is smaller than 100 nm they are called nanoliposomes. The lipid bilayer can merge with the bilayer of a cell and its contents can be released, enabling drug or cosmetic delivery.

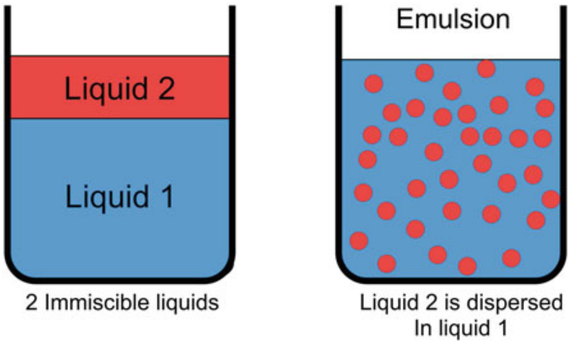
Transferosomes are more elastic than liposomes. They are more efficient delivery systems because they can penetrate spontaneously the stratum corneum.[1]

Niosomes are nonionic surfactant-based vesicles developed and patented by l'Oreal, a French company. They have a structure similar to liposomes but are more stable. They can encapsulate drug or cosmetic carriers soluble in water. Advantages of niosomes are that they better protect encapsulated products; they can improve the bioavailability and enhance skin penetration.

Ethosomes are noninvasive delivery carriers enabling delivery of drugs in the deep skin layers. They are lipid vesicles containing phospholipids, ethanol, isopropyl

[1] The stratum corneum is the outermost layer of the skin epidermis. It protects the underlying tissue.

Fig. 18.4 Schematic illustration of an emulsion of two immiscible liquids (*right hand part* of the figure). In the *left hand part* of the figure they are not emulsified while, in the *right hand part*, liquid 2 is dispersed in liquid 1



alcohol in high concentration, and water. Their size ranges from tens of nanometers to microns. Ethosomes are easy to make and safe.

Liposomes have been used for a relatively long time. An antiaging cream, manufactured by Dior, was the first liposome-based cosmetic introduced on the market (in 1986). Today, many products based on liposomes are commercially available but only a few use nanoliposomes. They are very useful for cosmetic delivery applications. Furthermore, they have the great advantage of being safe products. Transferosomes, niosomes, and ethosomes are supposed to further enhance the penetration of cosmetic substances across the skin.

An emulsion is a mixture of at least two immiscible liquids, such as oil and vinegar, in which one of the liquids is dispersed in the other. Vinaigrettes or milk are examples of emulsions. If we take oil–water as an illustrative example, we can have an emulsion of oil in water or an emulsion of water in oil. Both types are different. Figure 18.4 shows an emulsion in the case of two immiscible liquids.

Nanoemulsions are more stable than larger scale emulsions and are transparent or translucent. The active surface of the nanoparticles in the emulsion is much larger than in the case of microemulsions. Nanoemulsions are used in cosmetics, for example, for sun protection. They are regarded as safe and their small size increases their stability.

Solid lipid nanoparticles are particles of nanometer size with a solid lipid core (right-hand part in Fig. 18.4). The solid lipid nanoparticle can be stabilized against aggregation using surfactants, for example. Solid lipid nanoparticles are similar to nanoparticles present in nanoemulsions apart from the fact that in this latter case the core is a liquid lipid (left-hand part in Fig. 18.5). When solid lipid nanoparticles are used as a delivery system, the active agent is dissolved or dispersed in the lipid core. Encapsulated substances are protected from degradation.

Lipid nanoparticles are used in skin care cosmetics. There are several advantages in using lipid nanoparticles. Chemically unstable active ingredients are stabilized and a better control of their release is possible. Furthermore, the lipid enables better skin hydration and protection because of the formation of a thin film on the skin. Solid

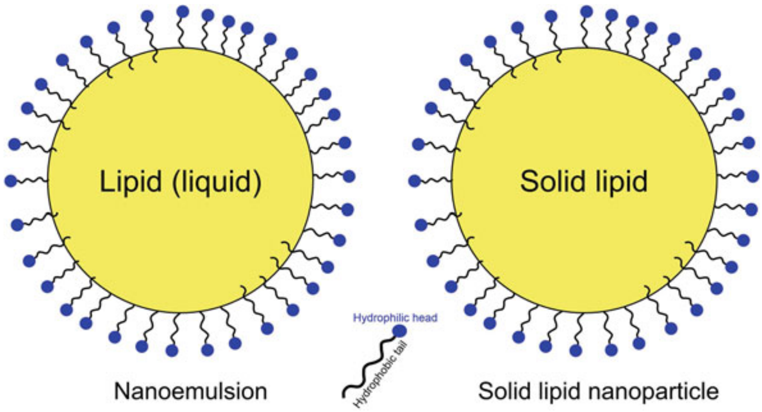


Fig. 18.5 On *left hand part* of the figure a lipid monolayer is enclosing a liquid lipid core. On the *right hand part* of the figure the lipid monolayer is enclosing a solid lipid core. See http://www.azonano.com

lipid nanoparticles improve the penetration of active compounds into the stratum corneum.

Dendrimers have already been presented in Chap. 4. They look like a tree with branches going out from a central point (see Fig. 4.15). They could find applications in cosmetics. These monodispersed micellar structures with a size of about 20 nm with end groups at the surface have a nanoscale container in their core which can be used for cosmetic agent's delivery. *Hyperbranched polymers* are unsymmetrical dendrimers which are interesting because they can be prepared in a single step. This is simpler and reduces the cost of synthesis. These products can be used in sprays, gels, and lotions.

Nanosilver has antibacterial properties. It can be used as underarm deodorants. It is claimed that it gives a 24 h antibacterial protection. *Nanogold* is also supposed to have a high disinfecting power in the mouth and can be added to toothpaste.

Nanocrystals are used to deliver poorly soluble drugs in pharmaceutical applications. Nanocrystals are formed with several hundred to tens of thousands of atoms ordered in a crystal structure. Their typical size ranges between 10 and 400 nm. They have physical properties in between those of molecules and macroscopic crystals. Their size and surface area can be tailored to provide specific physical properties. They need to be stabilized to prevent aggregation between nanocrystals. Rutin and hesperidin, which are poorly soluble plant glycoside antioxidants for dermal use, are now available commercially in cosmetics, thanks to nanocrystals.

Nanoencapsulation is a generic technique that has been used for a long time in enabling drug delivery for healthcare. A nanocapsule is basically a nanoparticle with a shell, where it is possible to load the interior with a drug. A nanocapsule can be made with hydrophobic or hydrophilic material depending on the application. It is also possible to functionalize the surface of the nanocapsule with specific molecules. For that reason polymers and biomolecules are often used to coat nanocapsules allowing an easier grafting of molecules. It is possible to use adaptive polymers responding to an external signal (such as pH, temperature, or ultrasound) to release the drug or cosmetic agent contained in the nanocapsule when it is required. Such products can be used for skin care and especially for skin repair. It has been shown, for example, that using nanocapsules can decrease the penetration of UV in the skin of a pig compared to conventional emulsions.

Cubosomes are bicontinuous cubic phase liquid crystals, first observed while studying food emulsifiers. A bicontinuous cubic liquid phase is a very viscous material, optically clear, with a very special structure at the nanometer scale. The surface area is also very large. They are self-assembled liquid crystalline particles of certain surfactants when they are mixed with a proper ratio of water. The most common surfactant used to make cubosomes is monoglyceride glycerol mono-olein.

Bicontinuous means that there are two distinct hydrophilic regions separated by a bilayer. These regions are continuous but do not intersect. This structure allows incorporation of water and oil-soluble materials as well as amphiphiles (a molecule that is attracted to both hydrophobic and hydrophilic molecules). Cubosomes have the same microstructure as the parent cubic phase but their specific area is much greater. Furthermore, they can exist at high levels of dilution, thanks to the relative insolubility of the cubic phase-forming lipid in water. So far studies of these products have been done only for cosmetic applications.

Hydrogels are three-dimensional hydrophilic polymer networks. They swell in water without dissolving thanks to their molecular crosslink. Hydrogels can anticipate changes and adapt their properties accordingly. They are used in facial masks, for example.

In Chap. 5 we introduced C_{60} "buckyballs" and other fullerenes. These molecules with a diameter of the order of 1 nm. It can be used in cosmetics in very expensive face creams because of their capacity for capturing free radicals.

18.3 Safety Aspects of Cosmetics

Nanotechnologies have already received considerable adverse publicity about their use in consumer products. Consumers must be assured about the safety of nanoparticles used in cosmetics. Products for application to the skin must ensure low cellular uptake of dispersed nanoparticles; zero stress on bodily organs resulting from the breakdown and excretion of nanoparticles; and no accretion of nanoparticles within the body. Nanoparticles may diffuse through damaged or weakened skin and enter the blood circulation.

In studying the health effects of nanoparticles, distinction should be made between soluble and biodegradable nanoparticles (such as liposomes, nanoemulsions, etc.) which disintegrate upon application to the skin, and insoluble nanoparticles (TiO_2, ZnO, etc.) for which health concerns related to possible uptake arise.

The conventional risk assessment methodologies used for cosmetics will have to be optimized for nanomaterials, validated by *in vivo* and *in vitro* tests. Raw material suppliers will have to disclose valid animal testing and satisfy specific legislative requirements before ingredients can be incorporated into finalized cosmetic products: cosmetics regulations Nr 1223/2009 (art. 16) imposes strict conditions and timelines, and testing will have to encompass skin and eye irritation, dermal absorption, mutagenicity/genotocity, carcinogenicity, and toxicity, including reproductive toxicity, repeated dose toxicity, and photo-induced toxicity.

On the basis of much scientific and technological data, the risk for humans from the usage of nanostructured TiO_2 or ZnO currently used in cosmetic products or sunscreens is considered to be negligible. Detailed microscopy studies show that TiO_2 pigments remain exclusively at the outermost layer of the human skin, with no dermal absorption. In addition, the safety of these metal oxides is confirmed by more than 25 years' human use of "nanocosmetics" without clinically adverse events. The benefits of UV-protective properties in sunscreen products outweigh any potential risk and "nano" TiO_2 and ZnO-based products as sunscreens are safe for human exposure.

In some cases, broad statements such as "more toxicological research is needed" can have the adverse effect of making the consumer afraid that an unknown threat exists.

In Fig. 18.6 some of the main causes of nanotoxicity are shown together with some of the possible consequences.

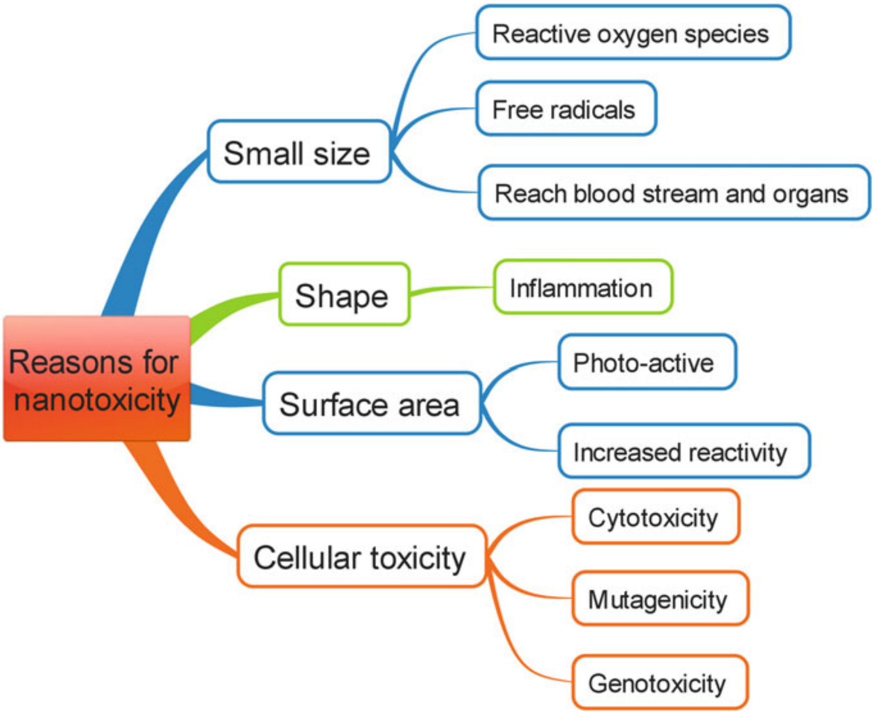


Fig. 18.6 Some causes of nanotoxicity and some of the consequences

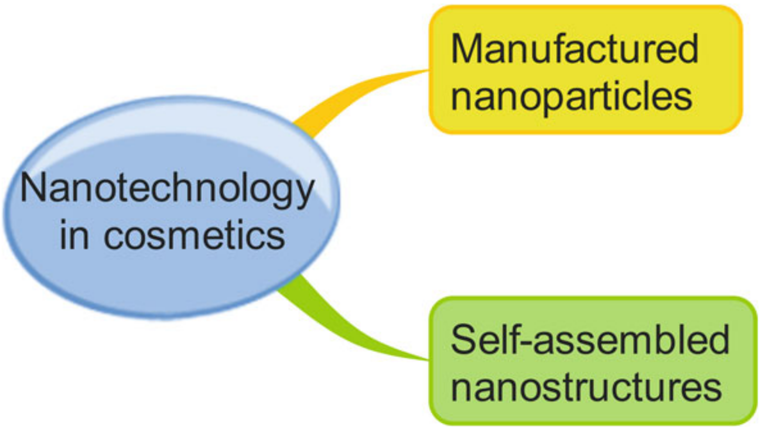


Fig. 18.7 Different types of nanostructures used in cosmetics

The small size of the particles enables them to possibly penetrate through physiological barriers such as the skin, especially if the skin is broken or damaged. Reactive oxygen species and free radicals can be formed which will lead to oxidative stress on cells, inflammation, damage to proteins, etc. Their shape may also cause specific inflammation. Their large surface area makes them more reactive. Dust of nanoparticles can explode: of course this is of no concern to the cosmetics user but is relevant in production areas. Nanoparticles have also potential cellular toxicity (cytotoxicity, mutagenicity, genotoxicity). All these potential risks should be carefully addressed at the research level in order to prevent any accident. More difficult is to foresee what may happen in the long term.

18.4 Conclusion

Nanofabrication can produce personal care products based on natural materials and extracts that are more environmentally friendly than current solutions. Cosmetics will be easier to apply and to remove. Cosmetic coloring will be controllable through pressure applied during application, reducing the amount of product needed to achieve the desired result. The division between cosmetics and pharmaceuticals may also blur, with the possibility of cosmetic products encapsulating drugs with controlled release, and stealth structures for dermal drug delivery and immunization, including DNA vaccines to create noninjection routes to delivery.

Cosmetics are an important field of application for nanotechnology. Large cosmetic companies invest a lot in research and development. For example, L'Oréal, a French company, has more patents in the nanotechnology domain than IBM.

In nanotechnology applications for cosmetics it is possible to categorize them according to the way the nanostructures are built (Fig. 18.7). Manufactured nanoparticles comprise, for example, titanium dioxide or zinc oxide used in sunscreens. Self-assembled nanostructures are for example nanosomes.

Chapter 19
Nanotechnology for the Textile Industry

During the next 10 years, the textile industry can benefit significantly from new nanotechnologies. The clothing and textiles industry has a significant turnover, but very little manufacturing of clothing now takes place in the European Union. Designs may be owned by European companies, but the items themselves are usually manufactured in Asia. Currently, clothing manufacturing is a low-tech industry; therefore, nanotechnologies offer attractive possibilities for developed countries and their economies.

19.1 Toward New Textiles

Clothing represents 60 % of the global market of textiles. Home and furnishing textiles represent about 35 %. The remaining 5 % of the world market corresponds to technical and nonconventional textiles such as medical textiles, sports and outdoor textiles, and military textiles.

19.1.1 Nanomaterials and Nanocomposites

Nanomaterials and nanocomposites can be used in textiles to bring new properties. New technologies have been developed to manufacture nanofibers at an industrial scale. Physical and chemical treatments are used for finishing of textiles and give them specific structural and functional properties. It is also possible to incorporate nanotechnology inside existing textiles.

Basically, nanoparticles can be dispersed into the matrix of the fibers or deposited on their surface. The goal is to obtain improved characteristics and performances and, eventually, new functions and properties. Several kinds of nanoparticles can be used: for example, silver (Ag), metal oxides such as titanium dioxide (TiO_2), carbon

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_19, © Atlantis Press and the authors 2014

nanotubes (CNTs), and clays nanoparticles. Of course the primary applications for nanotechnologies in textiles are in sectors where cost is not an issue in obtaining outstanding performances. This is the case for example in military, medical, sporting, and other specialist applications.

The development and application of fabrics, coatings, and fibers that enhance the functionality and ease of use for the wearer will create a revolutionary advance, a move from a low-tech, low-value labor-intensive industry to a high-tech knowledge-driven industry with high embedded value in the product and the possibility of a significant increase in the value of the global market. Of particular value to the European economy is the possibility to retrieve and redevelop a textile manufacturing industry with both a strong internal and export market. The potential impact could run into hundreds of billions of Euros over the next decade.

Because of new functionalities, industries as diverse as laundry and telecommunications can be affected by the new technologies. Nanoscience has already produced stain- and wrinkle-resistant clothing, and future developments will focus on upgrading current performance of textiles, as well as integrating novel materials and/or technologies to produce multifunctional textiles and clothing.

Nanotechnology provides conventional protective textiles with a multitude of new features and properties, often with reduced weight and increased strength. For example, nanosized particles can be used in finishing stages for better and more durable protective coatings, but the biggest impact in protective textiles will come from novel types of nano-enhanced fibers. Electro spun CNT or polymer nanofibers can be made into textiles which are soft and have good strength-to-weight ratio, and at the same time can act as a barrier against microorganisms. Nanometer-sized clay particles finely dispersed in a polymer matrix can be used to enhance stiffness, tensile strength, thermal stability, gas barrier properties, and the flame retardant properties of textiles. Nanosilver can be used to produce fabrics that kill pathogens, useful in medical and decontamination applications, including dressings that have antibacterial properties built-in. Very high strength “engineering” fabrics can be produced using nanotechnologies.

19.1.2 Self-cleaning and Dirt-Free Textiles

Nanotechnologies can be developed to mimic effects found in Nature. Microscopic bumps on a lotus leaf transform its waxy surface into an extremely water repellent (superhydrophobic) material. Raindrops roll easily across such a surface, removing any dirt.

Synthetic self-cleaning materials have been developed, some of which are based on this “lotus effect”, while others employ the opposite property, superhydrophilicity (water-attracting) as well as catalytic chemical reactions. Future developments may combine these two properties or use substances that can switch back and forth to control the movement of liquids (Fig. 19.1).

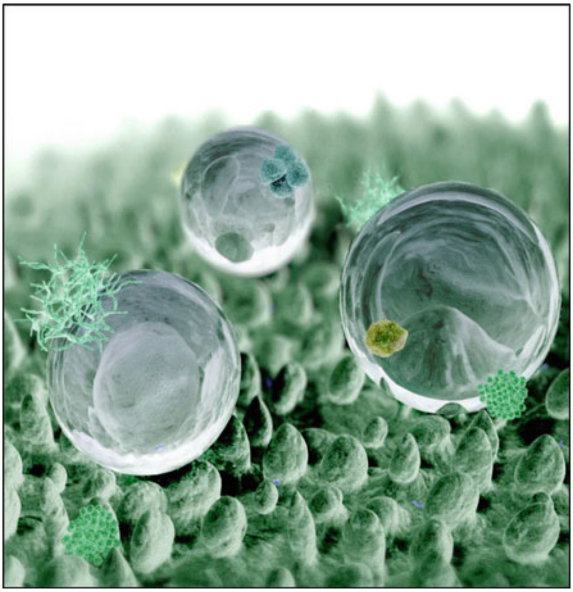


Fig. 19.1 Mimicking the effect of the lotus leaf in cleaning natural surfaces. Image courtesy of IoN, UK

Nanofibers using sunlight to break down dirt, organic materials, pollutants, and microorganisms, may make laundry a thing of the past: fabrics will be resilient, weather-proof, and dirt-proof. Through engineering the properties of individual fibers at the nanoscale, and through utilization of novel coatings exploiting nanomechanisms, fabrics will be able to automatically repel dirt, oil, microorganisms, and liquids. It may be possible to develop fabrics that never stain or require cleaning. Comfort will be improved through inbuilt moisture management. Water repellent and self-cleaning textiles can be obtained by nanoscale modification of the surface roughness, resulting in water and dirt rolling off the surface; while, water vapor may still pass through, ensuring breathability. As well as day-to-day clothing, this will take the current generation of sportswear to the next level of comfort and performance. High strength and abrasion resistant nanotextiles are also beneficial in sports applications.

19.1.3 Medical Textiles

The medical sector will reap particular benefits from nano-enhanced medical textiles. Wound dressings can be engineered to have bioactive properties, stimulating healing and skin regeneration while also providing antibacterial protection (for example, through nanosilver inclusion). Direct drug delivery will be possible, either through the skin generally or more directly on an affected area. Passive sensing in fabrics will indicate the presence of infection or the progress of healing, and dressings will be tailored to allow the passage of air, water, and medication, as appropriate. Flexible and stretchable ECG patches for cardiac monitoring with wireless signal transmission, and integrating biochemical sensors into textiles for continuous monitoring of a person's health are also possible options. These capabilities also offer an important survival tool to professionals operating in dangerous situations where the monitoring of physiological parameters and physical location can be of extreme importance. Antimicrobial dressings are commercially available (www.acticoat.com).

19.1.4 Security, Safety, and Military Textiles

The applications for nanotechnologies go beyond domestic clothing or leisure wear, to military, security, and safety applications. Multifunctional, personal protective textiles have the aim of eliminating or minimizing the risk of injuries, accidents, and infections; acting as shields against chemical, biological, and nuclear hazards; as well as protecting against high temperatures and fire, sharp objects, and ballistic projectiles. Fire resistant properties in textiles are of value not only for the emergency services but also in limitation of fire damage in buildings. Radiation-protective clothing will be less cumbersome and easier to decontaminate. Fibers can be made resistant to penetration by blades and shrapnel, and offer higher protection from blast and heat. The development of innovative technologies in high-tech domains such as the space and defense industries is driving development of nonwearable interior textiles for buildings, transport vehicles, and consumer products.

CNTs and carbon nanofibers offer the potential for very high strength composite fibers. Carbon nanofibers effectively increase the tensile strength of composite fibers owing to their high aspect ratio and high intrinsic stiffness. One CNT fiber already exhibits twice the stiffness and strength, and 20 times the toughness, of steel wire of the same weight and length. Applications in safety harnesses and explosion-proof blankets can be envisaged. Textiles containing inorganic fullerenes, or multi walled CNTs, have shown superior protection for ballistic impact. The innovative functional protective properties of nanotextiles surpass conventional protective textiles such as Kevlar, since these are heavy, bulky, and uncomfortable, with limited protective performance and restricted use.

19.1.5 Textiles for Automotive Applications

Nanotextiles with self-cleaning, antibacterial, antiallergy, antistatic, and improved wear and tear resistance will have widespread application in improving the comfort and durability of vehicle interiors in the automotive industry. They will provide improved noise reduction and acoustic performance, and better safety through flame retardance/resistance and impact absorption. Innovative textiles will also have a favorable effect on the weight reduction of vehicles and consequently on reduced fuel consumption and CO_2 exhaust levels. There are Al_2O_3, SiO_2, and ZnO nano-enabled coatings being tested by the automotive industry to protect textiles from UV damage. Methods for nanoparticle encapsulation to guarantee that the coating lasts for the entire lifetime of the car must be found.

To reduce noise within the car, a nanofibrous layer of nonwoven polyvinyl alcohol on a fibrous underlay may be used. Compared to conventional materials, this offers improved noise reduction while also providing good heat insulation and weight reduction. Cost reduction of these nanofibers is, however, necessary before adoption in the automotive sector.

19.1.6 Smart Textiles

Smart systems will combine electronics with textiles, by direct integration at the fiber level, allowing the wearer to be tracked and vital signs monitored. Electrical properties can be tailored to provide protection from electrocution or energy generation for the charging of personal electronics. "Wearable computers" can be foreseen, where the electronic systems are fabricated and integrated with the textiles. Functional technologies will provide access to the internet and telephony networks without the need for a separate handset.

Nanotechnologies will be a disruptive technology in textiles in the way that the iPad has revolutionized personal computing. Many functions that have traditionally been embedded in other devices such as telephony, music and entertainment, drug dispensing, light generation, sensing, etc., will be able to embedded into fabrics using nanoscale fabrication, partly as a consequence of the progressive reduction in size of the basic electronics and also because of novel manufacturing techniques for textile production. Nanoscience promises "smart" textiles that extend the function of clothing beyond simply protection from the elements to providing adaptive behavior based on local environmental conditions, and a range of new functions from entertainment to pathogen detection. Textiles will be able to give an indication of UV exposure in order to prevent sunburn, through to acting as an electronic "nose" for drug and explosive detection, providing instant response to a swab test without the need for additional analysis. Multipurpose applications of smart textiles are shown in Fig. 19.2.

As well as the development of new functionality for clothing, nanotechnologies can provide designers with new ways for styling, coloring, and using fabrics with inbuilt technologies for new fashions and cosmetic applications. Fabrics can be designed to alter color or texture in response to body temperature, or on demand, controlled by electrical or magnetic fields.

The huge technological benefits offered by nano-enabled protective textiles can create an innovation-driven market to relaunch the textile industry in developed countries. Problems to be overcome include process scalability, durability of the nano-enabled functionality under repeated wash and wear cycles, reduction of costs,

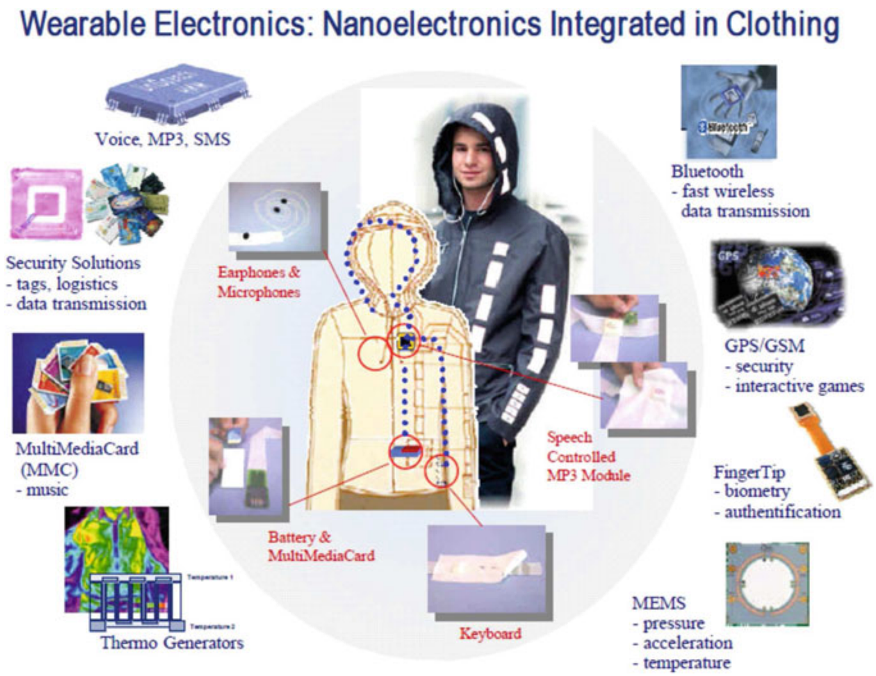


Fig. 19.2 Multipurpose applications for smart textiles. Image courtesy of Infinion, Munich

increasing education of the end user, and overcoming concerns about possible negative health effects.

Rising safety and health concerns for those exposed to dangerous environments or working in high-risk professions have increased the demand for improved protective apparel and accessories. In contrast, there are health and safety concerns to be addressed in the use of nanotextiles which may come in direct contact with human skin owing to the release of nanomaterials from clothing, due to abrasion or wear. At present, there are no specific regulations for either nanotechnology, or nanotechnology-related textile products. Much of the concern is focused on "free" engineered nanomaterials and their effects on the environment, health, and security. Regulatory schemes should go some way assuring the safety of this emerging field without constraining its growth.

19.2 Finishing Treatments

Finishing is an important step in textile fabrication. Its role is to give extra properties to the textile while maintaining the basic characteristic of the initial material. There is a strong demand for flexible, quick, and cheap treatments. Finishing treatments

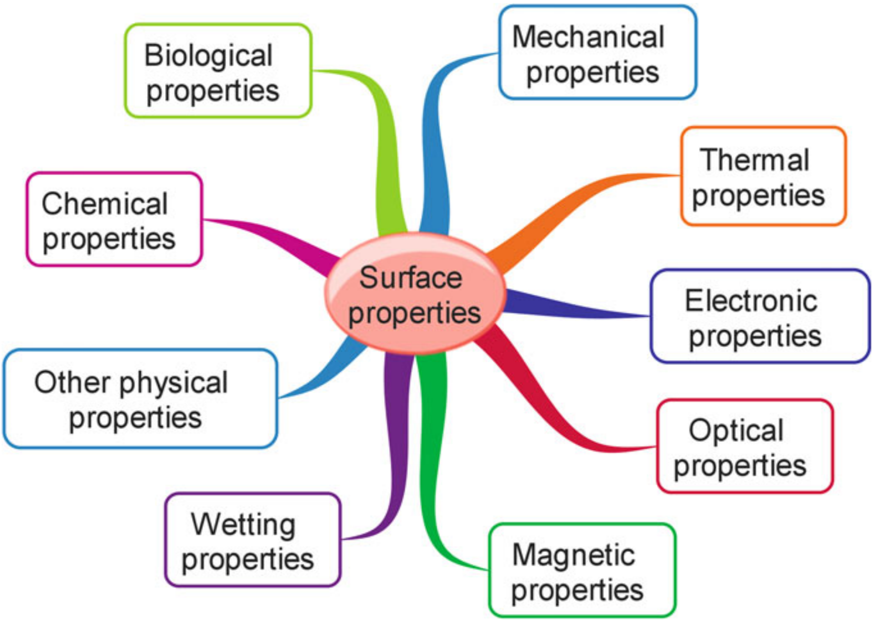


Fig. 19.3 Surface properties of textiles or fibers which are interesting for applications

mainly concern the surface of the fibers or of the textile. Various surface properties can be obtained. They are shown in Fig. 19.3.

There are two main families of finishing techniques:

- wet finishing where the chemical treatments are performed in a solvent, usually water. It is important to reduce the release of waste products and nanotechnology is helpful to achieve that;
- dry finishing which is a gas- or solid-phase treatment. The advantage is high flexibility and low environmental impact.

The main finishing processes used for textiles are indicated in Fig. 19.4.

Using nanoparticles, dyeing can be more environmental-friendly because the amount of dye used is smaller for the same efficiency and there is less waste water.

Many different techniques are used for coating and lamination: chemical or physical vapor deposition, electrodeposition, spray coating, etc.

Grafting enables functionalization of the surface of materials by means of chemical reactions.

Plasma treatments enable modification of the surface of the fabric while keeping the bulk unchanged. Enhancement of properties such as adhesion, or adapting the surface by metallization can be achieved. Several types of plasma treatment are possible: plasma-enhanced chemical vapor deposition is one of them.

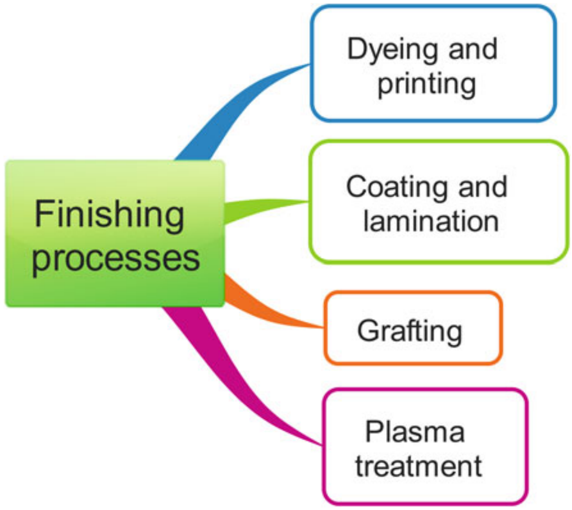


Fig. 19.4 Main processes used in finishing of textiles

One of the critical advantages of nanotechnologies is in the way that nanoscale emulsification enables vastly improved coating of fibers to confer the desired properties. Finishes can be applied to textile materials in a more thorough, even and precise manner, improving the look and texture of clothing and giving better colorfastness. Textile performance can be greatly enhanced for stain-resistance, antistatic properties, wrinkle resistance, wind proofing, waterproofing, and shrink-proofing. Using nanosize metal oxide and ceramic particles in coating formulations provides a much larger active surface area and hence higher efficiency than larger size particles; they also have the advantage that they are transparent, and do not blur the color and brightness of the textile substrates. Finishing with nanocrystalline piezoceramic particles can convert fabrics into sensor-based materials: the finished fabric can convert mechanical force into electrical signals enabling the monitoring of bodily functions such as heart rhythm and pulse if they are worn next to the skin. Novel finishes will also find use in fields as diverse as architectural applications and airbags.

19.3 Conclusion

There are a large number of potential or existing applications of nanocomposite fibers in the textile domain. Some of them are shown in Fig. 19.5.

To meet these applications several nanomaterials or composites exist and can be used. The most important are shown in Fig. 19.6.

Increasing awareness of risk prevention for those working in dangerous conditions (for example, in smelters or contaminated environments) or in the emergency services such as firemen, policemen, and security services has created a strong societal "pull" for innovative products providing high quality, performance, and greater protection. The textile industry stands to see major benefits from the advent of nanotechnologies,

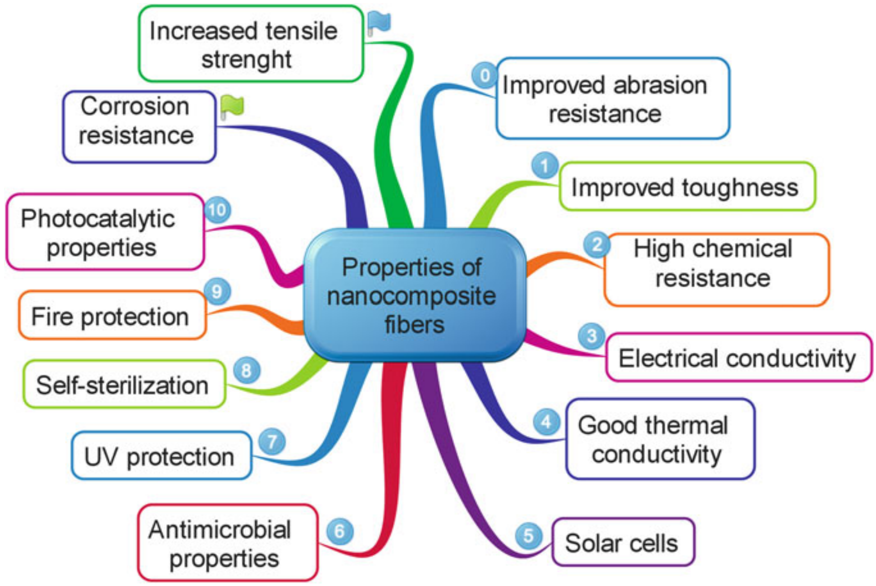


Fig. 19.5 Some properties of nanocomposite fibers which currently existor are under development

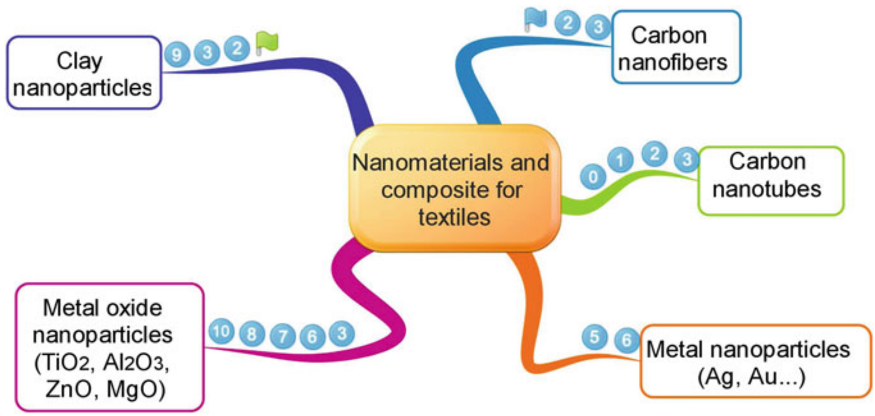


Fig. 19.6 Nanomaterials and nanocomposites used as fillers in textiles. The numbers and symbols indicate the properties in Fig. 19.5 that can be met

with step changes in performance of existing textile materials and the potential for completely new functions and applications integrated within the fabrics themselves. The potential rewards for investment in this field are very high, in redeveloping a global industry for the benefit of the world economy.

A high level of competence and excellence in multidisciplinary textile research is crucial to respond quickly to commercial needs.

Part VI
Nanotechnology and Daily Life

Conclusion

Daily life covers many different fields. The most important ones are shown in Fig. VI.1

In all these fields, nanotechnology can bring improvements or innovation. We have briefly described in this part applications relative to daily life, with a particular emphasis on cosmetics and textiles. However, many other fields are concerned (see Fig. VI.1). They are addressed in other chapters.

New consumer products will mean that nanotechnologies will become ubiquitous in our daily lives. Nanomaterials will revolutionize some products, bringing new functionality and performance; some industries will see incremental improvements; and in most cases consumers will be unaware of the nature of the materials that are being used for their benefit. Nonetheless, there will be a step change in the products that we buy and use in our homes, and our living environment will change as dramatically in the next two decades as much as it has in the last two centuries.

Because of the advantages that can be gained in deploying nanomaterials openly in the environment, the potential risks and health hazards of nanomaterials must be identified and addressed. Consumers will come into contact with nanomaterials throughout the day, from application of deodorants, through driving a car, to using a telephone. There must be open and rigorous assessment of the toxicity of nanomaterials throughout their life cycles to ensure public confidence and give assurance to industry that they can safely invest and deploy nanotechnologies for wealth creation.

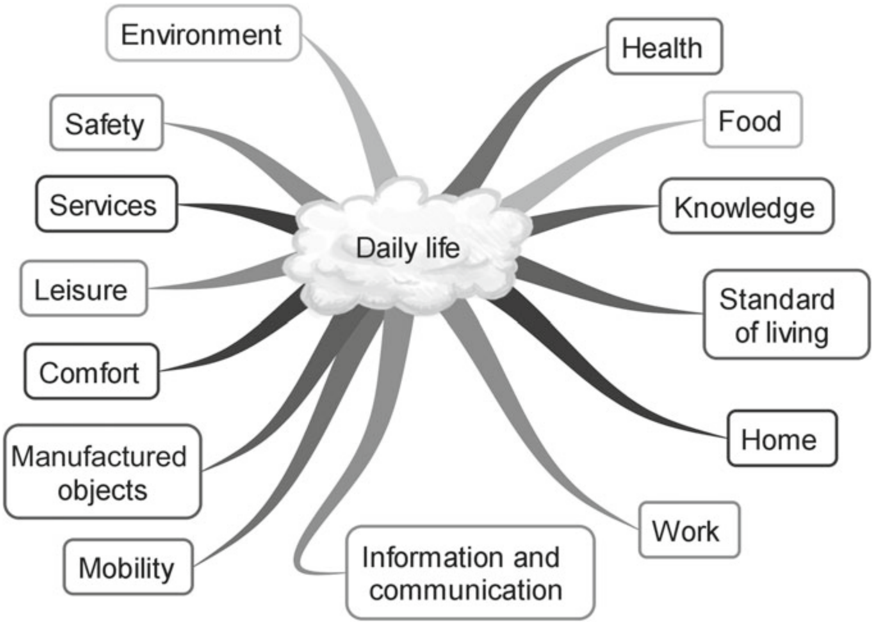


Fig. VI.1 The aspects of our daily life

Finally, new nanomanufacturing technologies must meet customer requirements, promote growth, and meet environmental and health safeguards in order to be competitive on the world stage.

Part VII
Energy and Nanotechnology

Introduction

Nanotechnology can play a significant role in providing solutions to the challenges of energy generation, storage, and transport. In industrial processes, it will introduce improvements and new solutions that will save energy and resources. The ability to work at the nanoscale, producing new materials and conceiving new architectures offers huge possibilities to achieve better results with fewer raw materials and with improved efficiency. It is also possible, in some cases, to create new functionalities. Reducing the amount of material used to perform the same function is vital for better raw materials conservation.

A large part of energy consumed in the world is devoted to space heating, space cooling, and the production of hot water. In France, for example, 40 % of the total energy demand was consumed in the residential and service sectors in 2010. This is about twice as much as the industrial sector consumes. Transportation consumes also a lot of energy, essentially from derivatives of oil. In France, for example, it represented close to 30 % of the total energy use in 2010. Agriculture in France accounts for around 8 % of transportation energy consumption.

In 2010, 61.5 % of the world oil consumption went into the transportation sector, according to the IEA (International Energy Agency). In terms of the amount of final energy consumption, the contribution from the different fuel sources is shown in Fig. VII.1. Industry uses electricity, natural gas, oil, and coal. The share of these different energy sources is shown in Fig. VII.2.

Table VII.1 shows the final energy consumption of the different energy sources in Mtoe (millions of tons of oil equivalent) and the share, for given energy sources among different sectors. The column "other" includes agriculture, commercial and public services, residential, and nonspecified uses. Much of the use of fossil fuels is for heating of homes and offices, and large savings can therefore be made by decreasing the energy consumption in the housing and service sectors. Nanotechnology can help to meet these challenges.

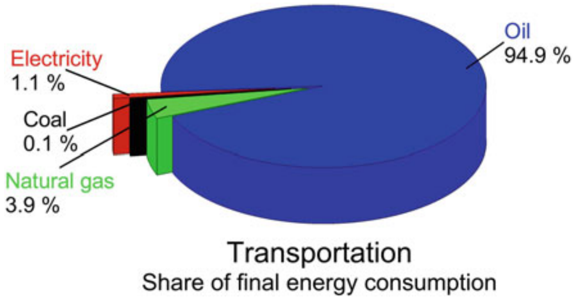


Fig. VII.1 Share of final energy consumption in the transport sector for the year 2010. Data from www.iea.org

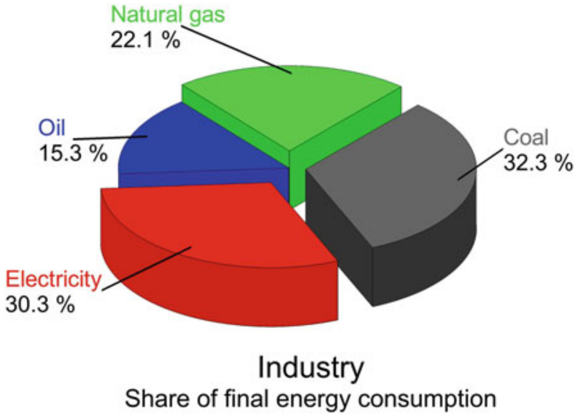


Fig. VII.2 Share of the different energy sources used in the industry sector for the year 2010. Data from www.iea.org

Table VII.1 Sectoral fuel share of different world energy consumption for the different energy sources for 2010

Final Energy	Mtoe	Industry (%)	Transport (%)	Other (%)	Nonenergy (%)
Coal	853	79.5	0.4	15.9	4.2
Oil	3570	9	61.5	12.4	17.1
Natural gas	1318	35.2	6.8	46.4	11.6
Electricity	1536	41.5	1.6	56.9	0

"Other" includes mostly agriculture, commercial and public services, residential. Data from www.iea.org

In the transport sector, which mainly uses oil derivatives, it is also valuable to decrease the quantity of energy necessary to travel the same distance. As we shall see, nanotechnology can help here also.

For industries in all sectors, decreasing the energy needed in processes is a priority. Catalysis is a way to make synthesis more easily while consuming less energy. Therefore, nanocatalysis has an important role to play in this area.

Chapter 20
Nanotechnology and the Energy Challenge

The primary global energy[1] consumption is increasing because of two effects. First, because the global population continues to increase (there are about 200,000 new inhabitants of planet Earth each day). Second, because many people on the Earth wish to increase their standard of living. Therefore, the global energy consumption increases faster than the world population. In 1800, the population was close to 1 billion while the primary energy consumption is estimated to be 0.2 billion toe.[2] A century later, in 1900, the population was about 1.7 billion with a primary energy consumption of about 1 billion toe. More recently, in 2000, the global population has reached 6 billion with a primary energy consumption of 10 billion toe. We have now reached 7 billion inhabitants, consuming around 12 billion toe. For more than a century, energy has been cheap and abundant. Today, with 10 or 20 cents of euros we are able, in Europe, to buy 1 kWh of electricity representing the work done by two manual workers during a day. Good and easy access to energy has many positive consequences at the economic and social level. In France for example, the life expectancy which was below 30 years before the French revolution (1789), was about 50 years in 1900 and passed 80 years in 2007. Today, in poor countries, the life expectancy can be below 40 years for people having poor access to food, energy, and other basics that are taken for granted in the developed world.

20.1 The Energy Challenge

Fossil fuels (oil, natural gas and coal) account for about 80 % of the total primary energy consumption, as shown in Fig. 20.1. Burning them produces carbon dioxide (CO_2) and increases the greenhouse effect of the Earth. Our energy usage comprises

[1] Primary energy corresponds to energy before any transformation or conversion, for example, crude oil, natural uranium, and solar energy. Gasoline or electricity are not primary energy sources. Electricity is actually an energy "vector:" a convenient way to transport energy.

[2] 1 toe = 1 ton oil equivalent. A unit often used to compare different kinds of energies. It is more a theoretical reference value than a real unit but allows comparing energy sources of different nature. Multiples of this unit often used are Mtoe (1 million of toe) and Gtoe (1 billion of toe).

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_20,

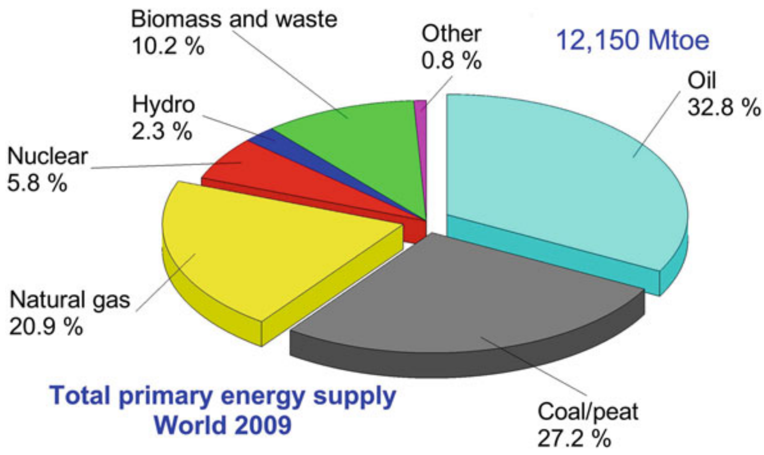


Fig. 20.1 Total primary energy supply in the world for year 2009. *Other* includes wind, solar, geothermal, etc. The share of fossil fuels is 80.9 %. In 1973, the world global primary energy consumption was equal to 6111 Mtoe, which is half the supply in 2009. The share of fossil fuels was 86.6 % in 1973. From www.iea.org, Key world energy statistics 2011

almost 85 % of total CO_2 emissions. Furthermore, fossil fuels, which were formed million years ago, exist in finite quantity. Therefore, they will eventually run out but prices will increase significantly as supplies dwindle.

We are now faced with two main facts. The first one is that there is too much emission of greenhouse gases, in particular of CO_2, due to human activities. We emit about two times more than nature can absorb. The second is that fossil fuels exist in finite quantities and will run out eventually.

The energy challenge (Fig. 20.2) is therefore twofold:

1. We should decrease the amount CO_2 emitted in the atmosphere. This can be done using carbon-free energy sources (renewable energies or nuclear energy) or by capture and sequestration of CO_2 when using fossil fuels. The timescale for this challenge is short.
2. We should progressively decrease our addiction to fossil fuels and reduce our consumption. This is required not only to retain fossil fuel reserves, but also to decrease the CO_2 emissions. However, while this is possible in rich countries, it is problematic in developing countries since energy is needed for economic development.

Energy must also to be used more efficiently and savings must be achieved. This is a high priority to fulfill the energy challenge presented above. Nanotechnology can be of great help in this respect in very many different ways.

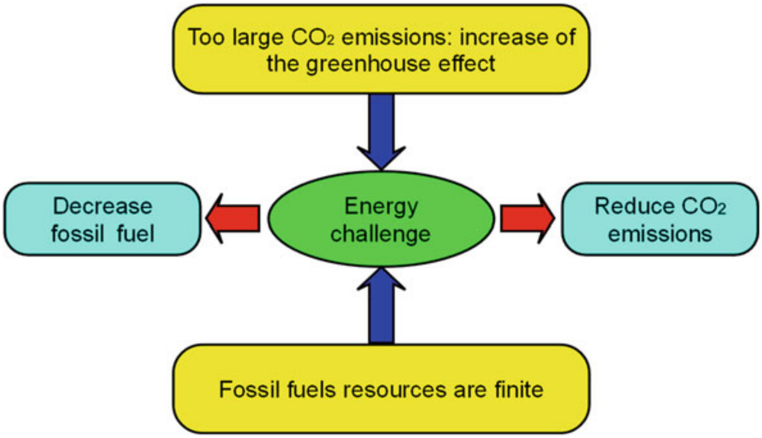


Fig. 20.2 Energy challenge: constraints and solutions

20.2 Nanotechnology and Fossil Fuels

Fossil fuels are today the dominant sources of energy. Before they are used by the consumer they are generally transformed through a series of processes, some of them being chemical processes. For example, crude oil has to be refined to produce gasoline for cars. The efficiency of the transformation processes in terms of yield and energy consumption is an important issue. Nanocatalysis, which is a natural extension of catalysis, plays an increasingly important role in this respect. Because of their economic impact, it is important to study ways to better prepare, characterize, and understand catalysts.

One way to still use fossil fuels while reducing carbon dioxide emissions in the atmosphere is to capture and sequester the CO_2 in an appropriate underground location. Carbon capture and sequestration (CCS) is now an important area of research and development, because it is a way to remove CO_2 emitted by large fossil fuel plants. Nanotechnologies are present in various stages: membranes to separate CO_2 from other gases, absorbents, molecular sieves, porous hybrid solids, etc. However, CCS can only treat a minor part of anthropic CO_2 emissions.

20.2.1 Petroleum Refining

Petroleum refining uses nanocatalysts in four main areas (Fig. 20.3): naphtha reforming, cracking, hydrocracking, and hydrotreating. Because of the large quantities of feedstock which are processed, any improvement of the yield has a major financial impact. A good catalyst has a large surface area to improve the efficiency of the interaction between the reacting products. The catalyst is usually a coating deposited

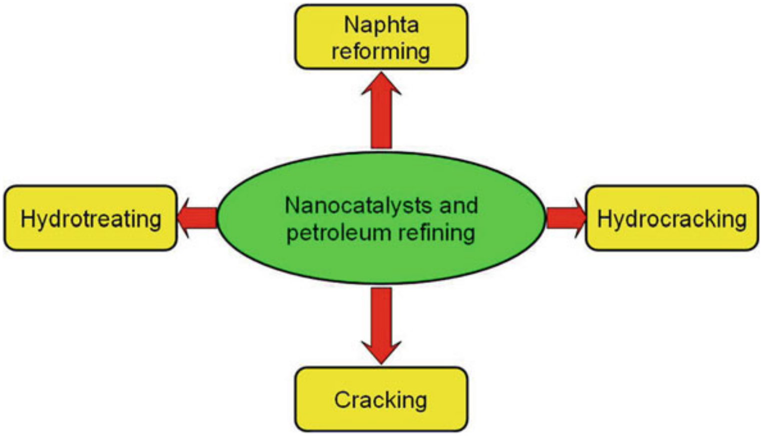


Fig. 20.3 In petroleum refining, nanocatalysts are used in four major processes

onto a passive high-area material, or a catalytic material structured to have a high surface area.

One of the first applications of nanocatalysts is naphtha reforming to produce high-octane gasoline. Since platinum (Pt) is used in the catalyst, there is a drive to reduce as much as possible the quantity of this precious metal used, while maintaining or improving the yield of the chemical reaction. This is done by dispersing Pt on an alumina support. It turns out that high-octane gasoline can be obtained if nanoparticles of Pt are used, but not when using larger size particles.

Cracking is a process in which the heavy molecules present in crude oil are broken down into smaller molecules more useful in applications. Although catalysts for cracking are usually large particles, new cracking technologies, like “fluid bed catalytic cracking” use nanoscale particles. Zeolite cracking catalysts utilize nanocrystals of zeolite dispersed in an amorphous silica–alumina matrix.

Hydrocracking is used when catalytic cracking is difficult. The feedstock is cracked in the presence of hydrogen. Generally, two types of catalysts can be used. Nanosize metal particles can be incorporated in a zeolite matrix or nickel, cobalt, or molybdenum oxides are put on an alumina support.

Hydrotreating uses extra hydrogen to remove contaminants (sulfur, nitrogen, metals). It also saturates olefins by hydrogenating double and triple carbon–carbon bonds. Cleaner products are produced in the end. Four metals are used in combination—Co, Mo, Ni, and W—to catalyze the reaction. Combinations of, for example, Co with Mo, Ni with W, or Mo with W can be used in the form of nanosize oxides or sulfides.

The future of oil may come from genetic breakthroughs in microalgae. If scientists succeed in producing synthetic oil from water, CO_2 sunlight and algae, the issue of oil reserves disappears. This dream may be realized in a few decades.

20.2.2 Syngas

Syngas (synthetic gas or synthesis gas) is also an important subject for energy applications. It is a mixture of carbon monoxide and hydrogen. It can be produced by various methods like steam reforming of natural gas, or gasification of coal. Conversion of syngas involves four main reactions (Fig. 20.4): water–gas shift, methanation, methanol synthesis, and Fischer-Tropsch synthesis.

In the water–gas shift reaction, carbon monoxide (CO) reacts with water vapor (H_2O) to produce carbon dioxide (CO_2) and hydrogen (H_2). The reaction was initially performed at high temperature with a catalyst, but today it is possible to do it at lower temperature using nanocatalysts such as Cu-ZnO.

Methanol is not used as a fuel in road vehicles because of its toxicity which is amplified by the fact that it can easily mix with water. However, it is an interesting hydrogen carrier and is also widely used in the chemical industry. Methanol can be formed from carbon monoxide and hydrogen. The catalyst used is generally copper in a metallic state on a ZnO substrate. For the low-temperature synthesis, the copper is present as a nanoparticle.

Methanol can also be decomposed at low temperature to produce hydrogen. This is interesting for the production on-site of hydrogen out of methanol stored in a tank. This is noteworthy for future applications such as small-size fuel cells supplying electricity to a laptop computer. Nanoparticles are present in the catalyst used for this low-temperature decomposition.

Methanation is a process where, in this case, methane is synthesized from carbon monoxide and hydrogen. This can be done using nanocatalysts, but the size of the nanoparticles can grow during the methanation process at high temperature and the efficiency can decrease.

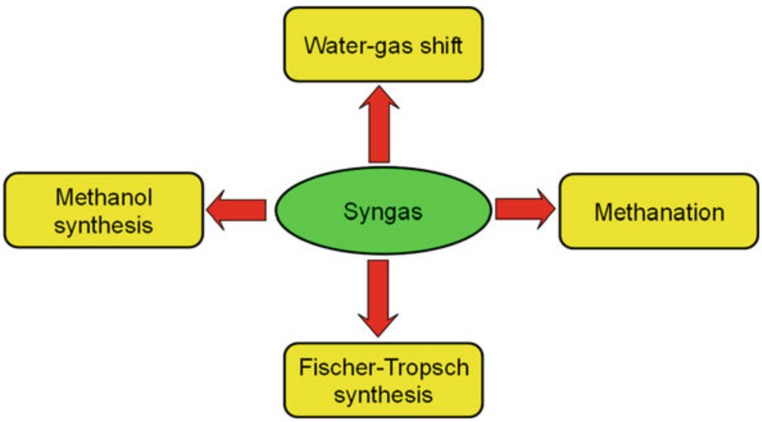


Fig. 20.4 Four major reactions where syngas is involved

Hydrocarbons can be synthesized from syngas by means of the Fischer–Tropsch reaction which has been used at an industrial scale in exceptional situations (by Germany in World War II, for example) for almost a century. However, nanocatalysis has been introduced only recently in this area, allowing operation at lower temperature in a slurry bubble column.

20.3 Nanotechnology and Renewable Energies

Renewable energy technologies are rapidly developing as part of the answer to the energy challenge. The main problem of renewable energy sources is that the energy density is very small, typically a million times smaller than oil and, furthermore, some of them are intermittent. To meet modern consumer demand more efficient methods of harvesting energy are needed. This requires sophisticated technologies where nanotechnology plays an increasing role.

Solar steam using nanoparticles

Scientists from Rice University (Houston, USA) have developed a new technology to produce steam using thermal solar energy and light-activated nanoparticles. The size of these particles is smaller than the wavelength of light but they are very efficient to capture the incident energy. Their tiny surface allows them to dissipate energy in a very efficient way. This energy is used to heat up water and change it instantly it into steam. Since there are a lot of nanoparticles present, steam is generated much more efficiently than by using a macroscopic energy transfer, such as solar concentration on water. One advantage of this technology is that it takes less room than a solar concentrator and has an overall efficiency of about 24 %. This is greater than photovoltaic panels where the usual global efficiency is about 15 %. Producing steam using this nanoparticles technology is interesting for sanitation and water purification in developing countries. It is also useful if a small amount of steam is needed in industrial processes. It is interesting to note that this technology is so efficient that it is possible to produce steam even from icy cold water.

Nanotechnology can be used in several areas and is sometimes essential to obtain efficient energy systems (Fig. 20.5).

As far as harvesting energy and transforming it into a more appropriate form (electricity, or potable fuels) is concerned, nanotechnology can be used to collect solar energy to produce electricity (photovoltaic cells), to make hydrogen, or perform artificial photosynthesis. Electricity can also be produced using thermoelectric phenomena from ambient heat. Nanocatalysts are used in biofuel production from biomass via syngas, a subject discussed earlier.

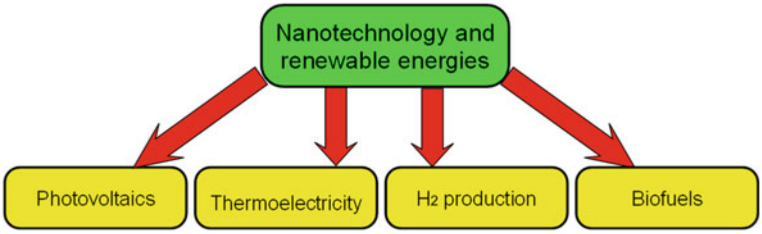


Fig. 20.5 Four domains where nanotechnologies are involved

20.3.1 Solar Energy

Photovoltaic cells are made with different semiconducting materials. Exposed to sunlight, the cell can create electron–hole pairs (excitons) which can be separated by a strong electric field present inside the cell. Collecting electrons produces an electrical current. Most photovoltaic cells used today are made of crystalline or polycrystalline silicon. This corresponds to a first-generation technology started in the 1950s. Until 2002, photovoltaic needs were met with by-products of the microelectronic industry. The strong demand in photovoltaic cells has led the industry to produce dedicated silicon for solar cells. With the present technology available at an industrial scale, a lot of energy is required to produce solar cells and the cost is still too high compared with other sources of electricity. Reducing the cost and the embedded energy is, therefore, a challenge for research, and nanotechnology is essential in this respect.

Second-generation solar cells correspond to thin films based on cadmium telluride (CdTe), copper indium gallium (di)selenide (CIGS), amorphous silicon, or micromorphous silicon. The production cost and energy consumption to make them turn out to be smaller than the first generation of solar cells, but the efficiency of conversion from sunlight to electricity is also smaller. The goal of photovoltaic technology studies is to produce low-cost solar cells with less material and less energy for processing. Thin films are therefore, the natural way to proceed to produce large and flexible areas. The active part of solar cells is often deposited on a substrate which has also to be low-cost and is often nanostructured. The ideal situation would be to have low-cost, long-life, and high-efficiency solar cells.

There is presently much effort to develop third-generation solar cells having a high-efficiency of conversion while keeping the cost the same or less. A nanostructuration of semiconducting materials can be used for that. Several paths are followed to reach this goal: multijunction photovoltaic cells: concentration of light on the cell; and thermal hybrid cells in which the extra thermal energy is used to increase the voltage and the collection of charge carriers. An example of a silicon solar cell is shown in Fig. 20.6.

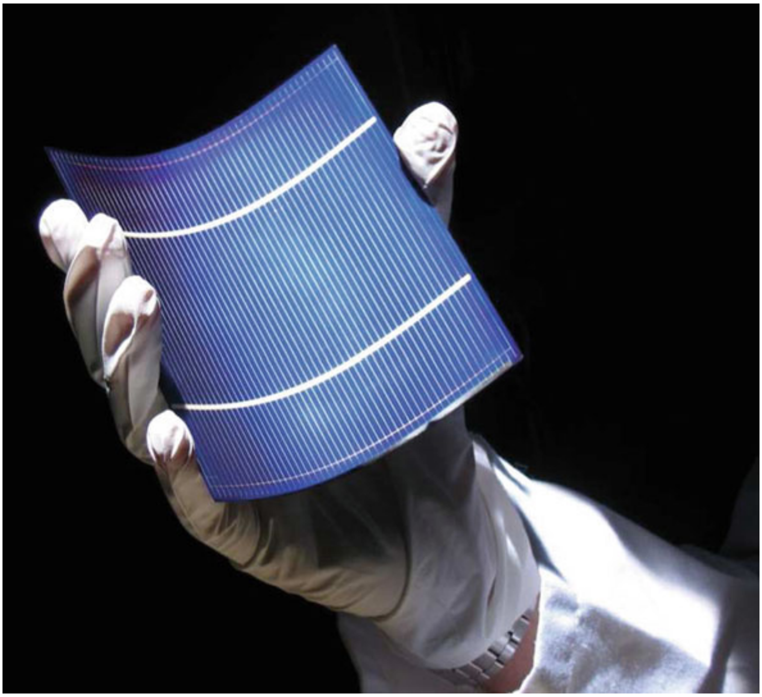


Fig. 20.6 Thin film silicon solar cell. Image courtesy of IMEC (Belgium)

Solar cells research: a dynamic growth

Many attempts are being made to develop new concepts to transform sunlight into electricity. For example, nanocrystals can be used in solar cells. The size of nanocrystal quantum dots can be tailored to obtain given absorption or emission wavelengths. Another possibility is to use nanocrystals of silicon producing two or three excitons per high-energy photon, whereas bulk silicon produces just one. Efficiencies twice as large as conventional solar cells can be obtained using nanostructured technologies. The nanocrystals have to be supported on a matrix of conductive polymers, or on the surface of mesoporous metal oxides like TiO_2*. Nanotechnologies can also be used to make thin layers and build tailored semiconducting structures. There are also studies on organic solar cells which can be produced as thin films. Some of them can be partially organic, like dye-sensitized photoelectrochemical solar cells, known also as Grätzel cells. Molecular engineering is used to obtain the most efficient dyes, which have to be properly self-assembled. The associated semiconductor substrate has also to be nanostructured. Organic or polymer cells (Fig. 20.7) aim to produce low-cost solar cells even though the efficiency of sunlight conversion is small, between 1.5 and 6.5 %. Other useful property, beside their low-cost, is that they are lightweight and flexible.*

Fig. 20.7 Organic solar cell on glass substrate. Courtesy of IMEC (Belgium)

20.3.2 Nanostructured Photovoltaics

Solar energy is the only source of renewable energy that has the capacity to fill humanity's technological needs. Major improvements in the conversion efficiency, cost, and stability of solar devices are needed for the increased application of solar energy.

Nanotechnology has considerable potential to realize cost reduction of photovoltaic cells, but must have cell efficiencies greater than 15 % and costs less than 100 €/m^2. The photovoltaic cell based on dye-sensitized nanoparticles of TiO_2 (Grätzel cell) can be fabricated in an inexpensive flexible plastic format.

There are many studies using various technologies to make efficient and competitive solar cells. The important point is that nanotechnology is more and more involved in this area of research. For example, nanotubes and fullerenes incorporated in the matrices of semiconductor materials greatly increase charge transfer and the efficiency of solar cells.

> ***Every silver-lined solar cell***
>
> *The future of lighter, cheaper, and more-flexible solar cells looks bright thanks to US research into silver nanoparticles. Scientists at Ohio State University have added the nanoparticles to their polymer semiconductor photovoltaic materials and observed a relative efficiency boost of 12 %. The discovery could pave the way to flexible organic photovoltaic with all the advantages of ease of manufacture and inexpensive starting materials.*

20.3.3 Wind Energy

Most of the power harnessed from wind uses large wind turbines. Small wind turbines are not widely used because they have a low-efficiency compared to large ones. This situation may change if nanomaterials are used to manufacture the blades. Carbon nanotubes make stronger and lighter wind blades. It also improves the efficiency of the turbine. In this technology, developed by a Finnish company, epoxy is used to bind the carbon nanotubes. Compared to traditional wind turbines, this technology increases power production by about 30 %. Carbon nanotubes are a hundred times stronger than steel, are lighter and the fabrication process can be automated. Therefore, the blades are about 50 % lighter than glass fiber blades. This gives the ability to increase the blade size, which in turns increases the energy which can be harnessed from the wind.

20.3.4 Thermoelectricity

Thermoelectricity is the phenomenon by which a difference in temperature is converted into electricity or vice versa. When electricity is generated from two metals at different temperature, it is called the Seebeck effect. It is the physical phenomenon used in a thermocouple to measure temperature. The converse is when a current is applied at the junction of two different metals, one side will heat up and the other cools down. The cooling property—the Peltier effect—is used in several applications.

As far as the energy domain is concerned, thermoelectricity is an interesting phenomenon to generate electricity from waste heat. It is also interesting for refrigeration because of better efficiency than conventional refrigeration methods. Furthermore, the quantity of pollutants generated is reduced. It turns out that semiconductors are better than metals as far as the Seebeck effect is concerned and nanoscaled-multilayered materials have a larger thermoelectric effect. Indeed, thermoelectric materials containing nanostructures are almost twice as efficient as existing thermoelectric materials. A factor of three in the performance, compared to conventional thermoelectric materials, would make thermoelectricity a competitive technology to produce electricity from waste heat and solar energy.

Nanotube thermocells

A great deal of thermal energy is lost industrial plants (chemical, automobile, nuclear, etc., as waste heat). Thermal energy is also lost along pipelines as well as in wastewater. Thermocells based on carbon nanotubes can be used to generate electricity from this waste heat. This has been developed in a collaboration involving US, Australian, and Indian laboratories. Compared to conventional thermoelectric cells, the yield can be up to three times larger. The cost per watt of this new technology is also smaller than the cost per watt of photovoltaic solar panels, and it works even if the sun is not shining.

In recent years, nanostructured materials have been discovered that have led to dramatic increases in performance of traditional systems. The differences come from the presence of interfaces that selectively allow electrons to flow across them, but block heat flow by lattice vibrations or phonons. Nanostructuring allows one to dramatically increase the density of the interfaces, which could improve the device performance more than three times that of conventional bulk materials. This may lead to nanostructured thermoelectronic materials and devices whose efficiencies are comparable to conventional engines and refrigerators.

20.4 Energy Vectors

An energy vector is a way to transport energy from one point to the other, but requires energy to be used in its production. Electricity and hydrogen are not *energy sources* but *energy vectors* because energy is needed to produce them. Electricity makes energy available at home but is usually produced in central power generation units. Hydrogen is another example of an energy vector.

20.4.1 Electricity

Electricity is increasingly used today because of its outstanding convenience. Hydrogen might be a future energy vector, useful among other things to store electricity produced by intermittent renewable energy sources, such as wind.

Electricity Transmission

About 7–10 % of electricity generated is lost in the transmission grid by heat dissipation. Transmission limitations can be responsible for blackouts throughout the world. Superconducting materials at high critical temperature have the potential to improve these limitations. They have no dc resistance and can accommodate about five times more power than copper cables with the same cross-section. The high-temperature superconducting material YBCO could fit this demand, but it is a brittle ceramic exhibiting large anisotropies in transport and physical properties, preventing any use over long distances. Nanotechnology provides the ability to control and tailor interfaces and multilayers with the hope to succeed in developing commercial products in the near future.

The use of engineered nanostructures at interfaces has potential for improving energy security based on advances in low-power electronics, efficiency energy in lighting, energy harvesting, and so on. The challenge is to create interfaces that are tailored to optimize transport of energy in forms of electrons, phonons, and photons. The possibilities include the fabricating interfaces using a wide variety of materials and chemical combinations, along with interface shapes patterned at the nanometer length scale.

Nanotubes Wires for Power Transmission

A major challenge is to develop new transmission line materials that are of lighter weight and lower loss than copper. Individual carbon nanotube fibers have an electrical conductivity better than copper at only one-fifth the weight and negligible eddy current loss. In addition, the mechanical strength is 10 times higher than other electrical conductors. Present production of single-wall nanotubes typically results in fibers that are 100 nm in length and have widely varying electrical conduction properties.

Power cables (superconductors or quantum conductors) using CNTs could be used to rewire the electrical transmission grid, and enable continental-and even worldwide—electrical energy transport. In addition, they could replace aluminum and copper wires in the windings of electric motors and generators. However, there are many scientific/technological challenges to be overcome: for example, how to manufacture CNTs cost-effectively into ropes and fibers with the desired electronic properties?

Lighting

The use of semiconductor-based light emitters for general illumination, composed either of inorganic (LEDs) or organic materials (OLEDs), is a rapidly developing technology that offers the potential of immense energy savings (Fig. 20.8). However, a number of technology obstacles must be overcome in order that solid-state lighting reaches its potential. The majority of these obstacles involve understanding electron–hole recombination at nanoscale interfaces.

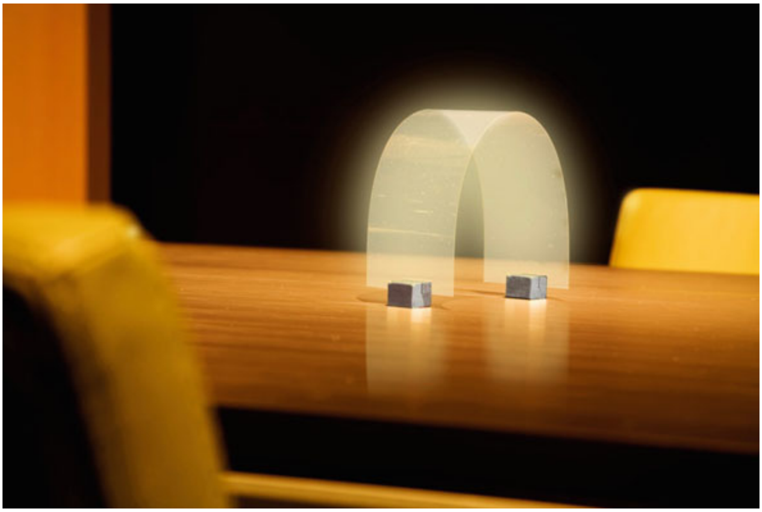


Fig. 20.8 Future vision of fordable lights based on OLEDs. Image coutesy of IMEC (Belgium)

20.4.2 Hydrogen

Hydrogen production can also benefit from nanotechnology. Hydrogen is the smallest and lightest of the atoms.

Synthesis

Hydrogen is mostly obtained today from natural gas but it is desirable to use more environmental-friendly processes. Electrolysis of water using electricity produced by renewable or nuclear energy is interesting because no CO_2 or other pollutants are emitted. New methods are at an early stage of development to produce hydrogen from water splitting: solar thermal, thermochemical, or photoelectrochemical water splitting. Photoelectrochemical water splitting, also called artificial synthesis, has a better efficiency when nanomaterials such as nanosized semiconductor particles are used. Nanostructured materials are expected to be more efficient photocatalysts. They are modified with the aim of adjusting the properties of the photoelectrodes to increase their efficiency. It turns out that nanosized semiconductor materials for hydrogen production from solar energy improve the efficiency of water splitting by photocatalysis techniques.

Hydrogen Storage

Hydrogen is one way to store electricity produced by intermittent energy sources such as wind or Sun. The energy density per unit of mass is large, about three times that of gasoline but unfortunately the energy density by unit of volume is small, even for liquid hydrogen. Apart from compressed hydrogen at pressures up to about 800 bars, one of the challenges of hydrogen storage is to find low-cost materials for storing large quantities of hydrogen in a small volume that can be repeatedly recharged. So far there is no material meeting the desired requirements but nanomaterials open possibilities, which have to be demonstrated at a commercial scale, to store large quantities of hydrogen per unit of volume, while being able to store and release hydrogen at ambient conditions and at the necessary speed for their target applications such as in automotive applications.

Producing Hydrogen from Sunlight

A promising route is to use of the energy of sunlight to split water into its constituent elements of oxygen and hydrogen. Solutions could be based on tuning the size of the catalyst particles into the nanometer regime as well as the addition of nanoscale additives using semiconductor catalysis such as titanium dioxide and ultraviolet light.

Fuel cells

Nanotechnology plays also a key role in fuel cell development. Fuel cells are energy converter devices using a fuel source like hydrogen or methanol to produce electricity by controlled chemical reaction rather than by combustion. The fuel reacts with oxygen from the air on electrodes separated by a membrane or an electrolyte. The electrodes act as catalysts for the chemical oxidation (anode) and reduction (cathode) reactions. The membrane or electrolyte is designed such that electrons cannot go through and hence the electrons are channeled into the external circuit and produce power. For example, in the proton exchange membrane fuel cell (PEMFC) technology there is a proton-conducting membrane separating the two electrodes but preventing electrons to flow through. Nanostructured materials improve the properties of the membranes and electrodes. Nanocomposite and nanostructured materials allow a fine tuning of the catalytic and ion transport properties of fuel cells. The size of the nanoparticles depends upon the technology and has a great influence on the final performances of the fuel cell. However, during cell operation a change of the nanoparticles' size can occur, which can decrease the catalytic efficiency.

Nanostructured Materials

Nanostructured materials offer exciting opportunities for the development of enhanced power storage and conversion. Fuel cell catalysts fabricated with nanoparticles of ruthenium–platinum (Ru–Pt) are outperforming traditional catalysts. They are much more resistant to carbon monoxide poisoning, operating 50 times longer than traditional fuel cell catalysts.

Nanostructured architecture employing a highly 3D structuring for power storage (batteries, fuel cells, ultracapacitors, photovoltaics) provide many advantages over existing technologies to minimize power losses, improvement charge/discharge rates, and enhance energy densities.

20.5 Energy Storage

Energy storage is an important issue and is currently the weak point of the energy domain. Fossil fuels provide an intrinsic storage of energy but this is not the case for wind or solar energy. We have already addressed hydrogen storage as one possible solution. Nanostructured materials can be useful for energy storage in the form of heat or chemical batteries.

Portable device batteries

About 1.1 billion of mobile phones are produced and sold each year. This corresponds close to 40 phones per second. By the end of 2011, there were about 6 billion subscriptions globally. There are more than a billion of portable computers around the world and tablets are now a fast growing market. All these mobile devices have a battery. The global market for portable devices batteries corresponds now to an energy stored of more than 15 GW/year. Any small improvement has a great impact at the global level because of the large number of these devices. There is, therefore, an enormous benefit to be obtained by increasing the energy and power density of batteries, and to increase their performance and their lifetime. For this a good durability of the electrodes under repeated charge and discharge cycles is needed. Because people want smaller and smaller devices, reducing the size and weight of a battery is a key issue. Li-ion technology today dominates portable device batteries. Nanotechnology can be used to nanostructure the electrodes of a battery. This increases the surface in contact between the electrode and the electrolyte. It also decreases the diffusion path of ions inside the active materials. Both effects have an impact on the power density of the battery. In the future, it may be possible to manufacture batteries by a printing process. An increase in the numbers of hybrid vehicles, plug-in hybrids, and electric vehicles will require more and more batteries with storage in the range of 10–30 kWh. There are already 7 million hybrid cars on the road but this number, together with the new plug-in hybrids and electric vehicles, is expected to increase rapidly.

20.5.1 Electrochemical Storage

Electrochemical energy storage is widely used, especially for portable devices. This means mostly batteries and also supercapacitors (Fig. 20.9). Electrochemistry of batteries is a difficult domain where the microscopic state of the electrodes plays

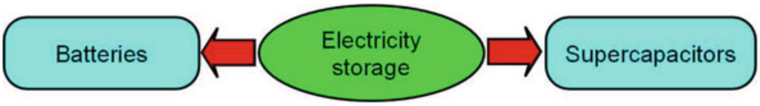


Fig. 20.9 Two domains of electricity storage where nanotechnologies have a key role

a key role and nanotechnology is now fully used in this field to improve performance. The particle size, the electrode structure, its texture, etc., are properties that can be controlled at the nanoscale to tailor electrochemical energy storage devices to specific applications. Because of the increased reactivity of nanoparticles compared to larger particles, due to their large surface-to-volume ratio, new reactions can take place and conventional ones can be boosted. For example, the number of electrons exchanged in a Li-battery per transition metal atom is much larger and an improved storage capacity is seen when nanoporous carbon is used in the electrodes.

Nanocarbons, which are interconnected pieces of graphene planes functionalized with heteroatoms, have a great potential in Li-ion batteries and supercapacitors. In supercapacitors, the porosity and the pore size have a large effect in controlling final capacitance.

20.5.2 Nanomaterials for Hydrogen Storage

Nanostructured materials promise to improve the conventional processing techniques by allowing them to be achieved at lower pressures and ambient temperatures. The best nanomaterial would achieve an optimum compromise between having the hydrogen too weakly bonded to the storage material, resulting in a low-storage capacity, and too strong a bonding to the storage material, resulting in high temperatures to release the hydrogen. Candidate materials are complex metal hydrides which have an intermediate bonding of the hydrogen and nanostructured carbon-based materials, such as carbon nanotubes.

20.6 Smart Energy Consumption

Close to half of the total *final energy* (48 %) used in Europe is devoted to heating. Heating, cooling, and refrigeration in residential and commercial building in the United States, for example, represents, respectively, 46, 9, and 10 % of the total energy consumption. Therefore, increasing the efficiency of thermal heating and thermal insulation of buildings is an important issue. Furthermore, the use of renewable energies requires efficient use of the energy that is generated.

Nanotechnology comes into play in several areas: in the low-emissivity coating of glass windows or nanoporous materials, and silica nano-aerogels for thermal insulation, for example. Smart windows, which are windows where the amount of visible light and solar energy coming into the buildings are actively controlled, rely on *chromogenic* technologies. In these technologies, the optical properties of the glass of the window can be changed by a signal controlled by measurement of the indoor temperature. Four major chromogenic technologies are possible: *electrochromic*, where the monitoring signal is based on an electrical voltage or current; *thermochromic,* which depends on the temperature; *photochromic,* depending upon the light irradiation; and *gasochromic,* which depends upon the exposure to oxidizing or reducing gases. Nanostructures turn out to play an important role in electrochromic materials and it is important to master processes of thin film deposition.

Electrochromic windows help to save energy

Using electrochromic windows can generate significant energy savings for internal temperature and lighting control. If the window is controlled for solar heat gain, the Californian Energy Commission has shown that an annual reduction of about 19–26 % of the peak cooling load is registered compared to the best window technology. If the windows are controlled for visual comfort, the energy for lighting could decrease by about 48–67 %. In hot countries, electrochromic technologies have a gain both in lighting and cooling, while tinted and reflecting glass windows decrease the cooling energy needs but increase the lighting demand. On the contrary, clear glass windows decrease the lighting demand but increase the cooling one.

In the early days of electricity, lighting was a large part of household electricity consumption. This share has decreased but still remains important. For example, in the European Union, close to 100 TW of electricity goes into lighting. In the United States, lighting represents about 22 % of the electricity consumption. There is a major drive to reduce this consumption using more efficient technologies. Light-emitting diodes (LEDs) are between about three and six times more efficient than traditional lighting. They are based on nanoengineered-layered structures of InGaN/GaN. Progress is still needed to increase the efficiency but a good understanding of the mechanisms at the microscopic level are needed to tailor the manufacturing processes.

The perspectives of nanomaterials in future energy technologies are represented in Fig. 20.10.

We shall come back to the sector of housing and transportation in Chaps. 21 and 22.

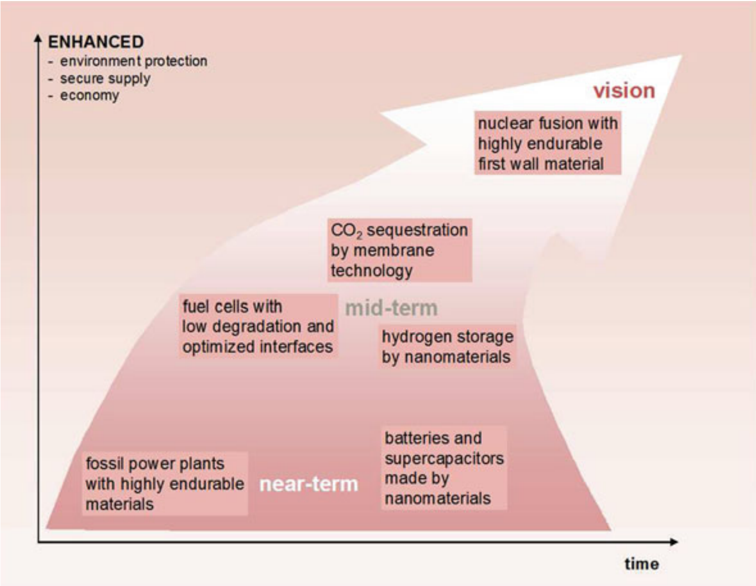


Fig. 20.10 Perspectives of nanomaterials in the energy domain

20.7 Conclusion

Many energy sources are now available to meet the demands of consumers (Fig. 20.11). Fossil fuels are still dominant and are likely to remain so for some time. However, their reserves are finite, their price is expected to increase, and they have the key drawback of emitting CO_2 when they are burned.

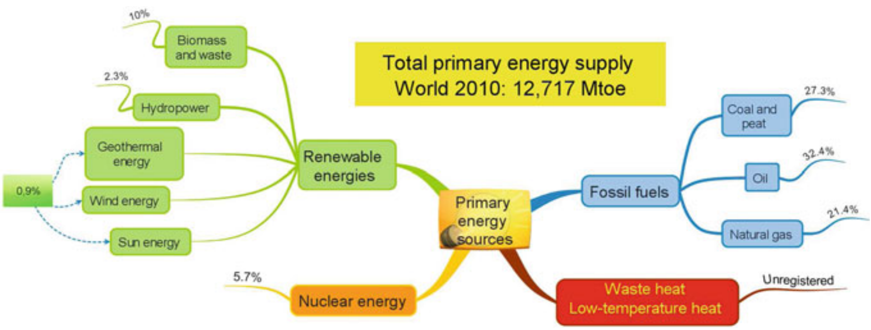


Fig. 20.11 Primary energy sources The total primary energy supply in 2010 was 12,717 Mtoe. The share of the different energy sources is indicated. Waste heat and low-temperature heat are energy sources used in heat pumps but are not registered for the statistics. Data from www.iea.org

Waste heat and low-temperature heat are not taken into account in the statistics. Energy can be harvested using heat pumps, a technology which has a bright future. This will contribute to meeting the increase in electricity demand.

It is necessary to reduce our energy consumption and to increase the yields at all the steps of the energy chain. Nanotechnology is perfect to help meet this demand. There is today a strong drive to develop renewable energy sources. They have unfortunately a low-energy density and some of them are intermittent, like wind. Technical progress must be made to counteract these drawbacks. In almost every area of renewable energies nanotechnology enables significant improvements. Biomass and hydraulics are the renewable energies that have been used for a long time: biomass essentially to produce heat and hydraulics to generate electricity. Both of them contribute today to just over 10 % of the primary energy share while other renewables still have a negligible contribution. Harvesting the energy coming from the sun and transforming it in to electricity is probably one of the greatest challenges of research where nanotechnology can be used to make breakthrough. Indeed, the amount of energy received from the sun is 10,000 larger than the present energy needs of humanity.

It should be observed that the renewable energy consumption per inhabitant is almost the same today as it was two centuries ago and today: about 0.2 toe. Whereas this was the only energy consumption two centuries ago, today the average energy consumption per inhabitant is about 1.8 toe. The extra 1.6 toe/inhabitant is coming essentially from fossil fuels with a very small contribution from nuclear energy. This extra energy usage is at the origin of the strong economic development of humanity since the beginning of the industrial revolution.

Chapter 21
Housing

A large part of the world's energy consumption is used in the housing and transport sectors. Any reduction in their energy consumption, for the same quality of product or service, is highly worthwhile. Housing can benefit from nanotechnology in many areas and we shall describe some of them here.

Nanotechnology has numerous present and future applications in housing. The development of renewable energy sources requires better building insulation because these energy sources have a much lower energy density than fossil fuels so their implementation needs to be matched with a reduction in energy consumption. Evolving toward green buildings will also reduce CO_2 emissions. Nanotechnology is not only an alternative solution to other technologies but in some cases is the only solution to respond to specific technical demands. Consequently, development of nano-optimized high-performance materials and smart materials for the building industry is urgently required.

Nanotechnology can make external building materials more efficient and indoors will save energy and life more comfortable for the occupants.

21.1 Nanotechnology in Construction Engineering

Construction engineering has relied on cement and concrete for nearly a century. Cement is a binder material which hardens like a glue. "Portland" cement is the most commonly used type of cement: it consists of limestone, clay, and gypsum that become hydrated due to a chemical reaction with water, making the material hard and extremely durable. Concrete consists of cement and cementitious materials, mixed with aggregates, additives, and water. Concrete offers a large compressive strength but has a poor tensile strength properties, and so reinforcements are needed if it is used in tensile stress applications, usually steel in the form of reinforcing wires or bars.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_21, © Atlantis Press and the authors 2014

Innovation in modern cement-based materials is often based on admixtures or chemical additives. Admixtures like silica fume, fly ash, or blast furnace slag—by-products from heavy industry—are used to boost performance: mechanically and against severe weather and corrosive conditions. However, the size distribution of such admixtures is of critical importance as they affect the reaction kinetics and the density of the final concrete product. A smaller grain size is beneficial and offers concretes with superior strength, and hence nanotechnology has high potentials for concrete engineering and structures. The specific active surface of admixtures is increased via grinding or milling techniques to the nanometer size. The comparatively high strength of modern concretes is based on crystal structures in the nanometer range.

Methods of construction are developing quickly. For example, as far as energy is concerned, 60 % less energy is needed to make one ton of concrete today compared to 1950. Over the same period, the CO_2-emission associated with cement manufacturing has been reduced from nearly 1 ton of CO_2 per ton of cement, to about 575 kg of CO_2 emission per 1 ton ordinary Portland cement (OPC), still the most utilized concrete binder system.

Nanotechnology is the basis for the development of new, highly-efficient products and technologies. It also enhances "traditional" technologies like those used in construction engineering; including construction materials like concrete, whose strength and durability are based on nanoscale physical, chemical, and mineralogical effects.

Nanostructuring by High Kinetic Processing (HKP), mechanical alloying (MA) or High Energy Milling (HEM) or Reactive Milling (RM) and/or subsequent solid state synthesis have already been proven to offer an economic and environmentally friendly technique to be successfully applied in large volume processing for cement or concrete. Major constitute phases of cement can be chemically transformed, and thus their effect on early strength or degradation can be tailored, for example, in the production of High Performance Portland Cement (HPPC). Achievable strength has been proven to exceed 1 GPa, 20 times greater than the 35–55 MPa of conventional Portland concrete.

The Rosenthal public bridge

In 2012 the "Rosenthal" public bridge at Olpe in Germany (Fig. 21.1) was built where high strength has been achieved through the utilization of activated GGBS (ground granulated blast slag; a waste product) giving a CO_2-emission saving of 20 %. Globally applied, a CO_2-saving of 0.5 % would be easily achieved with a marginal extra cost (<10 €/ton of concrete). Additionally, due to a substantial pore refinement, where the pores are sized (<30 nm, so water cannot penetrate, see Fig. 21.2), a significant increase of durability will result. In 2013, another demonstrator of advanced concrete so called "FuturBeton" based on nanostructured cement "FuturZement" has been set up at Siegen in Germany, see Fig. 21.3.

With such nanoscale-controlled material, construction industry in the future can build eminently faster, sleeker, higher, more cost-effective, more durable, and also significantly environmentally-friendlier structures.

Fig. 21.1 Concrete prefabrication: set-up of the Rosenthal bridge at Olpe in Germany on 14 November 2012

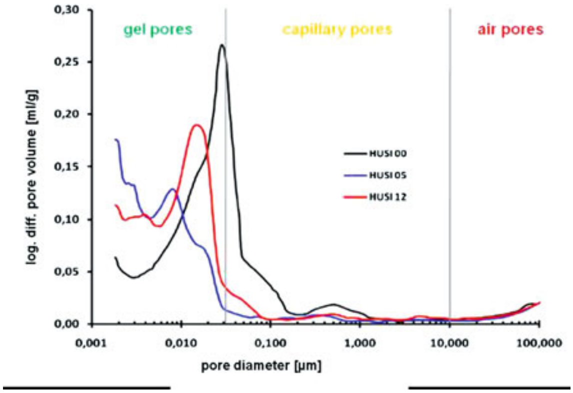


Fig. 21.2 Mercury Intrusion Porosimetry (MIP): GGBS untreated (*black*) and HKP-GGBS formulas (*red* and *blue*). Image courtesy Zoz Group, Germany

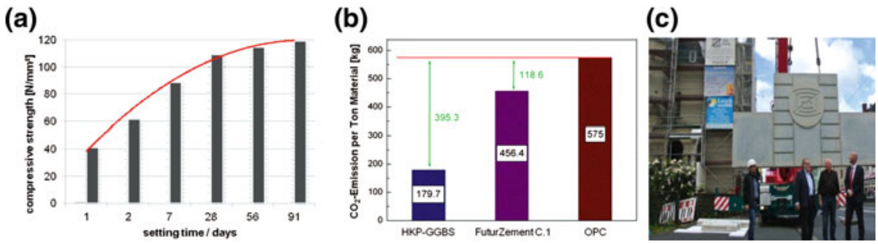


Fig. 21.3 **a** strength profile of Future Concrete “Futur Beton”. **b** CO_2-emission caused by the manufacturing of HKP-GGBS, Future Cement “FuturZement” C.1 and Ordinary Portland Cement (OPC). **c** Smaller demonstrator of about 10 tons set-up at Siegen in Germany on 21 June 2013. Image Courtesy Zoz Group, Germany

21.1.1 Potential for Nanoconcrete Materials

Concrete is by volume (over three million cubic meters per year) the most economically important material produced by humans. It is still the basis of all our modern infrastructures. Improvements by nanotechnology in this field will, therefore, have enormous technological and economic consequences.

The opportunities for improving properties of cement and concrete with nanotechnology far exceed the simple use of "classical" microparticles. By manipulating chemically and physically the structure of cement-based materials, using integrated technologies on the nanoscale, properties usually found only for engineering or fine ceramics can be achieved. At the same time, "smart concretes" can be developed, which exhibit mechanically-supporting and climate-regulating properties, or which can contribute to air-pollution control.

In addition to upgrading their properties, nanotechnology also has a positive effect in the manufacturing of cement-based materials. A major issue in the use of cement-based building materials is the high demand for fuel energy associated with cement production and the high CO_2 volumes released of 0.6 kg/kg of cement. This can be improved by the use of particle-optimized cements, using inert additives like slag sand, or nanosized silica.

A first step is toward ultra-high-performance concretes, which not only show a steel-like strength but are more durable against weathering. Much less materials is used for production of large building structures when high quality concretes are available.

Figure 21.4 schematically illustrates the multiscale character of building materials and structural design from the nanometer scale to the macroscale.

21.1.2 Nanocements and Concrete Developments

Cement has always been a material with nanoscale structures. With its physicochemical interactions that evolve with time it is a complex nanomaterial. The formation of concrete starts with the reaction of cement, other reactive fine additives, and water. Calcium silicate hydrate nanocrystallites act as nuclei for the cement phases and initiate and accelerate the hydration reaction. The reaction products develop within days and weeks to the microstructure shown in Fig. 21.5, which consists of dense nano- and microstructure of needle-like calcium silicate nanocrystallites phases that are responsible for the strength and durability of the concrete. The nano-SiO_2 seems to affect the cement microstructures and consequently the mechanical strength even in small quantities. Due to the small size of the crystallites, a high density of seeds is achieved. In addition, nanoparticles in the future might plug the voids and act as fillers. Finally, nanocrystals speed up early concrete hardening (crystallization process) significantly.

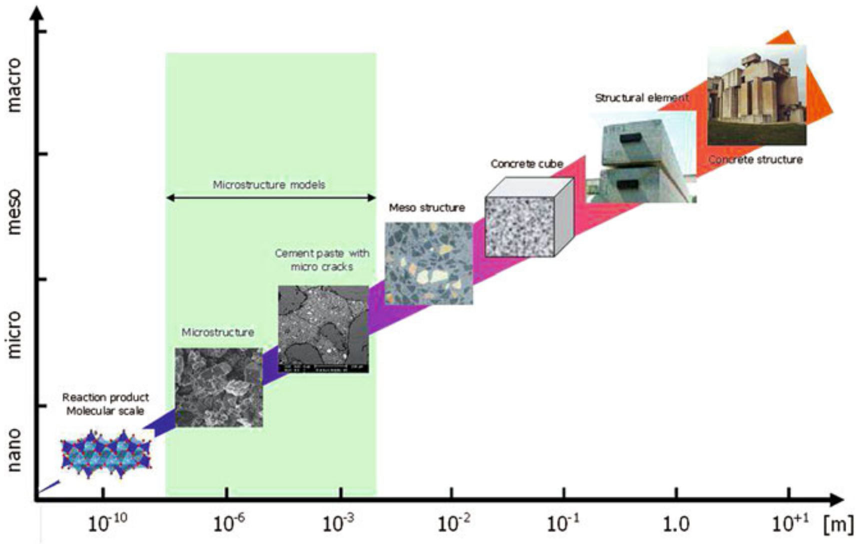


Fig. 21.4 Scale effect in building materials and structural design. Image courtesy K. van Breugel, TUD

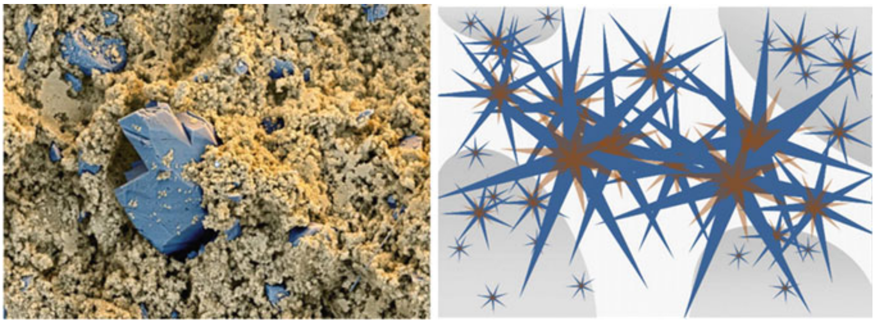


Fig. 21.5 Nanoparticle distribution in the nanoconcrete. Image courtesy of BASF SE Ludwigshafen

The density of the microstructure depends on the physical grain arrangement of the fine particles and on the so-called "water-cement ratio." Using nanofine SiO_2 leads to an even denser and stronger microstructure. Figure 21.6 shows at the bottom the very dense and capillary-pore-free, nearly ceramic-like microstructure of a packing-optimized ultra-high-strength concrete. Its compressive strength reaches the compressive strength of steel, up to 20 times the value achieved for normal concrete.

Nanomaterials play an important role in different applications, not only in classic Portland and calcium aluminate cements but also in the field of special cements like those used in dental applications. Nanobased cements can have better ecological and economic performance with reduced lifecycle costs. They can be easy to apply and

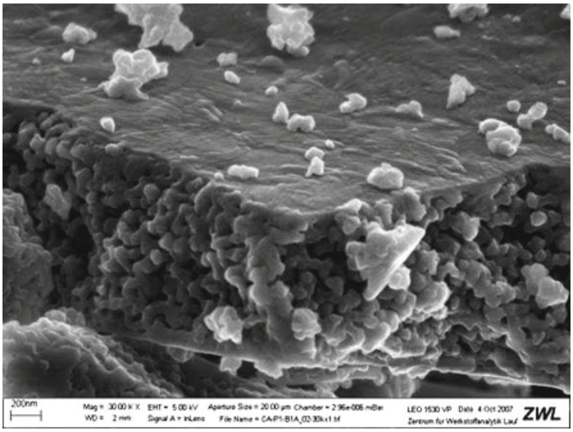


Fig. 21.6 Possibilities of using nanomaterials in cement and concrete. Image courtesy of BASF SE, Ludwigshafen

offer improved reparability than conventional cementitious products. In addition, nanocrystals speed up early concrete hardening significantly, making the production of precast elements more efficient and flexible in terms of time, cost, and energy consumption; and so can speed-up time-critical concrete work for roads, bridges, railways, and airstrips.

The production of high-performance concretes enriched with micro and nanoparticles requires very efficient flow improvers—nanoplastizers—so that the concrete can be liquefied in spite of low water content and so that it can be easily manipulated. In addition, to the compressive and tensile strength, the elastic modulus, the shrinkage on settings, and the resistance to attack by atmospheric acids are all improved. For this research, nanoscale analysis methods are of great importance like the atomic force microscope, which allows directly measuring the forces between the individual nanoparticles with and without the presence of flow improvers. As well as these experimental and technological developments also the evolution of multiscale (numerical) modeling techniques further discloses the potential of micro- and nanoparticles for application in the construction industry.

Nano-enhanced cement and concrete will be stronger, more durable, self-healing, air-purifying, fire-resistant, and easier to fabricate. Nanoparticles under investigation include nanosilica carbon nanotubes (CNTs) and carbon nanofibers (CNFs).

Nanoparticles are able to improve the durability of reinforced concrete by increasing the density of the concrete and hence its capacity to protect the steel reinforcement against corrosion by preventing moisture from reaching steel. Smart hybrid nanoparticles may be even more effective in protection of the steel. A drop of the pH in the concrete due to natural carbonation will cause the hybrid particles to release a healing agent while restoring the alkaline environment, thus preventing or postponing the occurrence of corrosion of the embedded reinforcing steel.

The tensile strength of concrete could be improved in the future by using textile fibers in place of steel. This would have advantages in weight, cost, corrosion resistance, and the lifetime of the concrete structure. Carbon nanotubes may be able to

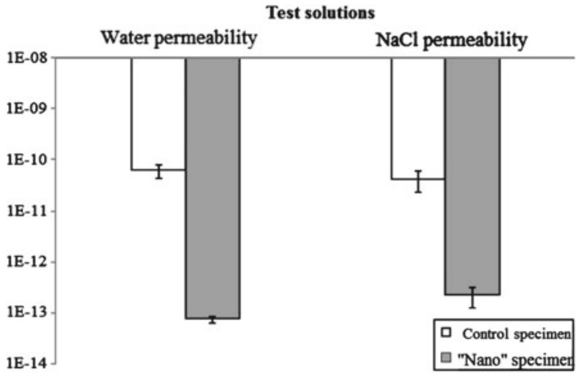


Fig. 21.7 Effect of nanosized particles ("hybrid vesicles") on the permeability of cement paste (after Koleva et al.)

offer cheap, widely-dispersed reinforcement to reduce the overall amount of concrete needed to fulfill a structural goal.

Figure 21.7 shows how the addition of nanoparticles to cement paste can result in a decrease of the permeability of the material, and hence enhance the resistance against ingress of substances that may impair the durability of concrete structures.

21.1.3 Smart Materials: Building Materials with Multiple Benefits

Nanotechnologies can produce building materials with additional functional capabilities: smart materials. Nanoscale titanium dioxide (TiO_2) can be added to concrete as particles or as coating to act as a photocatalyst (Fig. 21.8). When exposed to ultraviolet radiation, the TiO_2 induces processes, that which decompose many air pollutants. An additional effect is the breakdown of dirt on the surface, leading to self-cleaning properties; the materials can also attract water to help wash away dirt particles. Considering the enormous areas contained in the faces and roofs of existing buildings, this simple procedure provides achieving a major, sustainable contribution to air-pollution control; see Fig. 21.8.

"Smart concretes" based partially on nanomaterials, can also lead to heat-adjusting building faces and roofs, with auto-controlled reflection and storage properties. With other combinations of properties, road surfaces can be made skid-proof, quiet, and pollutant-reducing.

The dispersion of organic materials with nanoscale particles, where nanoparticles are combined homogeneously and inseparably with the organic dispersion and the nanobinder, enables coatings to combine different advantages of conventional coating types (Fig. 21.9). This results in a composite coating which offers an optimal balance of surface hardness and elasticity, increases resistance against dirt, cracking

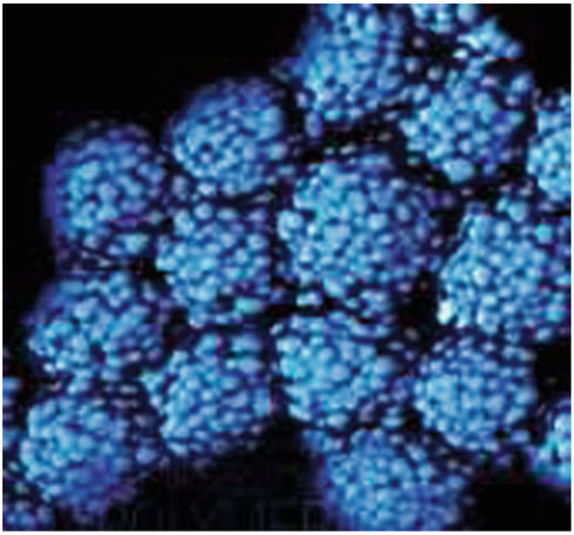


Fig. 21.8 Photocatalysis for cleaning air and walls: silica nanoscale particles embedded in an organic polymer matrix. Courtesy of BASF SE, Ludwigshafen

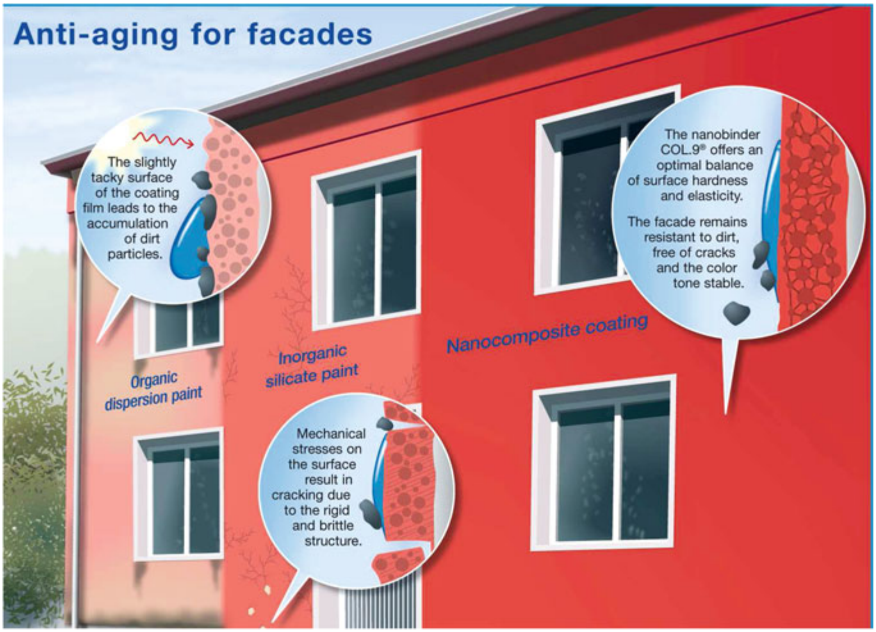


Fig. 21.9 Inorganic nanoparticles homogeneously incorporated in polymers provide ideal features for facade coatings. Image courtesy of BASF SE, Ludwigshafen

and scaling, improves color retention, and enables faster drying after rain and thus prevents the formation of mould.

The factors hindering the penetration of new nano-enhanced products in the construction world include higher costs for nanomaterials and associated process techniques, the lack of availability of large volumes, poor awareness of engineers and architects of these new materials and technologies, and finally the skepticism of society and builders in the use of new nanomaterials for reasons of reliability and human health.

21.1.4 Nanofillers in Construction Engineering

Nanofillers are excellent reinforcements for construction materials, owing to their extremely small filler particle size and their large surface area, and when well dispersed they have a great impact on materials properties such as compression strength, electrical conductivity, transparency, processability, and flame retardancy. Fillers can be widely used in construction engineering in adhesives and sealants, in paints and coatings, in plastics and rubbers, and in concrete (Fig. 21.10). In construction, nanocarbons can help to make new, lighter and stronger, concrete materials which last longer and are more able to resist shocks such as those generated by earthquakes because of enhanced ductility.

Nanofillers can also influence the manufacturing of construction materials through control of rheological properties, such as in ensuring free flow of powders and prevent the settling of pigments.

In addition to the conventional mineral fillers, synthetic nanofillers, the so-called ultra-fine grades, are now gaining importance because they allow the production of smaller particle sizes with controlled surface chemistry or tailored chemical functionalization. In addition, new innovations are being developed: organic-inorganic

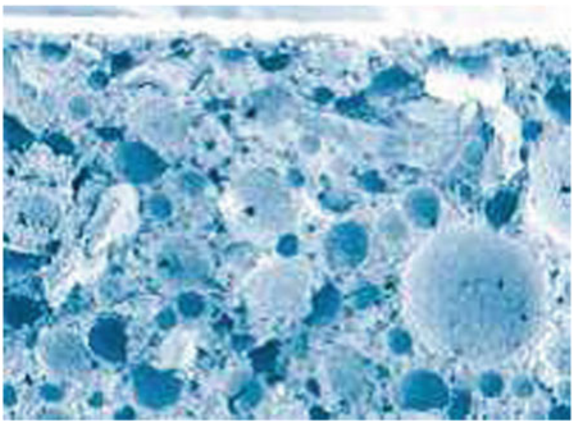


Fig. 21.10 Scanning electron micrograph of the cured isolation mortar: the *black* rubber granules with different particle sizes are embedded in a cement matrix. Image courtesy of BASF SE, Ludwigshafen

hybrid nanofiller materials such as polymer-CNTs in concrete, providing for longer lifetimes, improved reliability and excellent performance.

The spectrum of nanofillers is very large and parameters to play with are type (spherical, rod-shaped, or flakes), particle size ($<100\,\text{nm}$) to determine the specific surface area, composition, particle geometry (0-1-2-3 dimensional), chemical coatings, and functionality. Tuning of materials properties offers great potentials for innovations in construction engineering. For example, elongated nanostructures such as carbon nanotubes with high aspect ratios increase the reinforcing ability of the nanofiller to the surrounding matrix material. Therefore, nanotubes or elongated nanofillers excel over spherical particles in terms of reinforcement. Nanotubes, nanowhiskers, nanorods, nanowires, and nanofibres can be considered as nanoscopic reinforcing filler materials. Reinforcement of concrete using carbon nanofibres and carbon nanotubes allows for new high performance nanocomposite materials to be obtained, with excellent properties in fracture prevention, by resisting matrix cracks.

A variety of filler materials are available for integration in construction materials: some are minerals, others synthetic/polymer nanofillers, and finally aerogels such as fumed silica, precipitated calcium carbonate, titanium dioxide, organically modified nanoclays, carbon black and its 2-dimensional counterpart called graphene, carbon nanotubes (CNT), aerogels, and natural nanoclays.

21.1.5 Textiles in Construction

Construction textiles play an important role in the modernization of infrastructures and aesthetics for new and refurbished buildings. New textile materials and innovative techniques for their deployment offer huge potential in the construction of ecofriendly buildings that combine great design freedom with lightness and economy.

In order to reduce energy consumption and improve performance and to have greener, cleaner, lighter, high-performance, and sustainable construction structures, technical textiles are expected to contribute to the transformation of the construction sector into a modern, competitive, knowledge-intensive, and sustainable activity.

Finally, smart textiles, created using nanotechnology-derived sensors embedded into textile structures, find application in the monitoring of buildings, to sense material damage or stress, or the effect of temperature changes; and in geotechnical applications, to monitor distributed strain in slopes with stability problems.

21.1.6 Technical Ceramic Materials

Nanoceramics and ceramic coating materials bring new functionalities to construction ceramics. They find applications in floors, wall tiles and sanitary ware products (Fig. 21.11). Their main advantages over traditional counterparts are self-cleaning,

Fig. 21.11 Applying a nanocoating is straightforward: just spread and de-aerate. The very next day the tiles can be laid

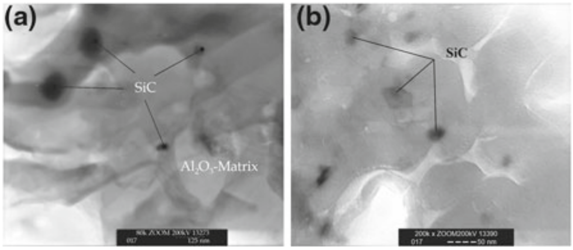


Fig. 21.12 **a** Al_2O_3-SiC nanocomposite powder, TEM Image courtesy Zoz Group, Germany. **b** Al_2O_3-SiC nanostructured plasma spray coating, TEM Image courtesy Zoz Group, Germany

anti-bacterial, hygienic, and scratch-resistant features. The problem is their high cost, limited availability on the market, restricted choice, and consumer reservations.

Nanostructured ceramics can substantially improve mechanical properties. The most utilized technical ceramic is alumina: aluminum oxide. Alumina is cost-effective and exhibits a very high hardness. However, during consolidation it forms a coarse grain structure resulting in high brittleness. By adding a nanoscale silicon carbide (SiC) phase, grain-growth can be substantially decreased resulting in quasi-ductile alumina. The left-hand side of Fig. 21.12 shows a micrograph of nanostructured alumina–SiC composite powder and right-hand side of Fig. 21.12 the same material after consolidation by plasma spray coating, proving that the SiC phase has hindered grain-growth by pinning of the grain boundaries.

The interesting challenge in the application of such nanostructures is in exploiting the desired nanofunction at an economic price and with bulk manufacturing capability.

21.2 Nanotechnology Inside Housing

Saving energy in the daily usage of buildings by decreasing the needs for heating or cooling air is an important issue. Nanomaterials can play a role in different areas and we shall illustrate here a few of them here.

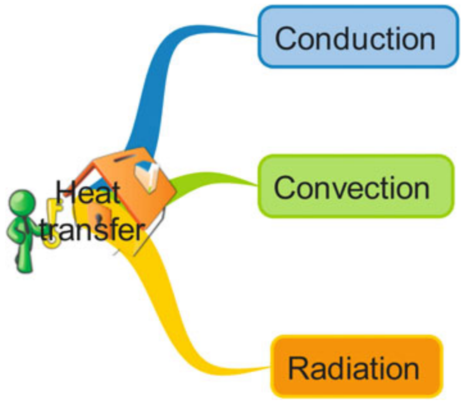


Fig. 21.13 Heat transfer can occur by conduction, convection or radiation

21.2.1 Insulation

The heat exchange between two objects at different temperatures goes always from the hotter object to the colder object. The exchange between two bodies in contact takes place spontaneously but can be slowed down enormously if insulating materials are placed between them. Insulating materials are those which provide a high resistance to heat transfer. This means that heat will escape slowly from a warm house or a cool one will warm slowly.

The transfer of thermal heat is done by three different physical phenomena (Fig. 21.13): *conduction* which is a transfer of thermal energy without flow of matter; *convection* which is a transfer of thermal energy with a transfer of matter, such as the circulation of air; and *radiation* which uses electromagnetic waves to transfer thermal energy.

Insulation is a key property in housing to keep people comfortable. Vacuum, the absence of matter, is an ideal insulator (often used in expensive vacuum flasks for hot drinks). The combination of reflecting surfaces and a vacuum provides a very efficient insulating system. Air is a good thermal insulator provided it is motionless, otherwise thermal exchange occurs through convection. Insulating materials based on air are made in such a way that air is trapped motionless in small volumes. This is the reason why it is not possible to make very thin thermal insulators.

Nanocellular insulating foams also reduce heat transfer, since a few gas molecules fit into the a nanopore, increases insulation efficiency, and reduce energy consumption (Fig. 21.14).

21.2.2 Nanoporous Materials

The most important parameter to reduce the energy consumption is in overall "buildings insulation". Nanotechnology offers ways of developing high-performance novel

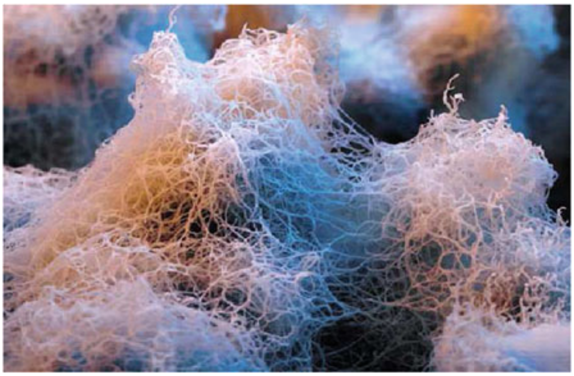


Fig. 21.14 Insulating foams with nanoscale pores. Image courtesy to BASF SE

insulating materials with an exceptionally high specific insulating performance, superior to traditional products but with substantially lower thickness, making them very attractive for building retrofitting. Nanoporous materials such as aerogels have an extremely low density with a nanoscale pore size: ideal properties to act as excellent insulators. They can be applied in textile roofing in sport stadia and the like, preventing heat loss and solar heat gain, while still allowing daylight transmission.

The thermal transfer through a solid made of nanostructures linked together turns out to be much smaller than with conventional materials. This is because the air is prevented from exchanging energy with other molecules because collisions mostly occur with the walls. For example, compared to expanded polystyrene, which is a widely used material in insulation, nanopore materials provide the same insulation using a volume twenty times smaller. Nanocoatings are also being developed for insulation, as a coating painted or spayed on the surface.

Several improvements in the insulation sector based on nanotechnology are underway. For example, processes are being developed to enhance the physical properties of silica aerogels by adding silicon multilayers. This increases the strength of the aerogel.

Today's insulation materials for buildings are extensively manufactured using recycled materials. Fiberglass insulation uses recycled glass, three quarter of slag wool is made of recycled content, and most of the cellulose insulation used comes from recycled newspapers. Several insulating materials used in buildings may have health effects and precautions should be taken during installation. Nanotechnology could increase the efficiency of insulation and make it less toxic while needing less fossil fuel in their manufacture. The good insulation properties of some nanomaterials are thanks to a high surface-to-volume ratio. A gain of around 30 % of the insulating power is expected using nanotechnologies. For example, it is possible to manufacture cellulose insulation material using by-products of the textile industry instead of recycled newspapers. Using electrospinning techniques, it has been shown at Cornell University that is possible to produce nanofibers from waste cellulose.

Aerogels

An aerogel is an ultra-low-density porous solid. More precisely, it is a gel in which the liquid has been replaced with gas. It is often called "frozen smoke" because it basically contains 95 % air and only 5 % of solid. Aerogels can be produced by extracting the liquid out of a gel by supercritical drying.
The first aerogels were produced from silica gels. It has been possible to achieve silica aerogels with a density as low as 1 kg/m^3. As a matter of comparison, air has a density of 1.2 kg/m^3: however, it should be noted that, by convention, the mass of air inside the aerogel is excluded to calculate the density otherwise such a material would float in the air!
Silica aerogels are the most common type of aerogels, but other types exist. Carbon aerogels, for example, are made of nanometer-sized particles bound together. Such aerogels have a very high porosity and, if their surface is made conductive, they can be used to manufacture capacitors or supercapacitors. Alumina aerogels, made with aluminum oxide, are used as catalysts, especially if they are doped with other metals such as nickel. Other types of aerogels have also been developed.

Aerogels are extremely good thermal insulators. They are two or three times more efficient than common insulating materials. One advantage of insulating nanogels is they also have good light transparency, up to 75 % transmittance. Furthermore, they are extremely light and can support over 2,000 times their own weight.

Aerogels available are mostly inorganic, with silica as the most common material. These aerogels are brittle, have poor humidity resistance, and are expensive. Organic aerogels are less brittle, have better mechanical properties, are lighter than their inorganic counterparts, and perform better as thermal insulators. New developments in the field of aerogels tend toward hybrid organic-inorganic aerogels which offer even better characteristics, and toward novel production processes.

Depending on the materials combination, nano-organic and hybrid aerogels can be up to 100 times more resistant to mechanical stress, can be inert against humidity, and can perform as an effective barrier against thermal radiation. They enable a wide range of applications in vehicles and buildings.

The challenge in this nanofield is to find ways to produce hybrid and organic aerogels at relatively low costs and in large volumes.

21.2.3 Radiation Insulation

Stainless steel nanofilms have the ability to absorb infrared radiation, and can be used as curtains to block a large part of the infrared heat from sunlight. As a consequence, the room temperature in buildings can be reduced by about 2–3 °C, so reducing air conditioning energy consumption. Using nanofilms in windows, it is possible to almost block entirely infrared and UV radiation and let only visible light pass through. Other nanofilms do not use metals which have disadvantages in corrosive environments, such as close to the sea, and can also perturb mobile phone reception.

An advantage of nanotechnology is that it also gives the ability to control the reflectivity of films. A ceramic-aluminum coating applied to cars can reduce the radiant heat and temperature inside the car by about 40 % and is corrosion-resistant. Such a nanocoating could be a good alternative to chrome-plating in the automobile sector because it is better for the environment.

21.2.4 Windows

Nanotechnology has been very successful in reaching the marketplace with the development of smart "multifunctionality" glasses. In the case of windows, they have features such as improved energy saving, self-cleaning, fire resistance (with addition of silica nanoparticles), UV absorption, and photovoltaic characteristics. Low-emissivity nanocoated glass reflects thermal radiation or because of its lower emissivity, reduces heat transfer through the glass. In winter, radiant heat generated indoors is reflected back inside, while in summer, infrared heat radiation from the sun is reflected away, keeping the interior cool.

Nanostructured films are also an interesting alternative to reduce the heat transfer through windows. These films are able to reflect specific wavelengths of light, without reducing the transparency of the glass. These films are made of a few hundred nanolayers of polymer that act as a filter to ultraviolet (UV) and infrared (IR) light while allowing visible light to pass through.

Self-cleaning, photocatalysis

Self-cleaning surfaces are highly in demand by consumers and can also be used on buildings surfaces to destroy organic pollution. Fig. 21.15 *shows example of that.*
(a) The lotus leaf is a naturally water repellent material. Drops of rain roll very easily across the surface and remove dirt. Scientists have developed artificial analogues which are self-cleaning materials.
(b) Coatings based on a titanium dioxide layer with a thickness smaller than 100 nm are transparent and invisible. When sunlight is present, droplets cannot be formed on the coating and water spreads over the entire surface and forms a thin film. As a consequence, dirt cannot adhere to the surface and organic pollutants are destroyed by photocatalysis.
(c) and (d) In photocatalysis, light is transformed into energy which has the ability to destroy organic molecules and kill microorganisms. This property can be used to manufacture self-cleaning windows but the product in solution can also be used in a safe cleaning spray.
Photocatalysis is a user-friendly means to prevent and remove pollution from volatile organic pollutants and is harmless with respect to the environment.

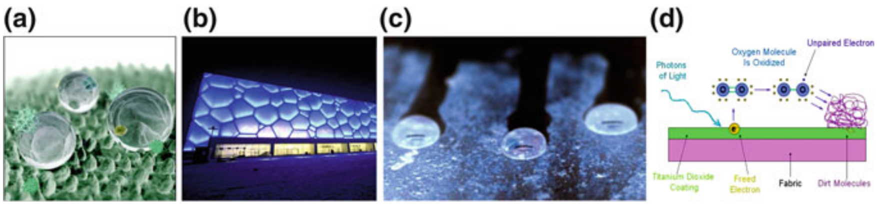


Fig. 21.15 TiO_2 self-cleaning surface and the mechanism of operation. Image courtesy of IoN, UK

21.3 Nanocoatings

Coatings play an important role on surfaces. Several methods exist to coat nanoparticles onto a surface such as chemical vapor deposition, spraying, plasma coating, and the like. Figure 21.16 presents some of the possible applications of nanocoatings. We have just discussed the possibility of thermal insulation or UV protection using nanocoatings. One of the advantages of nanocoatings is that it is possible to give to the surface a combination of several different properties at once.

Especially interesting is the use of nanocoatings on existing surfaces to dramatically increase insulation properties. This will allow easier, relatively noninvasive application to existing structures compared to using conventional insulation materials such as polystyrene, fiberglass, or cellulose. Nanocoatings will be especially useful in the case of old buildings.

Fig. 21.16 Nanocoatings have applications in several areas

21.3.1 Self-cleaning

A self-cleaning surface can be produced using titanium dioxide (TiO_2) nanoparticles, exploiting photocatalysis: a mechanism using ultraviolet light from the sun to destroy specific molecules. In the case of self-cleaning surfaces, the nanoparticles perform photocatalysis on dirt particles. The principle is to break up dirt molecules using the ultraviolet radiation of the sun, and the residues are then washed away by rain. TiO_2 nanoparticles can be put onto the surface in the form of a thin nanocoating film. Painting is also possible, as well as integrating directly the nanoparticles at the surface layer of the material. Nanocomposite polymers used in paints reduce dirt pick-up and help the paint to keep its color for longer.

Titanium dioxide (TiO_2)

One of the most promising and widely-used photocatalysts is titanium dioxide (TiO_2). The reason is that it is chemically-stable, abundant, and inexpensive. In the form of nanoparticles it is very reactive and can break molecular bonds. Dirt molecules can be broken down by the action of sunlight. In developing countries solar photocatalysis can be used for disinfection of water drinking. In developed countries using photocatalysis at large scale for wastewater purification is of great interest. TiO_2 nanoparticles are used already extensively in commercial products, as pigment in white paint and UV-absorber in sunscreens.

Clothing becomes soiled from daily wear. This has an impact on our energy consumption because they need to be cleaned frequently. Furthermore, in the case of dry cleaning, chemicals are used that can have a negative impact on the environment. Anti-stain coating of fabrics using nanostructures can be used. Without changing the natural characteristics of the fabric, nanotechnology provides new functionalities such as stain resistance or waterproofing, for example. The Nano-Tex company manufactures products where nanotechnology transforms the molecular structure of the fibers to provide new functionalities, as indicated in Fig. 21.17.

Self-cleaning surfaces can also reduce energy consumption needed for cleaning if applied to building facades. Furthermore, the quantity of cleaning chemicals is reduced which benefits the environment. As the surface self-cleans, depollution occurs because pollutants like nitrogen oxides and organic chemicals (formaldehyde, benzene, and volatile organic components) are broken into smaller, harmless molecules. Photocatalytic TiO_2 coatings are useful outdoors where sunlight is present. Indoors, other types of coating are necessary, like nanocrystals or double metal hydroxides. Their use reduces ventilation requirements by improving air quality, which in turns reduces the energy needed for the building.

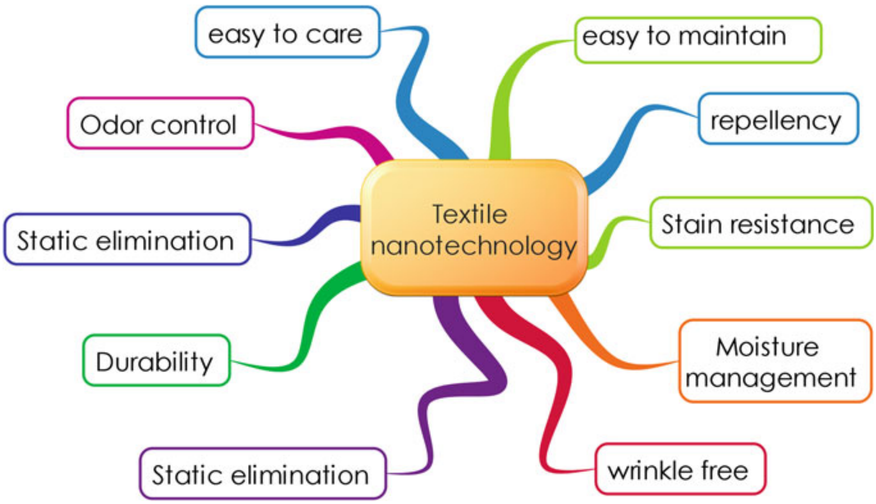


Fig. 21.17 Nanotechnology improve characteristics of fabrics. The different functionalities implemented in fabrics by the Nano-Tex company are shown in the figure

21.3.2 Nanoprotection

Nanoparticle additions into paints can influence the rheology, surface energy, etc. This will result in improved corrosion resistance and mechanical properties of paints. These nano-enhanced paints can be scratchproof, easy to clean, UV resistant, water repellent, flame retardant, and anti-bacterial. Nanoenhanced paints are quickly penetrating the market, mainly for building construction.

Surface scratches weaken materials and reduce their usable lifetimes. This increases the cost of maintenance and replacement as well as the energy needed to achieve these tasks. It also prevents the use of some materials in certain situations like plastics, wood or polymers, because they are not sufficiently resistant to wear and scratch damage. Nanocoatings can significantly reduce these drawbacks.

Harder than diamond

Until recently diamond was considered as the hardest material existing on Earth. However, German scientists have manufactured a new material which is harder than diamond: aggregated carbon nanorods. This material is made by compressing buckyballs at 200 times the atmospheric pressure at high temperature (2226 °C). This new material is so hard that it can scratch diamond. It has been also found, by simulation, that other materials could be harder than diamond: wurtzite, boron nitride, and a hexagonal diamond (lonsdaleite).

Reinforcing building materials with nanomaterials has the advantage of extending buildings' lifetime. A direct consequence is reduction in maintenance and replacement. Indirectly this also reduces the energy consumption and the impact on the environment.

21.4 Conclusion

Concrete is the most important building material in the developed world. There are enormous benefits, therefore, in making improvements to its processing, properties, and lifetime performance using nanotechnology. In order to realize the nanopotential benefits, research and development is required:

- mechanistic understanding of the chemistry of nanocement,
- better comprehension of the hydration process of cement and its nanocrystalline,
- hardening and setting processes of nano-enhanced cements and concretes.

Additives and admixtures play a key role in future developments of cement systems: in-depth characterization of the composition and size effects of additive materials is of great importance.

Nano-enhanced concrete materials are more expensive but represent much better properties; so research and development work is needed to fully quantify their benefits and to lead to long-term cost reduction to make them more attractive than conventional materials.

A major part of the energy consumed in the world is used for space heating and cooling. An efficient use of energy in the housing sector is important. This concerns all the stage in the life of a building, from construction to demolition. Embodied energy, or grey energy, is the energy necessary to build the house. Depending on the materials used and of the nature of the construction, this can be equivalent to the energy used during many years of operation. For example, in Europe, the energy required for the construction of a traditional house can represent the energy consumed for 30 or 50 years of occupancy. Since the lifetime of such a house is typically of the order of a century, grey energy represents a substantial contribution to the total lifetime energy cost of the building.

There are several steps in the lifetime of a house, shown in Fig. 21.18. The embodied energy is the energy necessary for the construction which requires materials, transportation, and manual labor. It is independent of the number of occupants. The operation energy depends on the number of occupants and on their lifestyle. Refurbishing can extend the lifetime of the house and improve its performances either for the same occupants or for new ones. It is beneficial to refurbish a house because the energy needed is smaller than for a new construction. Energy is also needed if the demolition of the house is done because it is no longer possible to live in it or because people want just to use the land to build something else.

In the majority of cases, the energy that people consider is only the energy used during operation and all the grey energy is forgotten. Nanotechnology, as we have seen in the chapter, can improve or bring new solutions at all the stages of the lifetime

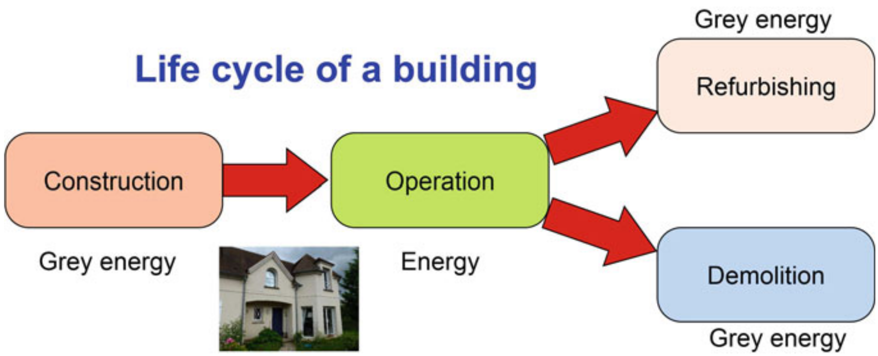


Fig. 21.18 Different stages in the life cycle of a house

of a building: construction, operation, refurbishing, and demolition (in the case where a re-use of materials is planned). Nanomaterials in the form of composites or coatings can improve almost all the sectors of housing with respect to performance, energy saving, and environmental impact.

Chapter 22
Road Transport

Automobile and freight transportation have an important place in society. They are essential for economic development. When the automobile replaced horses, at the beginning of the twentieth century, it was a step change in progress in terms of productivity, efficiency, and space (a car requires less area than a coach and horses). For example, in New York City, there were 175,000 horses and each horse produced between 10 and 15 kg of excrement every day, corresponding to a total amount of 2 tons per day. Part of it was collected, some washed into in watercourses. During the hot season some was transformed into dust, with a consequence of increasing respiratory and intestinal diseases. Furthermore, about 15,000 horses died in the street each year and their corpses were sometimes not removed immediately.

However, today there are so many cars and trucks over the world that they are becoming a serious environmental problem in several respects. Road transportation is more than 95 % dependent on oil and more than half the oil extracted in the world is devoted to this sector. We are close now to a billion vehicles over the world and any small improvement has great consequences at the global level in terms of energy consumption, pollution, and safety.

Although mobility covers many sectors, we shall deal mostly in this chapter with the automobile and illustrate, with some selected examples, the role played by nanotechnology now and in the future.

22.1 Improving Mobility

Mobility is important for individuals and automobiles. Nanotechnology has a great potential in the automobile industry. It can be used in three main areas: safety, comfort, and environmental protection (Fig. 22.1).

Safety is one of the first priorities. About 1.2 million of people die each year on the world's roads and 50 million are injured. Safety is steadily increasing and today's cars are intrinsically much safer than before.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_22, © Atlantis Press and the authors 2014

Fig. 22.1 Nanotechnology can be involved in four main areas of the automobile sector: safety, comfort, environment, and performance

Driving automobiles also has an environmental impact. Vehicle exhausts emit greenhouse gases and other pollutants. Road vehicles generate gaseous and particulate emissions and also noise, which is another aspect of pollution. Manufacturing a car has also an impact on environment, requiring energy and raw materials. Since we are close to a billion vehicles in the world, any positive or negative impact, even small, can have large local or global consequences.

Comfort is more and more demanded by consumers. Since speed is often limited and congested traffic more and more frequent, drivers like to feel at home in their car with a pleasant environment and facilities such as entertainment systems.

22.2 New Functionalities

Technical performance is also a goal of the automotive industry. Progress can be made along several lines. One way to decrease fuel consumption is to lower the weight of the vehicle using new materials. Another is downsizing, manufacturing smaller internal combustion engines while keeping or increasing the power and torque they deliver and consume less fuel to travel the same distance. Another is to introduce hybridization where an electric motor and a battery supplement the internal combustion engine. Another path is to improve fuel quality, especially for diesel, and to make better exhaust gas treatments.

Nanotechnology can provide several functionalities. The most relevant domains of application are shown in Fig. 22.2, all of which find use in the automobile sector.

Figure 22.3 shows nanotechnology applications of the different functionalities in the automobile sector. Some of them are already at an industrial stage and are used daily. They are indicated above a red branch. Others are still under development or used at a small scale. They are indicated above a black branch.

As far as mechanical properties are concerned, nanostructured materials can provide outstanding properties compared to conventional materials. Nanostructuration can provide higher hardness, increased breaking strength, improved fracture toughness at low temperature, super-elasticity at high temperature, and lightweight

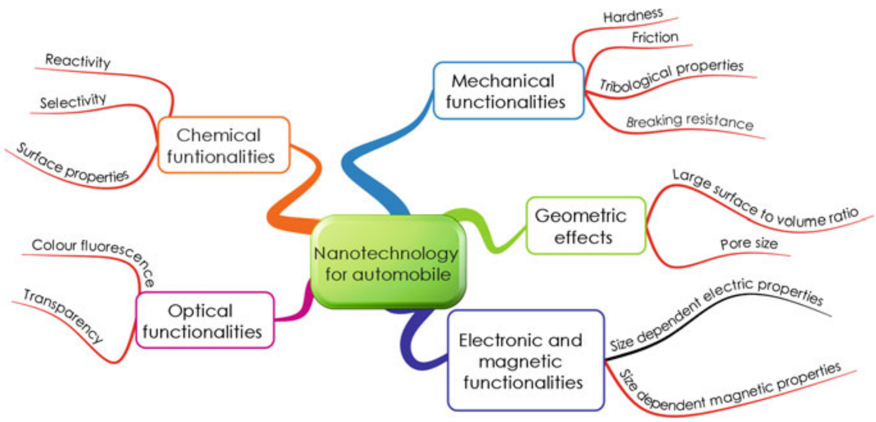


Fig. 22.2 Different functionalities offered by nanotechnology which can be applied to the automobile sector. This classification is taken from the report "Nanotechnologies in automobiles". Innovation potentials in Hessen for the automotive industry and its subcontractors, http://www.hessen-nanotech.de

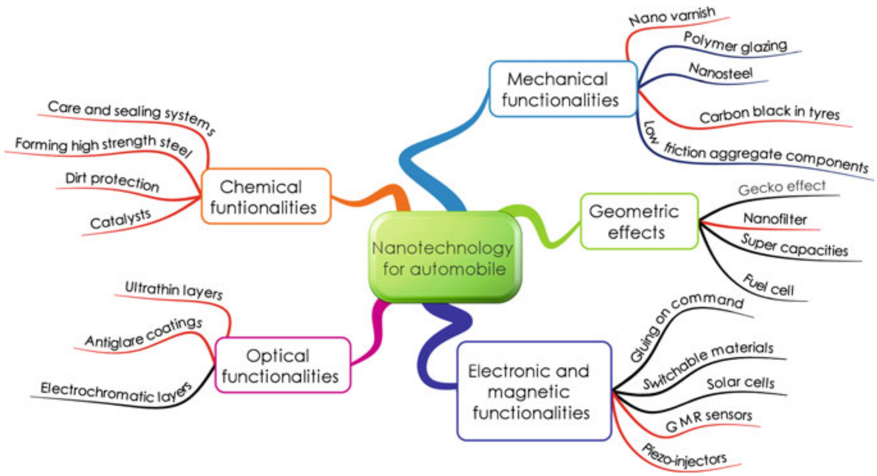


Fig. 22.3 Overview of possible application fields of nanotechnology in the automobile sector. Taken from the report "Nanotechnologies in automobiles". Innovation potentials in Hessen for the automotive industry and its subcontractors, http://www.hessen-nanotech.de

materials. Surfaces can be made more resistant against oxidation, corrosion, and mechanical abrasion.

At the nanoscale, quantum effects can be present. This has consequences on some of the electric properties. By adjusting the size of the grain of a material, it is possible to tune the electric properties of the material. Using nanoscale domains, the magnetic properties of materials can be modified on demand. It is possible, for example, to make glues containing nanoparticles where the adhesive property can be switched on or off using a magnetic field, providing new ways of joining and separating materials and components in a vehicle.

22.3 Outside a Car

The exterior of a car is subject to many interactions with the environment. The appearance should remain attractive and it should be resistant to degradation. Tires are also an important item connecting the car to the road at speeds which can be high, under weather conditions which can be awful, and on roads which can be in poor condition.

22.3.1 Body Parts

Steel is used extensively to manufacture cars. However, its share has decreased over the years. While it was about 75 % of the total weight in the mid-1970s, this has fallen to 50 % today. Today's materials for car manufacturing have to be light (to reduce fuel consumption) but also flexible to be efficient crash absorbers. Steels have improved continuously over time. It is now possible to produce high-strength and fatigue-resistant steels, using embedded metallic carbon nitride, with nanotechnology. Such methods, already used in other domains, could be applied to the automobile industry. For example, embedding 5–10 nm metallic carbon nitride particles inside steel can give to the material outstanding properties.

Another important issue is corrosion protection. It is no longer possible to use chrome-VI electrolyte in galvanic coating processes because of the health and environmental hazards of this product. Chrome-III or chrome-free protection is used but is much less efficient. However, including silica nanoparticles eliminates this drawback. In this case, galvanization is used to make an enriched Cr^{3+} layer covered by a layer containing silica nanoparticles embedded into a Chrome-III matrix. By covering steel with three successive layers, self-healing surfaces can be obtained. The deepest layer is zinc, the second is enriched with Cr^{3+} ions and the top one with nanoscaled SiO_2. This provides both corrosion protection and self-healing of the surface. This latter property is due to the fact that if a small damage occurs at the surface, the SiO_2 particles migrate to the damage location and cover it.

22.3.2 Tires

Tires are the only contact between a vehicle and the road. They are of key importance. A good tire has conflicting properties depending upon the circumstances. They need to have a good grip but with a low-rolling resistance. They should be resistant to abrasion but on the other hand avoid vehicle sliding. Tires are manufactured basically from natural rubber with additives playing a crucial role in their properties, typically, silica and organosilane. These additives are used in the form of particles of nanometer size. Their geometry as well as their precise size are important parameters to adjust the final properties of the tire.

22.3.3 Gluing

Gluing is often used in the automotive industry to assemble components. This is a simple technique to produce a joint between two components with low-cost and high-processing speed. Industrial glues need applied heat energy to work. Usually, glue is applied at the required locations and the whole system is warmed to around 180 °C for the two parts to firmly adhere. Apart from the energy consumption, this induces a thermal stress into the components which are assembled.

It is possible to mitigate these drawbacks using microwave radiation at a wavelength that interacts only with the glue, where the glue contains specific particles, such as nanoferrites, that absorb the microwave energy and disperse it throughout the volume of the glue. With this technique it is possible to perform "gluing on demand." It has the advantage, compared to other techniques, of consuming much less energy, to proceed faster and to avoid heat transfer to the components to be glued. It is also possible to have glues which can be unglued (or detach) on command. This can be useful in car repair.

Another path to have "stick and detach on demand" is to use materials biologically inspired from the Gecko lizard, which has limbs equipped with digits possessing adhesive pads. The adhesive properties come from the fact that it has tiny hairs on its limbs of nanoscopic size. A Gecko is able to climb on almost any surface, where the adherence comes from nanoscale attractive forces between the nanosize hair and the surface.

22.3.4 Car Protection

Nanoparticles dispersed in a material are much smaller than the wavelength of visible light (380–780 nm). However, they can disperse light by deflecting differently short- and long wavelengths. The size of the nanoparticles can thereby be adjusted to make coloring effects.

With nanotechnology it is possible to functionalize surfaces, for example to adjust the wetting properties or the chemical reactivity. It is also possible to protect a surface against external stresses using dedicated chemical groups.

The outside of the bodywork of a car has great importance. Usually, the body is painted and a varnish is applied on top to protect it. The body suffers many external stresses especially during driving, such as from small objects. The car is usually washed regularly and undergoes large temperature changes. A nanovarnish can provide a higher scratch resistance than conventional paint. Furthermore, it retains the paint brilliance for a longer time. A nanovarnish containing nanoscale ceramic particles has these properties. Furthermore, it can also be used for pigmentation stabilization.

Silica nanoparticles can be used in new car paints, in the form of spherical nanoparticles with a diameter ranging between 7 and 40 nm. The nanoparticles are distributed randomly in the paint solution. When applied and dried, these nanoparticles crosslink and the paint becomes very hard. By this mechanism, the scratching resistance is increased (actually, tripled) and the paint color is more brilliant. This process, involving nanotechnology in painting, is used today in some models manufactured by Mercedes-Benz.

Keeping clean the different parts of a car is important for the consumer. Anti-dirt products are being developed based on nanoparticles. Mist is also a problem when starting a car parked outside during the cold season. Anti-mist properties can be provided using nanoparticles. Water- and fat- repellent nanoparticles can be applied to glass, textiles, or plastic surfaces to prevent water, dirt, fats, etc. from sticking to the surface. For example, in the case of a water-repelling surface, drops of water just roll off the surface if the surface is correctly inclined. Dirt can be eliminated in the same way. However, there can remain dirt streaks on the bodywork after hosing and drying it. In the case of glass, it is possible to prevent this phenomenon by binding hydrophilic nanoparticles on the surface. This invisible nanofilm has the property that water can wet the surface evenly but then roll off faster which removes dirt more efficiently. The wheel rims of a car are often very dirty and are not easy to clean. Protecting them with specific nanoparticles give them excellent protection against dirt.

22.3.5 Windows and Optics

Modern cars have a large glass area, including the windscreen and the windows. The area of the windows can be of the order of 6 m^2 and that of the windscreen is usually a little more than 1 m^2. Reducing the weight of glass panes makes the car lighter and so less fuel is needed to drive the same distance. Replacing mineral glass by polymer glass is good, but polymers usually have a poor scratch resistance.

Polycarbonate is an interesting polymer because of its outstanding impact strength and lightweight. It is already extensively used in the automotive industry in lenses for headlight covers. The scratch resistance is usually improved by coating them with acrylate or polysiloxane paints containing aluminum oxide nanoparticles which are extremely hard yet maintain a high transparency of the polymer glass.

Progress is made also in coating processes, using techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and plasma polymerization. The thickness of the coating is of the order of 5–10 nms. An advantage of polymer glass is that injection molding techniques can be used which simplifies and decreases the cost of fabrication. Mastering this technique allows it to be applied to other parts of the car such as the roof or parts of the body work.

Mirrors and headlights use glass and plastic components. They need to have a good quality reflecting coating. This is currently obtained with a nanometer-thickness aluminum oxide layer. New techniques of deposition on the surface of the substrate material have been developed, requiring a lower temperature so giving a lower cost. Nanotechnology also allows making surfaces which are easy to clean because they are both hydrophobic and oleophobic, for easily cleaning dirt, sweat, and fingerprints. Water drops, oil, and fat are repelled.

Electrochromic glasses can also be used in the automotive sector. For this technology, an applied voltage can change the optical properties of the glass. It can be used, for example, as a coating on the rear mirror of an automobile. The applied voltage is driven by a sensor measuring the light coming from the following vehicles during night. The coating responds by changing its state and reducing the glare for the driver. As the lights disappear, the initial state of the mirror is restored automatically by changing the applied voltage.

22.4 Inside a Car

Because of traffic jams, drivers spend more and more time in their cars, and it is important that they feel comfortable inside.

22.4.1 Nanofilters

Air quality is very important inside a car. Air filters using nanofibers can be used to prevent most particles, gaseous pollutants, and odors from entering the car. Filters made with nanofibers are more efficient compared to conventional filters. One of the reasons for this is that the classical laws of hydrodynamics do not apply at the nanoscale, and air is transmitted more easily with a lower energy loss and lower pressure drop.

Nanofiltration can also be used to reduce pollutant emissions from the exhaust gas. Sooty particles can be trapped in the filter and burned continuously at temperatures above 200 °C.

22.4.2 Nano-Enabled Automotive Textiles

Nanotextile materials have an important role in the modern car of the future: to give lower weight, reduced energy consumption, reduced environmental impact, and improved comfort. Their use spans interior panels for doors and pillars, seats coverings and paddings, parts of the dashboard, to cabin roof and boot carpets, headliners, safety belts, airbags, air filtration, tire cords, and trimmings. In addition, natural-based textiles are easier to recycle and often replace conventional hard-surface structures.

22.4.3 Self-cleaning

Car seats can be in contact with dirt, sweat, water, and so on. The goal is to have seats which repel dirt and stay clean as long as possible. This is possible, by using nanocoatings to greatly reduce dirt adherence.

It is also possible to use nanocapsules containing fragrances to dispense different scents. The nanocapsules are injected at different depths in the fabric or leather and if they are stressed mechanically they release the fragrance. Only a few nanocapsules are needed to provide the fragrance and the system can operate as long as the nanoparticles are present.

There are often unwanted reflections on dashboards, instruments, and the windscreen. Structuring the surface in the micrometer range already does a good job in reducing this but significant improvement can be obtained by nanostructuring the surface in such a way that the refractive index changes gradually from outside to inside. In this case light is practically not reflected. It is possible to have the same effect using several coating layers but nanostructuration simplifies the process and decreases the cost.

22.5 Power Train

Great progress has been achieved on the power train of vehicles. For example, in 15 years, the specific power output of a diesel engine has almost doubled. The emission of pollutants is also decreasing. In France, between 1970 and 1996, the average pollution has been reduced by a factor of 30.

22.5.1 Improving Combustion

One way to decrease fuel consumption is to increase the combustion efficiency of internal combustion engines. This is done by optimizing the combustion process through variable valve control and precision fuel injection. Nanocrystalline piezoelectric materials can be used in diesel high pressure injection systems, allowing control of the injection valve in the nanometer range.

A portion of the fuel consumption is wasted on friction of the pistons on the cylinders of the engine. Friction can be reduced with a nanocrystalline coating, which also has the advantage of decreasing abrasion.

22.5.2 Exhaust Emissions

Catalysts reduce the pollutants emitted by vehicles. The exhaust pipe contains catalytic materials which can destroy carbon monoxide, nitric oxide and unburned hydrocarbons. Nanocatalysis is important because the specific surface in contact with the pollutant is substantially larger. The role of the catalysis is to transform pollutants into harmless molecules.

22.5.3 Switchable Materials

The properties of some materials can be switched using an external stimulus such as an electric field or a magnetic field. For example, the viscosity of magneto-rheologic or electro-rheologic smart fluids can be changed instantly and reversibly by applying a magnetic or an electric field. These fluids can be used in the automobile sector to make adjustable damping systems. For a vehicle, there is always a compromise between comfort and safety: a soft chassis is more comfortable but less safe than a hard chassis. The needs depend also on the type of road. Smart rheologic fluids can be used to make an adjustable damping system providing an optimal hardness of the chassis depending on the vehicle speed and the road conditions.

22.5.4 Supercapacitors

The number of hybrid vehicles in operation is now increasing rapidly. Plug-in hybrid and electric vehicles are being introduced in many countries. Hybridization saves fuel because of four functions: engine start and stop, regenerative braking, engine assist and electric driving. Hybrid vehicles have an internal combustion engine, an electric motor, and a battery. They can also have supercapacitors that store a small amount of energy but can deliver it very quickly to provide high power. They have a huge number of charge–discharge cycles which is not the case for conventional batteries. Nanomaterials and nanotechnology are essentials in the development of supercapacitors. High porous layer electrodes make a very large effective surface and therefore, provide the required high capacity.

22.5.5 Batteries

Nanotechnologies are also used in lithium ion batteries that are used in hybrid as well as in electric vehicles. They allow increasing the power density and, therefore, decreasing the weight of the battery for the same amount of energy stored. Nanotechnology is involved in the membranes of the battery which is a key point in battery development.

22.5.6 *Fuel Cells*

Nanotechnology is also applied in the membranes of fuel cells. The technology which is the most promising for transport applications in the future is the Proton Exchange Membrane Fuel Cells (PMEFC). For fuel cells, nanotechnology is also involved at the catalyst level through nanostructuration.

22.6 Conclusion

There are today more than 1 billion of vehicles in the world. In 2011, 76 million cars were manufactured and sold. Each second, 13 cars are manufactured and sold in the world. Automotive manufacturing is an important industry employing many workers over the world. The large development of the car industry is partly due to the fact that the automobile is very convenient and gives a freedom for transport which is not found elsewhere. You can leave at the time you want and bring with you an amount of luggage which is in most of the case far above what is possible with a train or a plane. However, road transportation relies heavily on oil and pollutant emissions are a big concern. Recycling of old vehicles is also an issue.

As we briefly discussed in this chapter, nanotechnology enters in many parts of an automobile and will be increasingly applied in the future. Ford predicts, for example, that by 2015, about 70 % of automotive materials will be modified by nanotechnology.

Although we have focused on road mobility with an emphasis on automotive transport, there are of course other modes of transportation. On the road, in addition to private cars which represent more than 70 % of the global fleet of vehicles, we have commercial vehicles. Buses, light duty vehicles, freight trucks, and powered 2–3 wheel vehicles are also used in road transport. Nanotechnology applies also to these categories of vehicles.

Air transport and ship transportation have also great importance. Ships are primarily used to transport goods. About one-third of the global ship tonnage is tankers. Ship transportation can be used on the oceans, seas, lakes, and rivers. Transporting goods over water is the most economical way, as far as energy is concerned. Airplanes are also used at large scale for passenger transportation. In 2007, for example, 831 million passengers took international flights and 1.25 billion used domestic flights. These figures increase regularly each year. Aeronautics is of course very eager to use nanotechnology to improve performance, energy consumption, and safety. Indeed, because of the high price of oil, the cost of fuel represents now a large part of the cost of a flight. Flying between Paris and New York corresponds to an emission of about 700 kg of carbon equivalent if all greenhouse gases are included.

Nanotechnology is expected to bring important improvements and breakthroughs in several areas related to mobility whether on the road, water, or air. Figure 22.4

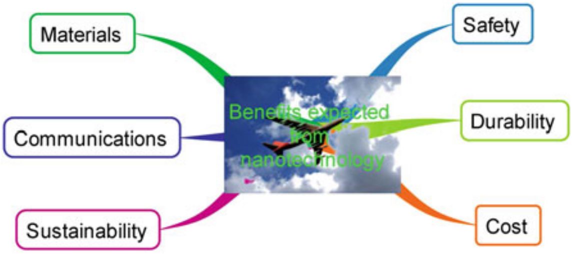


Fig. 22.4 Nanotechnology is expected to bring improvements and breakthroughs in the areas indicated in the figure

indicates some of them and we shall now very quickly go through these different items with one or two illustrative examples.

Safety is a big concern and nanotechnology can be used in several applications such as smart sensors for collision avoidance in cars or better catalysts for reducing or eliminating pollutants emitted by the engines.

Improving materials using nanotechnology allows increasing of the resistance against stresses and strains. The lifetime of the vehicles can be increased and the maintenance becomes easier. If the vehicle becomes lighter, it also needs less energy.

Reusing materials or developing materials to build vehicles requiring less fuel is required for sustainable development.

Better communications allows the development of intelligent and optimized transportation systems. Sensors can be used to have a complete monitoring of the infrastructure to optimize mobility.

Finally, most of the things needed are based on materials and nanotechnology gives the ability to develop tailored nanomaterials well adjusted to the demands of specific applications.

Part VII
Energy and Nanotechnology

Conclusion

Energy is a concern of everybody. It allows economic development and it is necessary to harness it in large quantities at the lower cost to meet the increasing demand of the world's population. Energy is the engine of development, and the reason why our standard of living has improved enormously during the last two centuries is the availability of energy in large quantities and at low cost. We are nevertheless subject to a challenge that we must reduce our CO_2 emissions and gradually reduce our consumption of fossil fuels. As we have seen in all chapters, nanotechnology and more specifically nanomaterials play and will play an increasingly important role in the development of new energy technologies. Figure VII.1 shows some of the sectors concerned by nanotechnology. As we see it covers almost all the energy domain.

Figure VII.1shows that many sectors are covered and nanotechnology is becoming an unavoidable technology to be competitive at the world level. The ability to understand, manufacture on demand, and use nanomaterials is a strategic issue to be competitive in the twenty-first century.

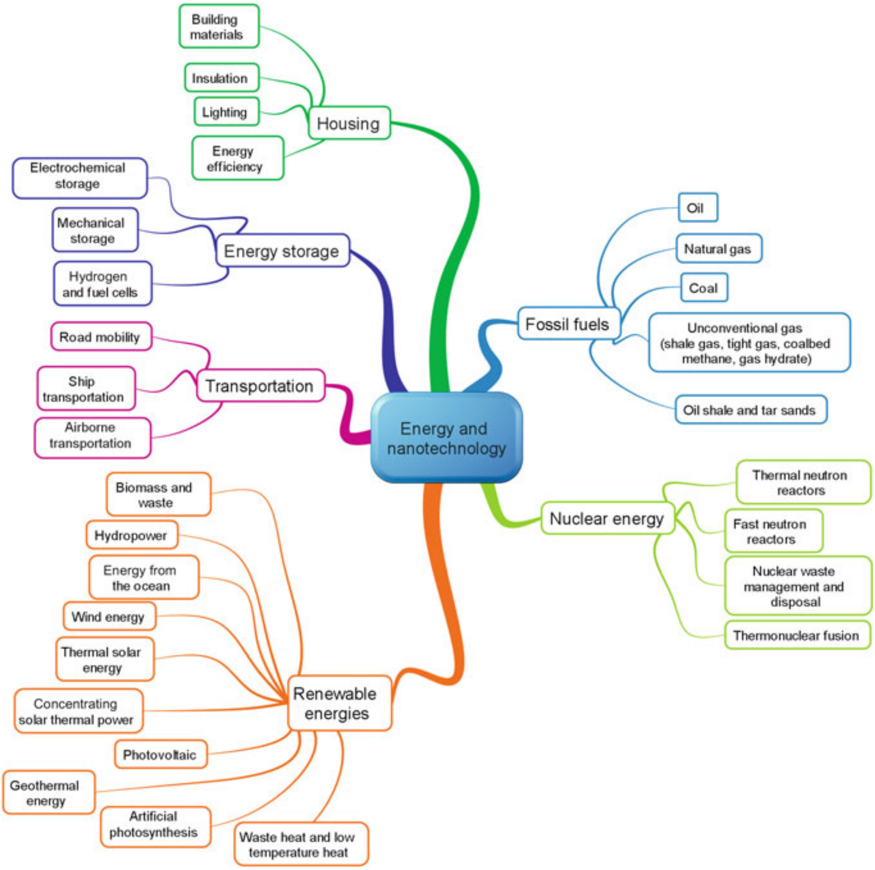


Fig. VII.1 Different sectors of the energy domain where nanotechnology can be useful

Part VIII
Nanotechnology in Industry, Defense, and Security

Introduction

It is predicted that in a few years the nanotechnology market will be worth hundreds of billions or even trillions of euros. Today, however, the field is still in its infancy. There are many exciting developments in the laboratory or at the project stage, but consumer products are limited to the application of technologies such as thin films, nanoparticle coatings, electronics with features below 100 nm, and some nanocatalysts. Most of the applications of nanotechnology achieved so far are just improvements to something that already existed, and only a few breakthrough innovations have arrived on the market. Very often, people making economic evaluations of the impact of nanotechnology include the cost of the whole product while the part which is really concerned with nanotechnology represents a very small part of this total cost.

Nonetheless, nanotechnology is without doubt a strong driving force for innovation and industry has to invest in this field to avoid losing market share into the future. In the global economic race, nanotechnology is an asset which cannot be neglected.

Industry is of course the entry point for the use of nanotechnologies. Nanotechnology will be able to create new products which are cheaper, safer, more reliable, smaller, faster, and stronger. That is the expected benefits to consumers: they expect to get better products with outstanding capabilities at the cheapest price.

Nanotechnology evolves toward more and more complex systems. We are today in the third generation of products. Each generation lasts about 5 years:

- the *first generation* started around 2000 with passive nanostructures such as nanostructured coatings, nanoparticles, and nanocomposites. Improvements to existing products could be achieved: sunscreen with nanoscale zinc dioxide or titanium dioxide; carbon nanotubes in golf balls, etc.;
- the *second generation* started about 5 years later, around 2005, with active structures such as transistors, actuators, targeted drug delivery, etc.;

- the *third generation* began around 2010 with more complex systems: three-dimensional nanosystems, multiscale architectures, bio-assembly, etc.;
- the *fourth generation* ($\approx$ 2015–2020) is expected to concern molecular systems where the function is realized by a single molecule, tailored materials designed using knowledge of the physics and chemistry of the nanocomponents, etc.

  All industry sectors are affected by nanotechnology. Let us just quote a few examples:

- in the food sector, nanotechnology has applications in the way that food is grown, how it is processed and in its packaging. Nanotechnology can modify the taste of food and make it safer and healthier.
- in the energy domain, nanotechnology allows to manufacture solar cells at a lower cost than conventional technology. In fuel cells, nanotechnology can reduce the amount of catalyzer needed and improve the efficiency of the membranes.
- in the space sector, nanomaterials allow lightweight spacecraft reducing the amount of fuel needed to reach orbit. A further reduction can be obtained with nanopropellants.

Industrial processes are major consumers of energy. Many processes use catalysis to achieve high reaction rates with a good yield and with minimum energy consumption. Nanoscale catalysis can make real advances in this domain although nanocatalysts have been used for a long time without real understanding of their nanoscale mechanisms and effects. This is the reason why we have devoted a whole chapter to the nanocatalysis domain.

Societies are more and more faced with insecurity: terrorism, counterfeiting, identity theft etc. Furthermore any country should have a defence system in order to protect peace. Nanotechnology offers many opportunities to prevent malicious and terrorist attacks. It is important that a country uses nanotechnology to develop an efficient defence system against the new threats which are now emerging at the global level.

Chapter 23
Nanomaterials in Industrial Application

The spectrum of nanomaterials now manufactured by industry is already quite large, with synthetic approaches aimed at producing high-quality nanostructured materials with tailored bulk and surface profiles and properties. Nanostructured materials and products have been developed such as nanocomposites, nanoporous foams for improved insulation, a wide range of agricultural products, construction materials, cosmetics, and pharmaceuticals with controlled delivery of active ingredients. Nanostructured surfaces aim to place the functionality precisely where required for catalysis, functional coatings, pigments, and electronic components (e.g., printable electronics and e-paper). These innovations create competitive products and contribute to sustainable development.

Across various sectors, nanotechnologies will provide new products, technologies, and processes: a combination of incremental improvements and/or revolutionary step changes which are far reaching and that will yield new and unanticipated developments. A short flavor of nanoproducts in industrial development or fabrication is provided in the following sections. Research and development has had a long incubation time but a breakthrough in nanoindustry is expected and it is difficult to imagine that industries in the 2020s will be able to competitive without being involved in nanotechnology manufacturing.

23.1 Electronics, Information, and Communication

Electronics, information, and communication will be the defining technologies of the twenty-first century. Advances will take place in all aspects such as new computers alongside flatter, lighter, and more energy-efficient displays for monitors and televisions, and higher density data storage. Nanotechnology can provide true "electronic paper" and novel sensing technologies based on interactions at the nanoscale.

As fabrication using conventional top-down approaches reaches its theoretical limit, bottom-up self-assembly will allow the fabrication of electronic devices in the

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_23, © Atlantis Press and the authors 2014

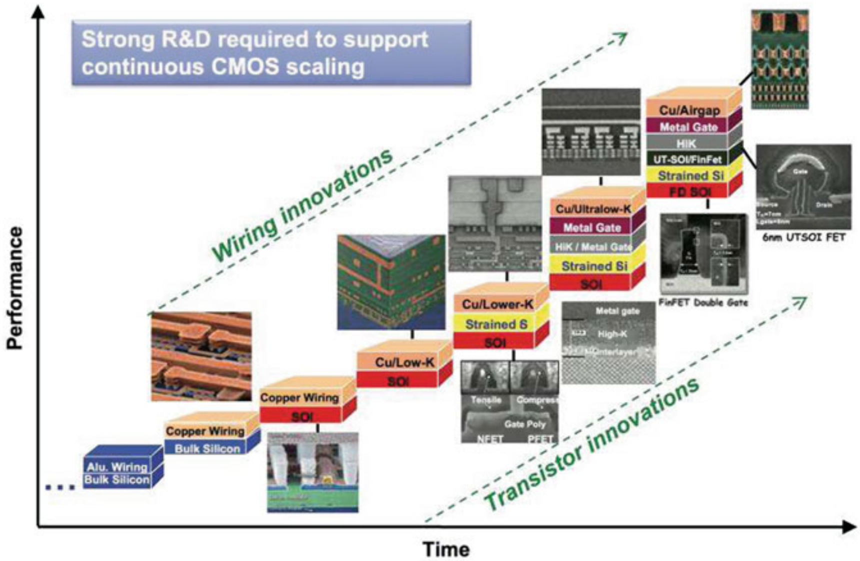


Fig. 23.1 Developments in semiconductor technology during the years: image courtesy of Research IBM—Zurich

scale of 10–20 nanometers. Figure 23.1 shows the "Semiconductor Roadmap" the innovative CMOS-scaling technology goes toward 22 nm currently in development and to beyond 10 nm in research.

With the year-on-year increase in consumption of electronics goods around the world, any improvement offered by nanoelectronics in energy efficiency has a major impact on carbon emissions. Figure 23.2 gives an overview of the use of silicon-based nanoelectronics in various industrial and consumer sectors.

23.2 Materials

Nanostructuring opens the possibility of materials and products with new and improved properties, in applications as diverse as optoelectronics, catalysts, cosmetics and skin care, building materials, textiles, and medical analysis techniques. As an example, Fig. 23.3 highlights the opportunities for nanomaterials and components in aircraft technology.

23.3 High-Value Industries

Very high-value industries will see particular opportunities, such as in nanomaterials for aerospace, space exploration, and satellite applications; Fig. 23.4. This includes

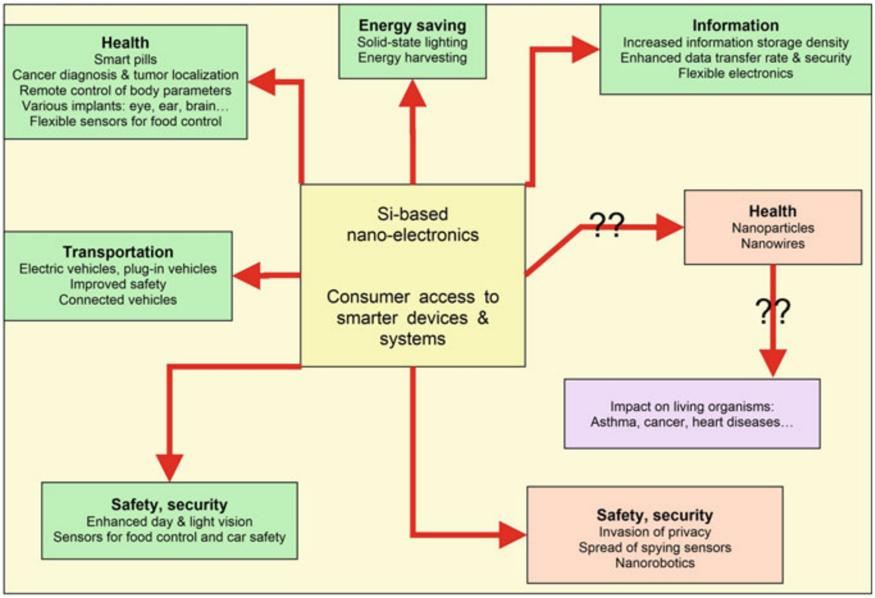


Fig. 23.2 Overview of spin-off applications of silicon-based nanoelectronics

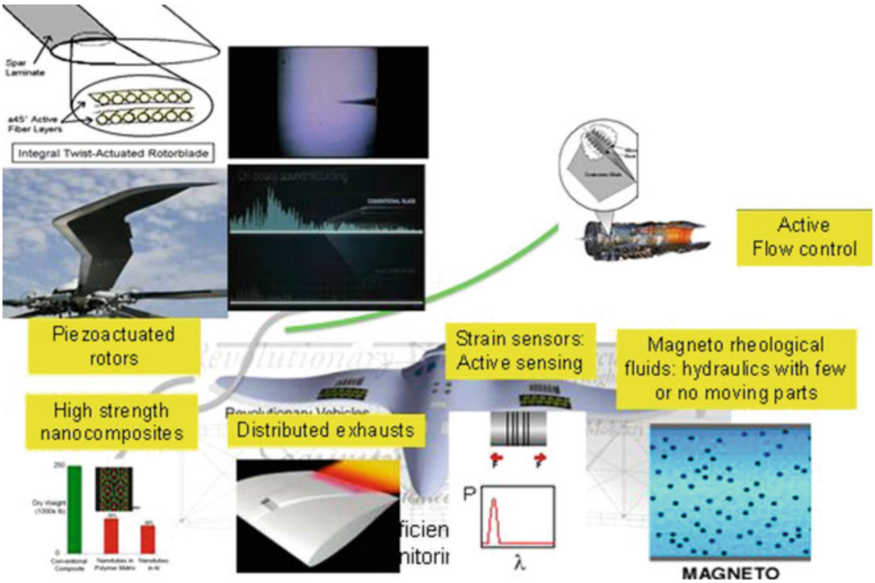


Fig. 23.3 Overview of nanomaterials and components in aircraft. Image courtesy of P.J. Withers Manchester University. GENNESYS conference, Barcelona, 2010

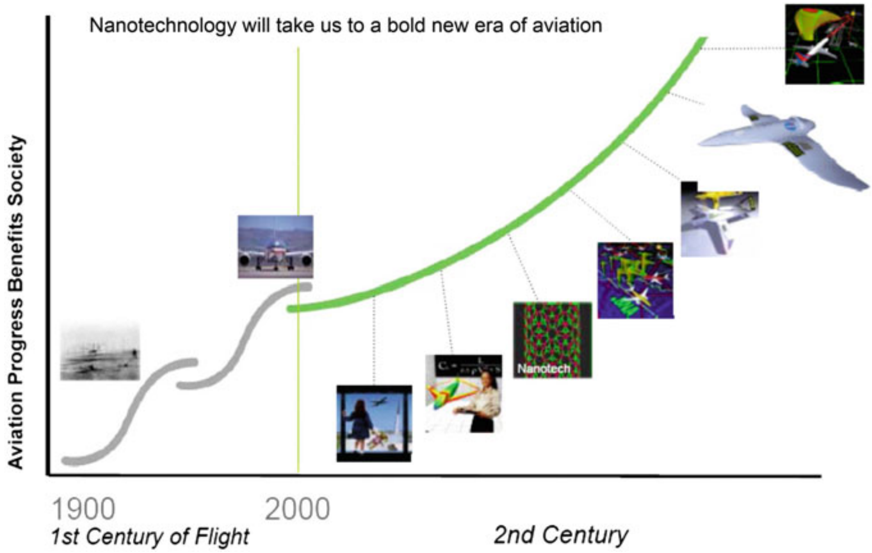


Fig. 23.4 "A journey into the future": prospects of nanotechnology in aircraft engineering. Image courtesy of P.J. Withers Manchester University. GENNESYS conference, Barcelon, 2010

new concepts in the deployment of miniature "swarm" robots where functions can be distributed across many individual devices. This new concept also has spin-offs in other technology branches such as nanorobots in medicine. These industries often demand for special materials and designs and nanomaterials will play here a unique role. Developments led from high-value applications will find their way into traditional sectors including construction engineering, the textile industry, and metallurgy.

23.4 Manufacturing and Processing Industries

Manufacturing industries will benefit from longer life tooling that will reduce the cost of component production. Super-hard components that improve wear resistance and lubricants that respond to operating and environmental conditions will reduce energy losses in manufacturing and processing, and all applications involving moving parts. New catalysts produced from nanoparticles will improve the efficiency of chemical production processes and the effectiveness of exhaust cleaning systems.

The fabrics industry will benefit as clothing will gain self-repair and dirt-repellant features, with future fabrics that are less prone to wrinkling, staining, and electrostatic charging. The leisure industry will see advances such as the fabrication of skis with low-friction nanocoatings.

23.5 Meeting Food and Water Demand

The growing global demand for energy, food, and water can only be met by using efficient and sustainable new technologies. Rapidly developing economies are faced with increased demand for clean water and processed and packaged foods, whilst striving to protect the local and global environment. Nanotechnologies can help in the purification of drinking and waste water through nanoenhanced filtration processes. Agriculture yields will be improved through targeted fertilizers and nutrients engineered at the nanoscale.

Global problems associated with the supply of clean, disease-free water can be solved by the application of membranes that exploit nanoscale filters, which will also find application in the treatment of sewage and the reduction of pollutants in industrial discharges.

23.6 Energy

Perhaps the highest impact for nanotechnologies in global industry lies in nanotechnologies for energy applications, from improved (rechargeable) batteries offering lighter storage with greater energy density, to alloys and coatings for more efficient fossil fuel power plant. Improving household insulation to maintain year-round comfortable temperatures can have an enormous effect on domestic carbon emissions. Photo- and thermovoltaics, fuel cells, and nanocrystalline hydrogen storage materials are all potential applications of nanotechnology. Developing high-efficiency solar photovoltaic panels and solar-thermics will make the economics of distributed solar power generation much more attractive.

The way that we transport energy must be revolutionized if the challenge of reducing carbon emissions from vehicles—one of the largest contributors to global CO_2 levels—is to be met. A particular challenge is the safe storage and transport of hydrogen to enable its use in clean fuel cells. The transport industry will also see improvements in nanostructured materials that will provide crash-resistance through safer car bumpers, improved braking systems, improved tyres for automobiles and aircraft vehicles (see Fig. 23.5), self-cleaning windows, more efficient fuel consumption, dirt-resistant paints, corrosion resistant materials and fabrics, and exhaust gas treatment systems via catalytic convertors or filters (see Fig. 23.6).

23.7 Security

In security, much greater safety and monitoring can be provided with small, multifunctional detectors that can be widely distributed. The market for security systems is growing as more companies want to have secure buildings for workers and

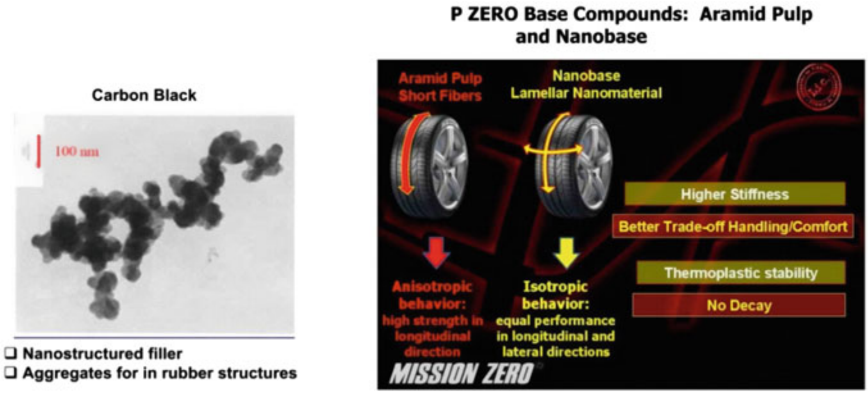


Fig. 23.5 Effect of nanocarbon particles in automotive tires. Image courtesy of P. Perlo Torino e-district, IFEVS—GENNESYS conference, Barcelonna, 2010

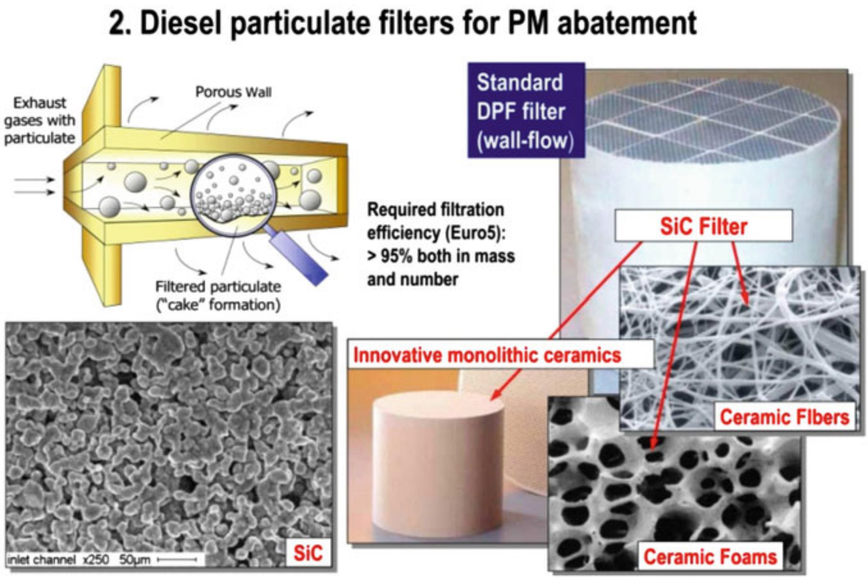


Fig. 23.6 Nanomaterials in diesel exhaust applications. Image courtesy P. Perlo Torino e-district, IFEVS—GENNESYS conference Barcelona 2010

visitors. Miniaturized surveillance systems will provide better monitoring at reduced costs. For the security services, detectors and detoxifiers of chemical and biochemical agents will become more effective. The increased drive for safety and protection will underpin the growth of the sector.

23.8 Consumer Products

Nanotechnologies are already providing advances in consumer products such as sunscreens and cosmetics. New applications, including sunglasses with protective and anti-reflective nanocoatings, better fabrics, and improved sporting goods, are all ready for market. Better performance in products will always be attractive to the consumer, and this will lead to the acceptance of nanotechnologies more broadly.

By building functionality directly into a surface, greatly enhanced products can be developed. Nanostructured surfaces can be exploited for applications such as coatings for windows so that they are cleaned naturally by sunlight and rain without the need for human intervention; another example is stain-resistant coatings for clothes. Taking this one step further in development, concepts of self-repairing coatings are envisaged, such as self-repairing paints and adhesives.

At present, the primary purpose of food packaging is to protect the contents against dirt, contamination, and/or oxidation. It is now becoming possible to devise packaging materials that provide information on the food quality through novel sensing: for example, materials that respond to the decay of meat, and will provide a more reliable indicator of freshness than an estimated indication of shelf life on the packaging. Furthermore, it is possible to protect the food against UV-degradation and oxidation by employing suitably nanomodified polymer films in the packaging.

23.9 HealthCare Industries

The healthcare industries (Fig. 23.7) have a very large market where new technologies can provide improved diagnostics and treatments. Reliable and accurate self-diagnostics for the general public at low cost—self-diagnostics at home—will mean that the efforts of healthcare professionals can be better targeted toward those in

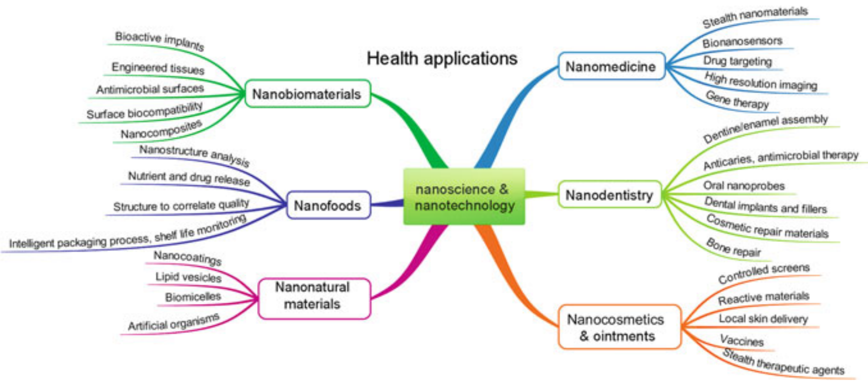


Fig. 23.7 Application of nanotechnology in health care

most need and make health care more cost-effective. Imaging agents and diagnostics will allow clinicians to detect cancer in its earliest stages. More rapid diagnostics, "lab-on-a-chip" testing, and improved therapies for disease management will all see major improvements.

Improved drug delivery for chronic conditions and pain management will mean better quality of life for people. New and better systems for the encapsulation of drugs and nutrients based on the concept of nanostructured carrier systems can be developed, that will respond to physicochemical changes to trigger the release of an encapsulated compound. For instance, the pH near a cancer cell is slightly lower than near healthy cells: a carrier could be made that responds to these minute pH changes and then releases the drug. New methods to manage the debilitating symptoms of cancer will become available.

Better prostheses (bone, tissue, and tooth substitutes), "intelligent" implants, and synthetic organic products including blood will become a reality.

Nanotechnologies are being used to develop a new generation of smaller and potentially more powerful devices to restore lost vision and hearing: for example, attaching a miniature video camera to a blind person's glasses in order to capture visual signals which are then processed by a microcomputer worn on the body and transmitted to an array of electrodes placed in the eye. For hearing, an implanted transducer can be pressure-fitted onto a bone in the inner ear, causing the bones to vibrate and move the fluid in the inner ear, which stimulates the auditory nerve. An array at the tip of the device uses nanoscale electrodes, much smaller than current devices, to stimulate a fuller range of sounds. The implant is connected to a small microprocessor and a microphone in a wearable device that clips behind the ear. This captures and translates sounds into electric pulses transmitted by wire through a tiny hole made in the middle ear.

23.10 Magnetic Nanopaper

Magnetic nanopaper is a new material with great potential. It is based on natural cellulose, and finds special use in preventing the falsification of paper money and official documents. However, its unique combination of properties could also see it being used in surprising applications including implants in the human body and in the construction of small motors and sensors. It is easy to manufacture: nanoparticles are integrated into the paper, followed by a magnetisation process. It is extremely light, strong, elastic, and flexible compared to magnetic metallic materials. The production of nanopaper offers great future potential and challenging new possibilities for the wood industry.

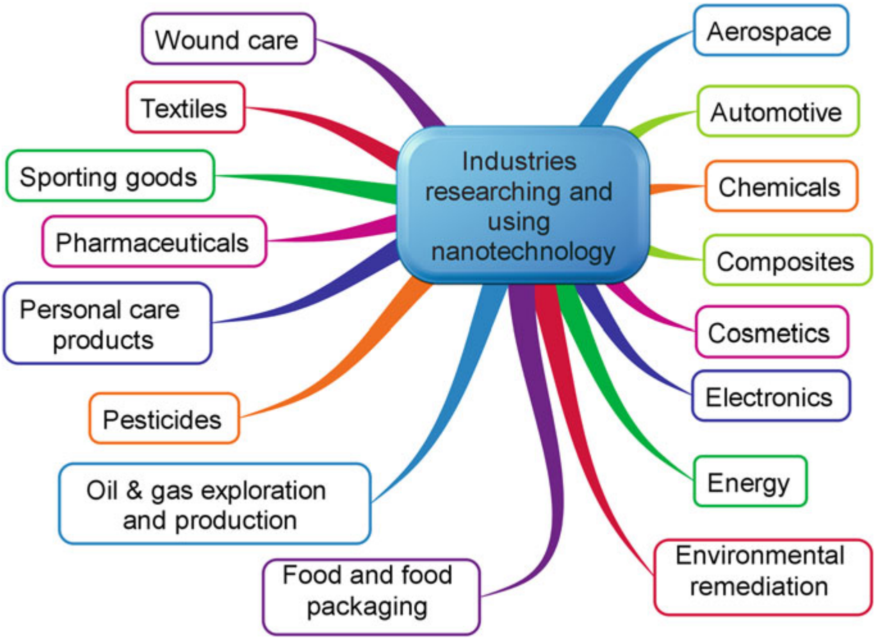


Fig. 23.8 Industries researching and using nanotechnology. Compiled from www.nanotox.com

23.11 NanoAdhesives

Mechanisms for adhesion are primarily either mechanical or chemical. Mechanical mechanisms provide an interlocking mechanism, typically by the substance filling small pores in each of the surfaces to be joined. Chemical mechanisms invoke direct chemical bonding, with the development of intermolecular forces. However, new mechanisms can be derived from nanoscale interactions, such as mimicking the attractive forces of the hairs on a gecko's foot that allow it to walk upside down.

Nanotechnologies will contribute to the reshaping a range of industrial and commercial applications through the development of nanoadhesives. Nanoadhesives can have significantly improved products, and entirely new or novel capabilities. Nanoadhesives can be produced that are targeted to activate when in contact with specific surfaces or materials. In addition to their adhesive properties, it will be possible to achieve multifunctional characteristics: for example in the automobile industry, making adhesives with tailored mechanical and thermal strength, and corrosion and abrasion resistance. Nanoadhesives may have special electrical, chemical, or biological properties. The goal is that adhesives contribute to the overall performance and function of a structure, and not just act as an inert interlayer.

In medicine and health care nanovelcro bio-bandages, dental nanoadhesives, and nanoadhesive plaster will improve conventional technologies. In aerospace, nanomaterials will provide enhancement of conventional epoxy adhesives.

During application, nanomaterials can help an adhesive to have optimal rheological properties: low viscosity, and the prevention of slumping after application, so more uniform layers can be produced during application. Nanosized metallic particles can help the adhesive process, such as for electrostatically applied adhesives. Even dry nanoadhesives based on nanotube arrays are possible.

23.12 Conclusion

Nanotechnology will be more and more used in the industry as source of innovation and to improve existing products. Industries will be effectively forced to be involved in this domain or they could become uncompetitive. Several industries are already researching and using nanotechnology. Some of them, compiled by www.nanotox.com are shown in Fig. 23.8.

Besides the advantages brought by nanotechnology, research should be pursued to find out the hazardous effects of nanoparticles. Means must be used to reduce the risks of exposure to workers and consumers.

Chapter 24
Nanocatalysts: Fascinating Opportunities

Nanoparticles have been used as catalyst in the industry since the beginning of the twentieth century, though the nanoscale mechanisms were not fully understood at that time. Catalysts are important because they facilitate chemical reactions. About 90 % of chemical products are synthesized using a catalyst and 60 % of industrial processes are based on catalytic reactions. In the living world, catalysis is essential for life, and enzymes, which are large biological molecules, mostly proteins, are biocatalysts involved in almost all chemical and biological reactions.

The challenges of our changing world call for new technological answers. Solar energy and biomass are becoming vital technologies for sustainable energy generation. However, they lack the convenience and wide applicability of the hydrocarbon raw materials that are presently in use. For biomass, conversion into other forms is essential and catalysis will play a major role.

24.1 What Is a Catalyst ?

Catalysts can make chemical reactions occur faster and in easier conditions such as lower temperatures or pressures. Many chemical reactions would be useless without using a catalyst because they are too slow or require too hazardous conditions to proceed. The principle of catalysis is shown in Fig. 24.1. A catalyst lowers the activation energy barrier making the transition from the initial state (two initial chemicals, for example) to the final state (one or more chemical products) easier and faster. In Fig. 24.1 we illustrate this with a classical model where a particle has to overcome a barrier. At the microscopic level the system behaves quantum mechanically and there can be tunneling through the barrier. The height of the barrier is an important parameter with respect to the ease of achieving the chemical reaction and catalysis is used to lower the barrier.

Catalysis can be homogeneous or heterogeneous (Fig. 24.2). In homogeneous catalysis, the catalyst is in the same phase as the reactants. In heterogeneous catalysis

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
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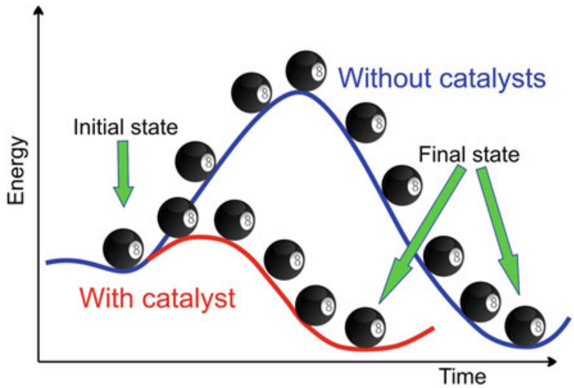


Fig. 24.1 Principle of catalysis

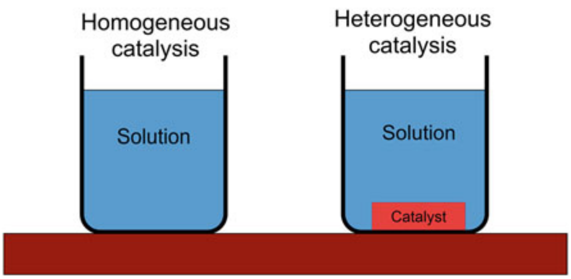


Fig. 24.2 Difference between homogeneous and heterogeneous catalysis

the catalyst is in a different phase from the reactants. An advantage of heterogeneous catalysis compared to homogeneous catalysis is that the catalyst can easily be used again.

The main functions of a catalyst are shown in Fig. 24.3. A good catalyst should increase the rate of a chemical or biological reaction and increase the yield. It should be able to reduce the amount of undesirable products. The catalyst should have a high stability and keep its physical integrity during the process. This means that it should have a low volatility, a high resistance to rapid changes in temperature, and a long-term lifetime. A catalyst needs also to have a large surface area to be very efficient. This point favors the use of nanocatalysts.

A catalyst has several influences on chemical reactions. They are shown in Fig. 24.4. A good catalyst is active, selective, and stable.

It is important for a catalyst to have a large area in contact with the reactants. The larger the surface, the more efficient is the catalyst. This is why nanostructures are so interesting: they offer a much larger surface area. The efficiency of a catalyst depends on many parameters. The most important ones are shown in Fig. 24.5.

The nature of the catalyst is important. Any particular reaction can be catalyzed by specific materials only. The size and the shape of the catalyst govern also the efficiency. A catalyst is often put on a support or substrate and the properties of

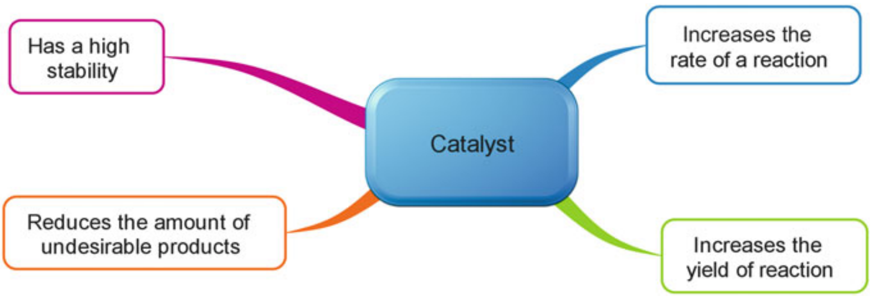


Fig. 24.3 Main functions of a good catalyst

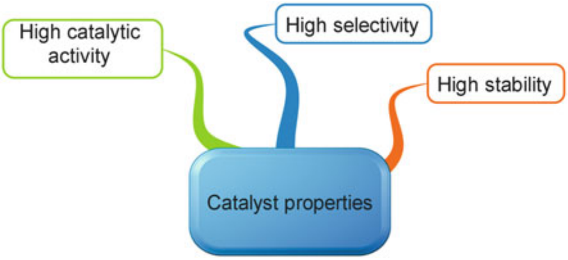


Fig. 24.4 Properties that a catalyst should have

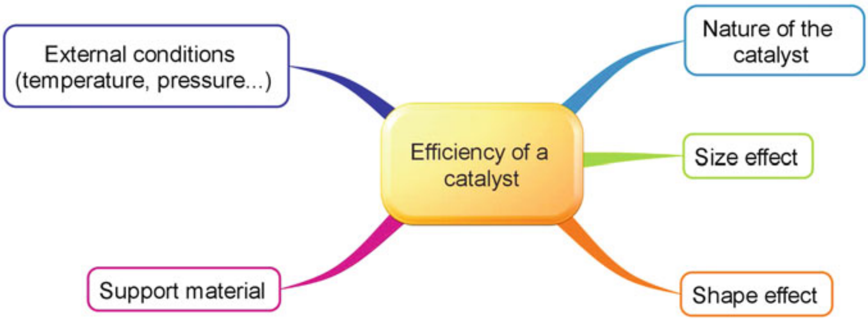


Fig. 24.5 The efficiency of a catalyst depends on several parameters

the substrate can affect the efficiency of the catalytic process. Finally, the external conditions also play a major role in the process.

24.2 Catalysis and Nanoscience

The chemical, petroleum, and pharmaceutical industries are largely based on catalysis: it has contributed enormously to efficiency and lower environmental impact. For example, a nanocatalyst made of Ni, Mo, and Zr is used for the polymerization

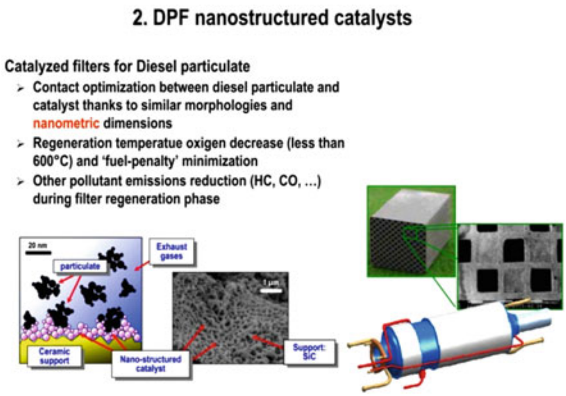


Fig. 24.6 Nanocatalysts for exhaust reduction in cities. Image courtesy of P. Perlo, IFEVS Torino, GENNESYS Barcelona Conference 2010

of butadiene in the rubber industries. A Co/Mo/zeolite nanocatalyst can be used for sulfur reduction in diesel.

In the world of the consumer catalysis is crucial as well. Without catalytic convertors transport would make modern cities unpleasant to live in. The application of nanocatalysts in an engine is given in Fig. 24.6.

Nanostructured materials offer exceptional properties to drastically improve catalytic performance. Recent developments in nanoscience enable a jump in synthesis of novel catalysts. A grand challenge for nanoscience in catalysis, in this century, is the rational design of novel catalytic materials: to achieve atomic precision in two and even three dimensions, allowing design and synthesis atom-by-atom, molecule-by-molecule, nanounit-by-nanounit. The geometrical and electronic structures of nanoscale catalyst particles play a major role in selectivity; so a highly controlled particle size, shape, architecture, and distribution on nanotemplated surfaces of oxides is desirable.

For example, the yield of converting nonedible oil (from plant or food production waste) into biodiesel can change dramatically according to the process and the catalyst used. The method based on transesterification produces conversion efficiency of between 20 and 29 % to biodiesel while gasification with crude oil at 300 °C with a Ni nanocatalyst produces 38 % plus other by-products such as benzene and propene. With photocatalysis more than 90 % conversion to biodiesel can be achieved in 5 min.

A spectacular discovery is that gold-based catalysts exhibit extremely high activity in several reactions: this was a surprise as it was generally reasoned that gold should be inactive, being one of the most inert metals. However, it was discovered that nanosized gold particles are remarkably active: e.g., they efficiently catalyze CO oxidation far below 0 °C, and they have the ability to decompose environmentally hazardous gases such as sulfur dioxide. The efficiency of this catalyst material is many times greater than that of commercial catalysts today. The challenge now is to target the spectrum of the chemical reactants as they interact with the nanostructured catalyst materials. The choice of materials, structural parameters, and the experimental design must be guided to the understanding of the structure-function relationships of the nanostructured catalysts.

24.3 Catalysis Engineering

It is useful to realize that catalysis is a multiscale discipline (Fig. 24.7), covering:

1. the materials: nanostructured solids, including membranes and multifunctional catalytic materials, open completely new avenues for catalytic processes;
2. the catalytic reactor: microreactors open the avenue to miniaturization, allowing the development of labs-on-a-chip and high-throughput experimentation;
3. the process: structured catalysts and reactors are instrumental in miniaturization and the achievement of higher precision. They are powerful tools in re-engineering chemical plants providing process intensification aimed at more compact, safer, and waste-free chemical production plants.

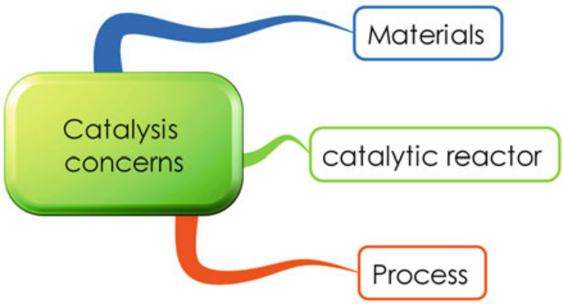
Examples of new technological developments are in self-assembling chemistry and lithography. These methods provide unique opportunities to design and construct nanostructured catalysts with ultimate precision.

Undoubtedly, catalysis is a success story. A genuine step-change in progress is within REACH provided new ideas are put in practice and smart solutions are found for several key barriers; Fig. 24.8 gives an overview of nanocatalysts in multiple technologies.

A wealth of catalytic processes forms the basis of the modern chemical industry and it is expected that the area will expand dramatically, e.g., with future applications in biorefineries, photocatalysis, and electrocatalysis.

Catalysis can be used in the production of biodiesel (see above), in the conversion of biomass for energy generation, and to produce domestic cleaning products by replacing harsh chemical action by catalytic oxygen activation. Another example is in fuel cell energy production: platinum is the key catalyst in PEMFC fuel cells, catalyzing hydrogen, or alcohol oxidation at the anode and oxygen reduction at the cathode. In the case of platinum nanowires grown on carbon black substrates, they are cost effective to fabricate fuel cells and provide, for the oxygen reduction reaction, a 50 % higher mass activity and a threefold better specific activity than the platinum nanoparticle catalysts.

Fig. 24.7 Main fields of catalysis



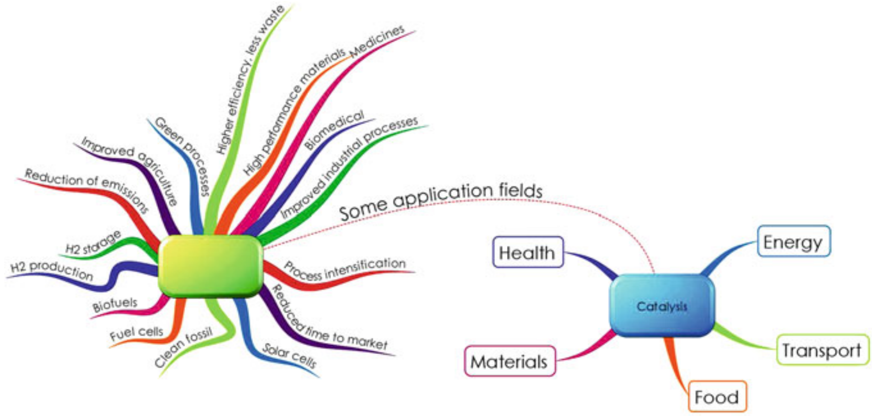


Fig. 24.8 Summary of the role of catalysts in multiple technologies

Superthermites

A thermite is a mixture of a metal powder and a metal oxide. The metal is typically aluminum, magnesium, zinc, or titanium and is the fuel. The metal oxide, which is the oxidizer, can be iron oxide, copper oxide, boron oxide etc., A thermite can be ignited by heat and temperatures above 2,200 °C can be reached in the course of the oxidation-reduction process. The thermite reaction was discovered by the end of the nineteenth century. It has civilian applications (such as cutting or welding steel rail track, and purifying metal ore) and military applications (hand grenades, destruction of sensitive military equipment in case of retreat, disabling of artillery pieces, etc.,).

A superthermite or nanothermite is a metastable intermolecular composite. It is a nanoscale mixture of an oxidant agent and a reducing agent, typically a mixture between a metal oxide and a metal. Superthermite produces much faster and intense reactions than thermite. They have military use as propellants and explosives, or in pyrotechnics.

If nano-aluminum is used in solid fuels for missiles, torpedoes or munitions, the projectiles go further and faster than with conventional charges. One advantage is that the projectile can reach the target much faster, often before any countermeasure can be taken.

An advantage of using nanomaterials in munitions is to decrease the cost and to require less material to get the same characteristics.

Nanomaterials are highly beneficial for the remediation of pollution in the environment. Catalysts can provide abatement of atmospheric pollutants such as CO, NO_x, VOC, unburned hydrocarbons, and aerosols emitted by industrial, transport, and domestic activities. Nanostructured materials can be used for the separation and capture of CO_2, and nanocatalysts can be used in water treatment. In wastewater, pollutant oxidation and microbial detoxification can be achieved with a thin photo active layer, and nanoparticles supported on a high-surface area-oxide semiconductor can be used to remove industrial organic pollutants.

The chemical industry is important for Europe, but its market position can be lost! It is fair to state that from both the US and the Far East in the field of catalysis real competition is growing. In the past, Europe and the US formed the cradle of new developments. The Far East is investing heavily in the field and for Europe the challenge is now to rejuvenate its research in catalysis.

24.4 What Can Emerge from the Nanoscience of Catalysis?

We can envision new catalysts that will allow economical one-step conversion of methane into methanol or other liquid fuels. Similarly cellulosic raw materials or CO_2 may be converted into liquid fuels. Improved catalysts may lead the way to economical fuel cells for conversion of H_2 or methanol or even gasoline. This would allow small, lightweight devices in automobiles for on-board conversion of liquid fuels into H_2 for the fuel cells, eliminating the need for hydrogen storage. All these new possibilities are summarized in Fig. 24.9.

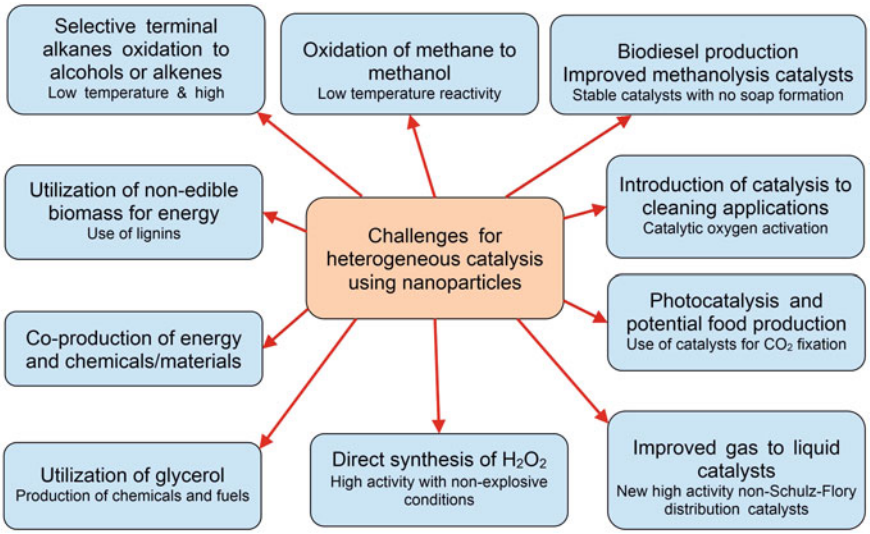


Fig. 24.9 Challenges for heterogeneous catalysis using nanoparticles

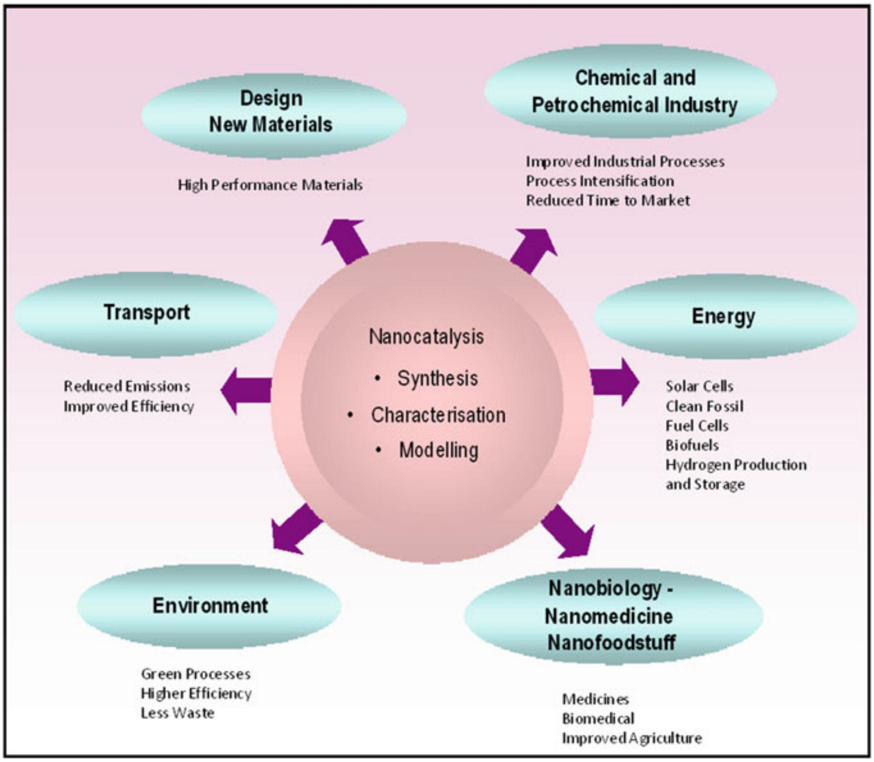


Fig. 24.10 Applications of nanocatalysts

24.5 Conclusion

Nanocatalysis is an essential area in the chemical and biotech industries. It is a broad field covering a wide range of applications as shown in Fig. 24.10. However, a lot of physics remain to be understood to master the field and be able to completely control the synthesis of tailored nanocatalysts. In particular, a good understanding of the relationship between the structure of the catalyst and its performance has to be developed. Today, most of commercial nanocatalysts have been developed by trial and error and more science must be introduced for the development of tailored catalysts.

The goal is to obtain a catalyst which is completely selective, with high activity, a long lifetime, and a low energy requirement. This requires a good understanding and control of the size, shape, electronic structure, spatial distribution, surface composition, and so on.

There are several nanocatalysts derived from carbon derivatives: carbon black, graphite, carbon nanotubes, buckyballs, fullerene, graphene; as well as inorganic nanotubes such as tungsten/boron nitride. Metal and metal oxides are also often used. Finally, nanoclays and quantum dots can also be used as nanocatalysts.

Chapter 25
Nanotechnology for Defense and Security

Defense and security are industrial sectors that are necessary to ensure that our citizens can lead peaceful lives. Nanotechnology has many possible applications in these sectors. It can be used to update existing equipment and weapons or to introduce new functions and devices. It is a broad field which can contribute to conventional as well as unconventional weapons. Some current and potential applications of nanotechnology related to defense and security are displayed in Fig. 25.1.

Nanoelectronics helps to increase the performance of information systems. Nanomaterials can make guns lighter, with more ammunition. In combination, these new technologies can lead to guns, that can target and fire automatically if an enemy is detected with self-guided bullets.

Nanorobots can be programmed to attack and destroy weapons, metals, or other materials. Bionanorobots could be developed in such a way to be lethal to individuals, based on a preselected DNA profile.

Nanoelectronics as well as nanomaterials will help to make virtual reality systems more powerful and less expensive. Virtual reality systems are important for training or for battlefield reconstruction.

Nanomedicine can monitor the health of soldiers and provide vastly improved wound treatment occurring in the battlefield.

This chapter will address two main aspects. One is about defense and security in the sense of attacks against civilians or industrial accidents. The second addresses more directly applications of nanotechnology in the military domain.

25.1 Detection

Civilian societies are now faced with threats ranging from terrorist attacks to problems with drugs or counterfeiting. Industrial accidents can release toxic chemicals. Detection is essential to prevent these threats and, if the worst happens, to identify the products which have been dispersed during an incident. It is essential to find the

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DOI: 10.2991/978-94-6239-012-6_25,

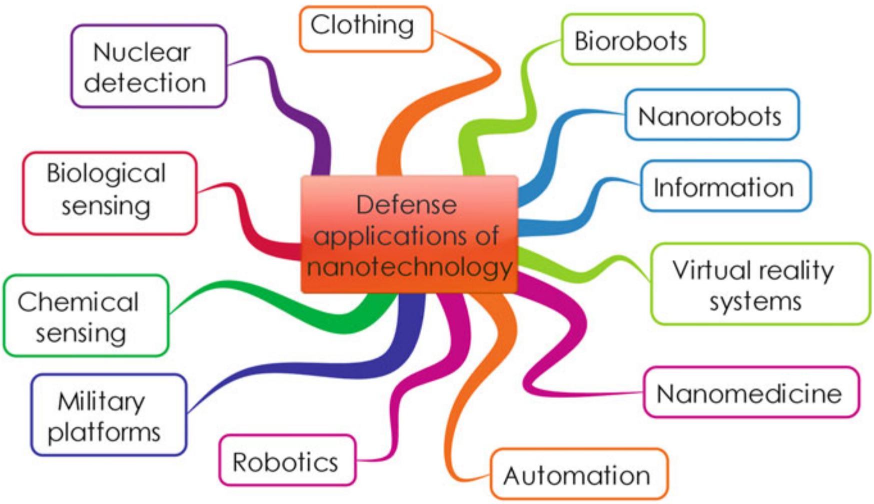
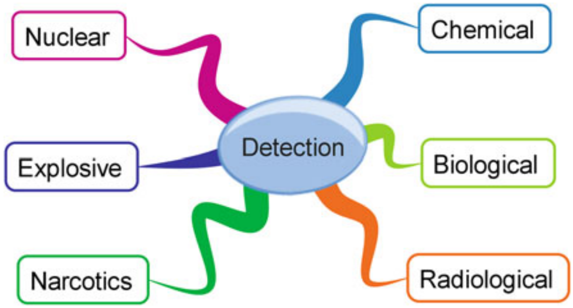


Fig. 25.1 Main sectors in the defense and security domain where nanotechnology can play a role

Fig. 25.2 Main sectors where detection is needed



most appropriate response, and where relevant, the persons responsible. The main sectors of detection are shown in Fig. 25.2.

25.1.1 Chemical Detection

The detection of chemical weapons and toxic chemicals requires sensors which are sensitive, specific, and cheap to be deployed at a large scale. Figure 25.3 shows the different categories of toxins that can be faced during an accident or a terrorist attack. It illustrates each category by a few examples.

Detections tools using nanotechnology, at least in one of the components of the device, are shown in Fig. 25.4 taken from the observatorynano project. There are many potential techniques, some of which are at commercialization stage while others are still at the research level.

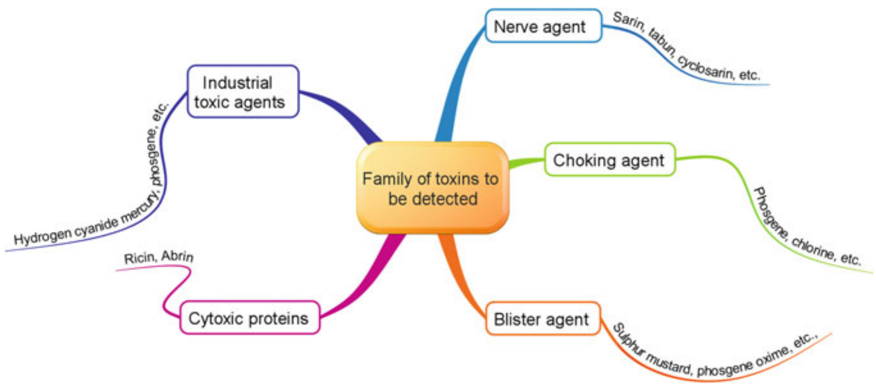


Fig. 25.3 Different families of toxins. Classification from the ObservatoryNano project

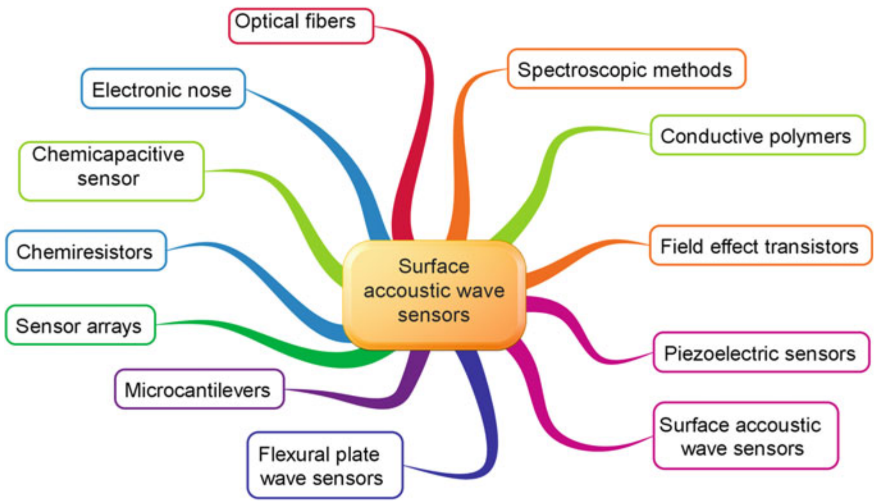


Fig. 25.4 Different methods to detect chemicals where nanotechnology can contribute. Classification from ObservatoryNano project

The air can be contaminated by toxic agents. A gas molecule has a tiny weight which can be detected using piezoelectric sensors. If a gas molecule is absorbed at the surface of the detector, the resonance frequency of the crystal changes and this can be measured. Field effect transistors, used as potentiometers, can detect toxic gases if their gate is made sensitive to them. Conductive polymers connecting two electrodes are sensitive to volatile organic compounds. Carbon black can be included in sensing arrays to detect nerve agents such as sarin.

Nanomaterials are essential to develop the best sensors. The main challenges for chemical sensors are selectivity, sensitivity, reliability, and ease of manufacture. Conventional analysis techniques such as using mass spectrometry, chromatography, or spectroscopy require larger samples and a longer time before the measurement is achieved.

Acoustic waves traveling on the surface of transducers are sensitive to gas molecules absorbed on this surface because of a frequency change or a phase shift. Detectors based on this phenomenon are called surface acoustic wave sensors (SAWS). Flexural plate wave sensors work in a similar way their high sensitivity gives them the ability to detect concentrations in the range of parts per trillion.

Microcantilevers, manufactured in particular out of silicon, can be coated with specific nanofilms. This gives them the ability to detect chemical gases with a higher sensitivity than piezoelectric or SAWS.

Sensor arrays can detect, process, and classify a large amount of data measurements with sensitivities in the range of the parts per billion. They are used to detect nerve or blister agents.

Chemiresistors are sensors based on the change of electrical resistance induced by absorption of gases. Single carbon nanotubes, belonging to this family, are able to detect nerve agents. Chemicapacitive sensors are based on the change of capacity of a dielectric which has absorbed volatile organic compounds.

Electronic or artificial noses can detect the presence of toxic gases and biological agents using several sensors that generate electrical signals which are processed before giving the final result.

Optical fibers can be used as sensing devices by coating one end with a nanosensing material or by replacing the cladding by a sensing material.

In spectroscopic methods, nanotechnology comes into play mainly in the hardware necessary for data processing.

25.1.2 Biological Detection

Biological threats include viruses, bacteria, and toxins that can be deliberately spread among the population, livestock, or crops, with the aim to kill or incapacitate people. According to security agencies, there are 23 bacteria, 43 viruses, and 14 toxins which could be used as biological weapons in terrorist attacks. Some of these biological agents are shown in Fig. 25.5.

Detection methods for biological threats are based on nucleic acids and immunology techniques. Optical biosensors can also be used to detect a change in the transducer surface of a detector where a biochemical reaction takes place in the presence of a threat.

25.1.3 Radiological and Nuclear Weapons

Dispersal of radioactive matter in a dense area of population is a terrible threat. Nuclear fission or fusion weapons are more the concerns of attacks by a sovereign power although homemade bombs are also possible.

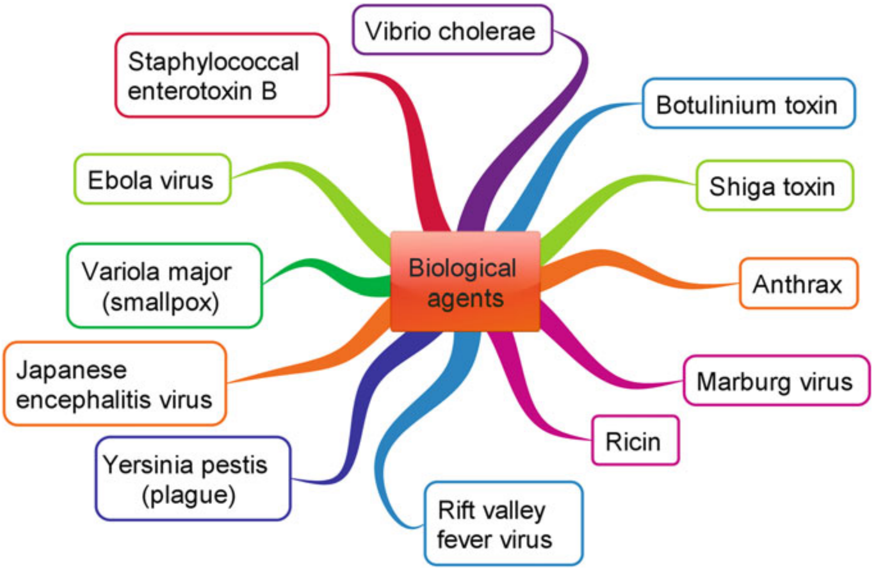


Fig. 25.5 Examples of biological agents which could be used in biological weapons

Nuclear detection is an important issue and high sensitivities can be obtained with existing detector technologies but they are usually bulky and expensive. Nanoscale materials for detecting radiation have great potential. They could replace existing single crystal detection of gamma rays or be used in scintillators to enhance light output. Nanowire arrays of detectors are required for imaging techniques and high rate counting.

Since high resolution germanium detectors used to measure gamma rays need to be operated at very low temperature, alternative portable solutions based on nanomaterials operating at room temperature would be useful especially in the case of nuclear incidents where measurements have to be done quickly out of the laboratory.

25.1.4 Explosives

Detecting explosives in luggage, vehicles, cargo, aircraft, or carried by people, is a great challenge in the sector of security. More than a hundred explosive categories have been reported in the literature.

Several methods have been developed to detect explosives. The first one detects traces of volatile compounds leaking from explosive compounds into the air. The second uses spectroscopy to see if there is a chemical compound present associated with explosives. A third method uses several detection methods at the same time in order to increase detection efficiency. There are several families of detection methods (Fig. 25.6) which have the ability to detect explosives.

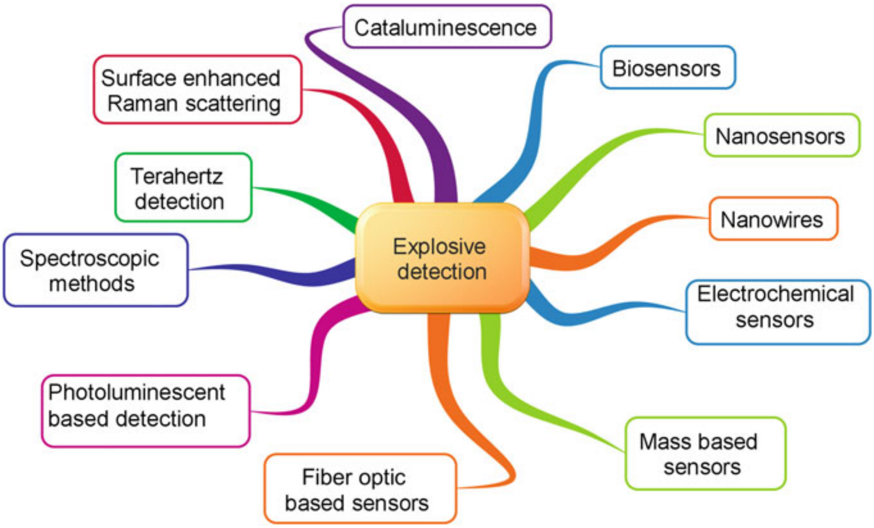


Fig. 25.6 Some families of detection methods available to detect explosives. Classification from ObservatoryNano project

Most of the techniques rely on the fact that absorbing volatile molecules found in explosives changes a physical or chemical property of a nanomaterial. This is the case for electrochemical sensors, mass-based sensors, fiber optic sensors, photoluminescent-based detection, surface-enhanced Raman scattering (SERS), nanosensors, nanowires, and biosensors. The sensor is usually a nanosize material with specific properties. Other methods are possible which do not use nanotechnology, such as spectroscopic methods or terahertz detection, exploiting wavelengths between microwaves, and infrared radiation. This technique has great potentiality, not only in the defense and security but also in nanocatalysis.

25.1.5 Narcotics

Spectrometric methods are mostly used to detect narcotics. However, SERS can be used to detect drugs and narcotic molecules with high sensitivity in blood, urine or saliva. SERS is combined with other methods to detect cocaine, heroin, amphetamines, etc. Thermal neutron and fast neutron analysis can also be used to detect narcotics and researches are presently being carried out into membrane methods.

Narcotics detection needs cheap, selective, small sensors with high sensitivity. The accuracy, time of detection and lifetime of operation are also key characteristics. Detectors have to be operated under various conditions of temperature, humidity, etc. Nanotechnology can be used in these developments as we have seen in the chemical detection section. Selective membrane electrodes are used as sensors to detect fentanyl, which is 40 times more potent than heroin.

25.1.6 Counterfeiting

Counterfeiting is growing all over the world. This concerns counterfeiting of brands, intellectual property, and equipment. This includes pirated copies of music or videos. On one hand it weakens companies and can lead to loss of business and, on the other hand, it can provide customers with potentially dangerous products. Therefore, it is a threat both to companies and customers.

25.2 Response

If an attack on a civilian population occurs because it has not been detected and prevented in advance, it is necessary to respond to the consequences and prevent further damage. There should be medical attention for injured people and contaminating species should be removed or neutralized. Figure 25.7 gives some of the responses involving nanotechnology which will be presented below for some specific examples. This figure has been built from the results obtained in the European ObservatoryNano project.

25.2.1 Prompt Response

Nanoparticles can be used to efficiently deliver antidotes to people at risk (antibiotics, anti-inflammatory drugs, anti-infective medicines, and vaccines) before any potential attack. Nanoparticles can improve the stability of drugs, carry larger concentrations, and provide a better-targeted delivery. Depending on their structure, which can be designed on demand, nanoparticles can carry hydrophilic or hydrophobic molecules. This is done by the same methods as described in Chap. 12.

It is important to make a correct diagnosis and, depending on the result, to deliver the relevant drug to the patient. This is field of *theranostics*, a combination of drug delivery and diagnostics. It is possible to develop arrays of biosensors with the ability to detect a large number of viruses in parallel (up to almost a hundred), to recognize proteins, DNA and RNA fragments, and to identify toxins and microorganisms released during an attack. In this field, carbon nanotubes, nanoparticles, or quantum dots can be extensively used in detection or imaging.

As far as radioactive materials are concerned, only a few studies based on nanoparticles have been carried out. For example, magnetic nanoparticles can absorb low-level radioactive material. This is the case for nanomagnetite composite particles which can absorb radioactive cesium atoms. Other examples concern remediation of nuclear waste. Cesium and strontium radioactive materials are often mixed together. Nanostructured sodium silicotitanate can selectively remove cesium ions while nanostructured sodium titanate can remove strontium ions.

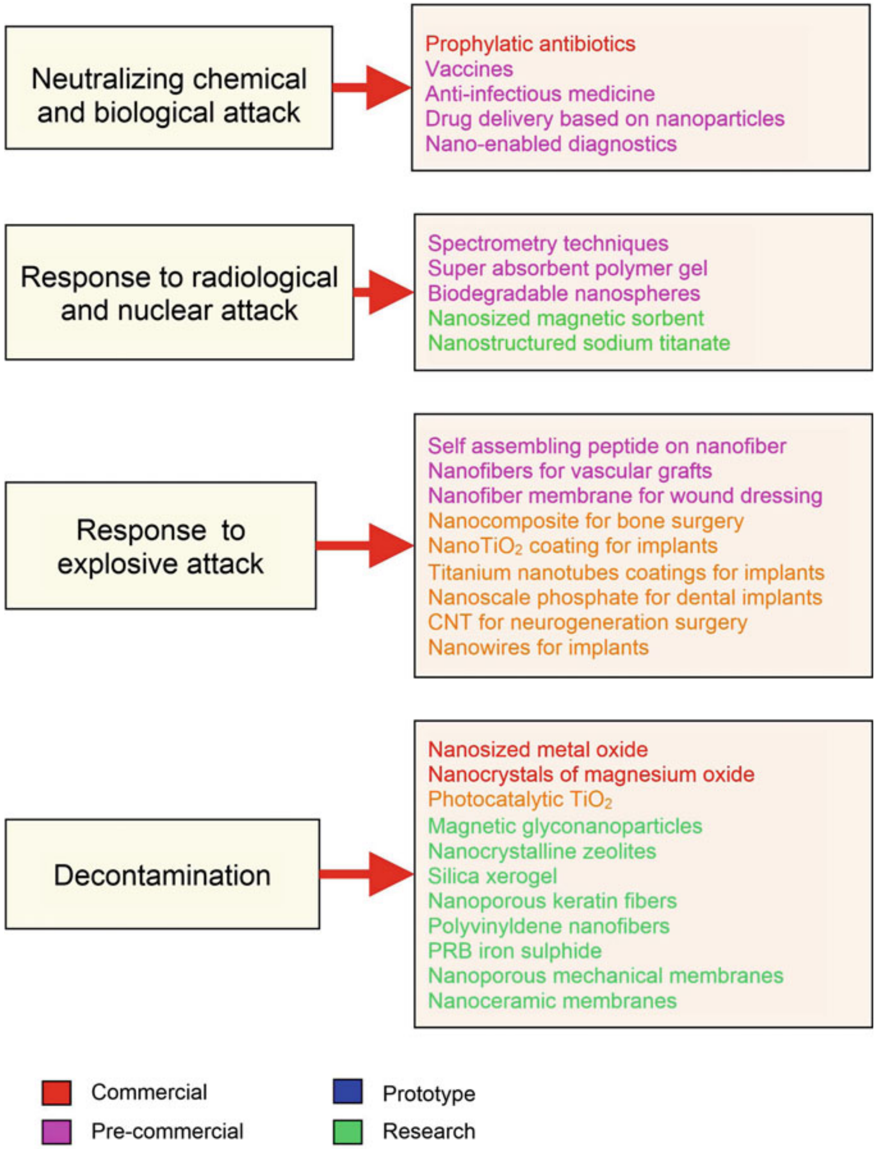


Fig. 25.7 Some responses to various attacks as compiled from the ObservatoryNano project. *Colors* indicate the state of application reached for each technique

In case of a radiological attack, a foam obtained by spaying polymer gels in suspension in water can trap radioactive particles, which bind to nanoparticles contained in the gel. Nanoparticles can be coated with proteins responding to the specific toxins generated in a radiological or nuclear attack. These nanoparticles, injected into the blood of the contaminated person, can detoxify the blood. In order that they are not attacked by the white blood cells, they are prepared in such a way that they are invisible to them: they are "stealthy" with respect to the immune system.

In the case of an explosive attack, many people can be seriously injured. Self-assembly methods can be used to build a nanofiber barrier to stop bleeding without requiring cauterization, pressure, or adhesives. Nanotechnology is also useful in surgery, wound dressing, and implants. Nano-objects such as titanium nanotubes, nanocrystals, nanofibers, and nanoparticles can be used to treat injuries induced by an explosive attack or incident.

25.2.2 Decontamination

After an accident or a terrorist attack, it is often necessary to decontaminate the environment from chemical, biological, or radiological products.

Nanotechnology can be used to develop filtration membranes for water and air. Metal oxides of aluminum, titanium, or cerium in the form of nanoparticles can be used to destroy bacteria and viruses: macrocrystals are useless in this respect because of their much lower surface reactivity. Magnesium oxide nanocrystals can chemi-absorb organophosphorous compounds at room temperature. They can be useful in the case of an attack with chemical weapons. Bacteria such as *Escherichia coli*, *Bacillus cereus*, or *Bacillus globigii* can be decontaminated in a few minutes using nanopowders of calcium and magnesium oxides. Carbohydrate-coated magnetic glyconanoparticles can be used to quickly decontaminate bacillus anthrax.

Photocatalysis, based on TiO_2 nanoparticles, can be used to destroy various organic pollutants and toxic agents. TiO_2 is an inexpensive material that can be manufactured in nanoparticles with size ranging from 3 to 5 nm. Photocatalysis can be extended with photocatalytic nanowires or membranes. In this latter case, the membrane can be used in protective masks because it stops toxic gases while allowing oxygen and nitrogen to pass through. Another example is nanosponges manufactured from mesoporous silicon dioxide which can remove toxins from water. Their nanopores, with a size of 6 nm, can be filled with self-assembly layers permitting capture of mercury or other chemicals. Filters carrying nanocrystalline silver are also used to decontaminate water from *Legionella pneumophila*, for example.

25.2.3 Forensics

Forensics uses science and technology in criminal investigations. It concerns the identification of criminals, weapons, and methods used to commit a crime. DNA identification is important in forensics: this technique is greatly advertised in television detective series. DNA can be extracted, amplified, and identified in microdevices where nanotechnology can play a significant role. The goal is to get low-cost and fast devices using sample volumes in the nanoliter range.

Fingerprints are frequently used to get evidence from a scene of crime. They are of three kinds: visible, indented, or latent. Visible fingerprints can be seen explicitly. Indented fingerprints are those obtained from malleable materials. Latent fingerprints are invisible and more difficult to detect. Different methods are used to reveal them and nanotechnology offers new possibilities.

Fluorescent nanoparticles or quantum dots can be used to detect latent fingerprints. Because of their small size, nanoparticles have the ability to detect greater details and are more accurate than conventional techniques. For example, metal nanoparticles, such as gold or silver nanoparticles, can be used in latent fingerprint detection. Metal oxide nanoparticles, such as TiO_2 or nanostructured zinc oxide, are able to detect fingerprints on surfaces. Metal sulfide nanoparticles, in the form of nanocrystals or nanocomposites, are especially useful in fingerprint detection on soft drink cans and aluminum foils.

Scanning probe microscopy, which is a technique working at the nanoscale, is used to detect fingerprints and also forged documents. It is a slow detection method but is nevertheless useful in difficult cases. For example, it has been used to recover information from mobile phone subscriber identity module (SIM) cards after an explosive attack. Scanning electron microscopy is also often used in forensic and counterfeiting analysis as shown in Fig. 25.8.

Biosensors are used in forensics to identify, for example, sexual crime perpetrators. Identification of prostate specific antigen (PSA) gives the possibility to detect semen and other body fluids. Various nanoparticles and nanostructures are used: nanoparticles can be coated with antibodies and strands of DNA; antibodies can be coated on a silicon nanowire field effect transistor.

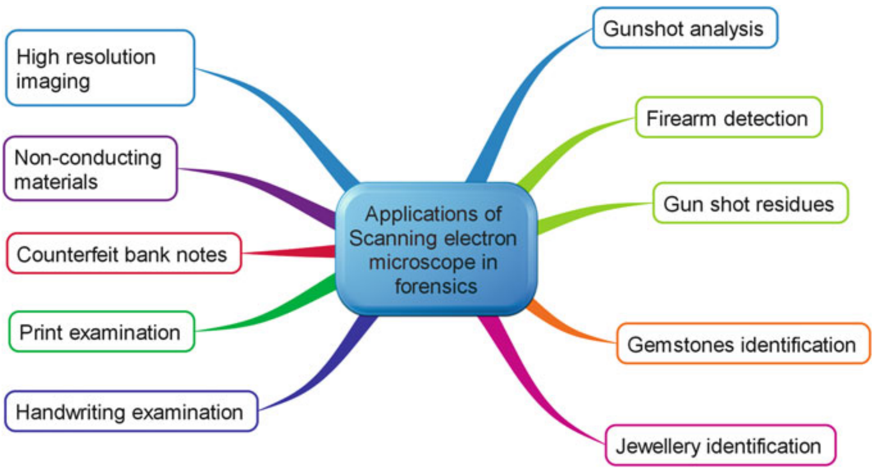


Fig. 25.8 Some applications of scanning electron microscopy in forensics. Examples from the ObservatoryNano project

Beyond fingerprint identification, DNA identification is of great interest in modern forensics. It is for example possible to apply genomagnetic nanocapture to collect trace amounts of DNA or mRNA strands and identify just a single base difference. In order to do that, magnetic nanoparticles are functionalized with strands of DNA which are able to recognize particular gene sequences. High sensitivity and selectivity can be reached and the magnetic properties of the nanoparticles allow collect of these strands of DNA, mRNA, or proteins.

Electrochemical sensors can also be used. They are based on hybridization and allow selective genetic identification. Low-cost and sensitive sensors can be made with good reliability.

A lab-on-a-chip is the ultimate device allowing, us to perform portable, low-cost, and high sensitivity analysis. The whole chain of detection, from the collection of the sample to the data analysis can be done in a single shot. One advantage for forensics investigations is the portability and the fact the sample cannot be contaminated during the different steps of the analysis by external products.

25.3 Protection

Protection of people before, during, and after an incident or attack is an important issue for civilians as well as military personnel. This concerns clothing equipment and various protections against chemical, biological or radiological agents, and explosives.

25.3.1 Protection of People

Protective clothing contributes to personal protection. Impermeable and selectively permeable clothes are one of the solutions. The Protective clothes should be lightweight and long lasting. This is not the case when charcoal, used today in many protective clothes, is used. Magnesium oxide nanoparticles loaded into nanofibers are more efficient than charcoal. More generally, nanofibers have a highly specific area and can include active chemistry as well as other functions. They can give a better protection against aerosols.

Protective gear is used daily by security personnel who can be faced with hazardous situations. They need to be lightweight while giving a high degree of protection against various chemical or biological agents. Nanocomposites will be more and more used in their manufacturing.

Protection against explosives, bullets, etc., is also needed. Fabrics made using carbon nanotubes offer better shielding than fabrics based on steel and are much more lightweight.

25.3.2 Protection of Infrastructure and Equipment

Buildings can be damaged or destroyed by explosives or by fire. Electronic infrastructure, essential for communication, data processing, and equipment control can be disabled in an electromagnetic attack or disrupted by malicious intervention. Figure 25.9 summarizes the response to these threats.

Infrastructures such as buildings, houses, etc., can be destroyed or seriously damaged in case of an attack or a severe natural event. Their mechanical resistance can be increased through incorporation of nanomaterials. For example, we have seen, in Chap. 21, how the properties of concrete can be improved with nanomaterials. In the same way, nanometer-size precipitates increase the strength of steel alloys against shock waves and metal foams give a high protection against ballistic projectiles. Other nano-objects, such as carbon nanotubes or inorganic fullerenes can be used to reinforce structures against explosions, earthquake, and so on.

Nanocoatings and nanoadditives can significantly improve fire resistance. Nanotitanium or nanosilicon dioxides improve fire resistance of coating materials. This is also the case of nanoclays for acrylate and polymer nanocomposites. It turns out that buckyball nanocomposites are also flame retardants. Furthermore, carbon nanotube membranes are used to reduce flammability of glass fiber composites.

We now exploit electromagnetic radiation far more than in the past. Frequencies in the range of 1–5 GHz are emitted by many devices in daily use (smartphones, WiFi, transmitting antennas, etc.). This large variety of electromagnetic sources can interfere with critical electronic equipment. Electromagnetic interference is a serious issue. Electromagnetic shielding can be provided by conducting polymers or nanocomposites containing conducting polymers. Nanocrystalline silver particles can also be used. Carbon nanofibers or carbon nanotubes can eventually be used

Fig. 25.9 Protection of infrastructures against the three main threats where nanotechnology can play a role: mechanical destruction of structures, fire, and electromagnetic interference

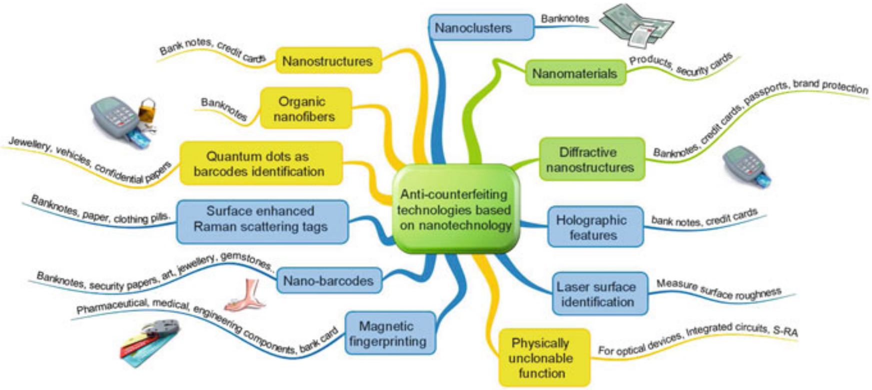


Fig. 25.10 Main anti-counterfeiting techniques based on nanotechnology (list from the ObservatoryNano project). Techniques which are either commercial or precommercial are displayed in *blue*. Techniques at the prototype level are indicated in *green* and those which are at the research stage are shown in *yellow*

but their cost is high. There is also a need to protect electronic equipment against electromagnetic bombs (E-bombs) which may disable entirely any electronic equipment in the range of the explosion.

25.3.3 Anti-counterfeiting

Many techniques are being developed to protect products and consumers against counterfeiting. More and more are based on nanotechnology. Those concerning brand theft and prevention of intellectual property theft, investigated in the ObservatoryNano project, are summarized in Fig. 25.10.

The goal is to obtain cheap intelligent materials and packaging allowing precise tracing and automated identification.

25.3.4 Authentication

Nanotechnology can also play a role in authentication of individuals. Some methods such as fingerprints are common in forensics but need to be easier to apply. Nanotechnology can be applied to several of the identification techniques (biometrics) that are used based on fingerprints, iris, retinal, facial, and hand characteristics. It is also necessary to safeguard the related information and its communication.

Nanocomposites can be used as a medium for recording biometric information. Opal-based nanocomposites are used in authentication technology.

As far as anti-counterfeiting is concerned, optical fluorescent fibers can be used to protect brand clothing or pharmaceuticals.

Quantum cryptography, which we already discussed in Chap. 9, can be used to securely transmit information from one place to another. It is based on quantum mechanics and uses entanglement effects.

25.3.5 Identification

It is increasingly necessary to know the path followed by an object from its manufacture to the user. This is important for products as diverse as pharmaceuticals to aero-engine components. Positioning and localization techniques provide quality assurance and the ability to trace back a deficient or dangerous product. It is also useful in the case of counterfeiting.

Radio frequency identification (RFID) tags are widely used to identify objects or goods. Metal nanoparticles or carbon nanotubes have been shown to enhance their characteristics.

25.4 Nanotechnology and Military Applications

Nanotechnology is also able to bring innovation and improvements in the military domain. Some applications of nanotechnology are purely civilian, others purely military and some overlap. This is summarized in Fig. 25.11. The drive for dual use comes from the fact that it is expensive to have a dedicated military industrial sector in all fields. For example, as far as electronics is concerned, progress is very fast in the civilian domain and it is more efficient to use civilian components, with variants or slight improvements rather than developing bespoke military components which will be difficult to maintain in the future. A similar situation is observed with supercomputers which are now developed with thousands of conventional microprocessors rather than with a few supermicroprocessors.

25.4.1 Military and Dual Nanotechnology Applications

According to Schilhuizen and Simonis,[1] nanotechnology for defense can be divided in four main sectors: materials, information, energy, and biology. Applications in the pure military domain are summarized in Fig. 25.12. Dual applications, which can be used both in the civilian and military sectors, are shown in Fig. 25.13. Most of these have been presented in previous chapters.

[1] *Nanotechnology, innovation opportunities for tomorrow's defense* F. Simonis and S. Schilthuizen, TNO Science and Industry, 2006.

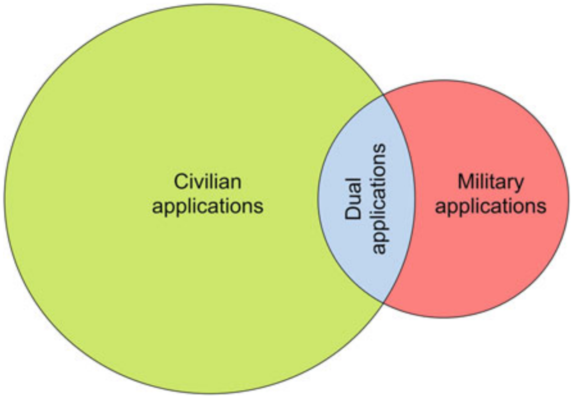


Fig. 25.11 Civilian applications and military applications have a common domain corresponding to so-called dual applications. Technologies in this common sector can be applied both to the civil and military

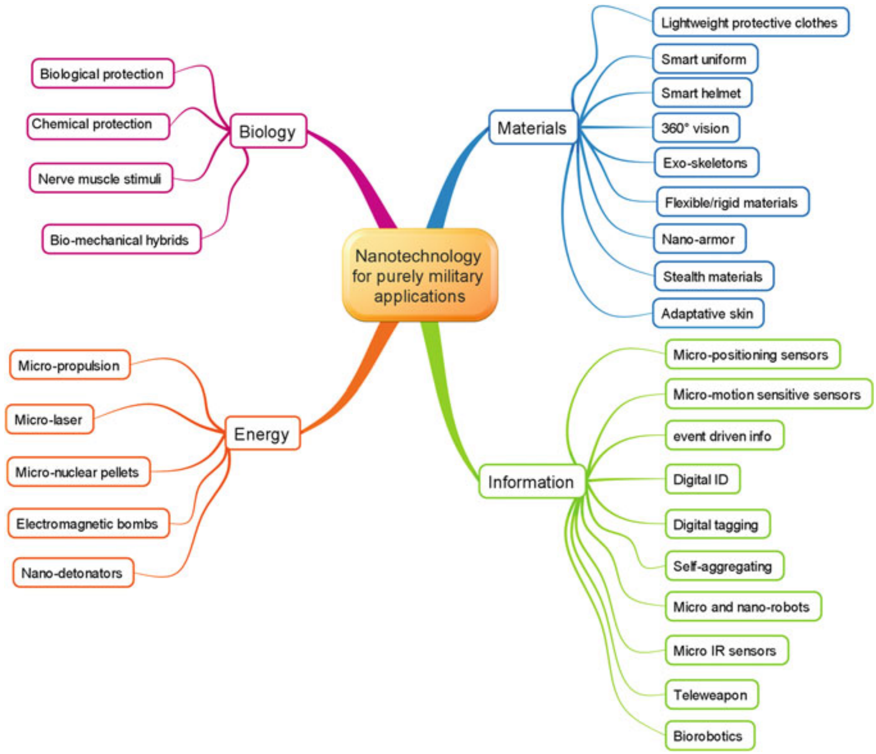


Fig. 25.12 Different applications of nanotechnology in the military domain are shown. The compilation of these technologies has been made in the report of Simonis and Schilthuizen

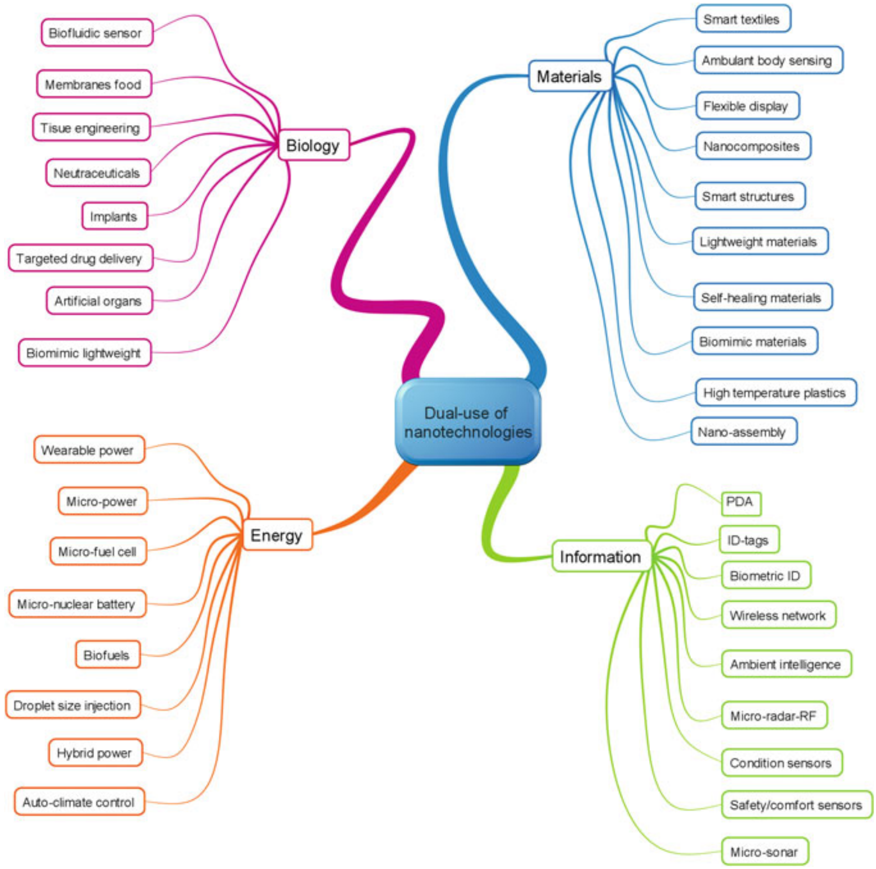


Fig. 25.13 Dual use of nanotechnology. Compiled from Simonis and Schilthuizen

25.4.2 Nanotechnology for Human Beings

The soldiers of the future are quite different from the soldiers of World War II. They have better protection against various projectiles coming from weapons, their physical performance will be enhanced and they are connected in real-time with logistics which provide them with necessary information and orders. This real-time feedback gives a group of soldiers a shared intelligence for more effective action. Their mental state and health has to be continuously controlled in real time. They should be equipped with survivability means and have what is necessary to be able to treat themselves if they are wounded. All these requirements demand for lightweight materials and devices which are enabled by nanotechnology. Figure 25.14 shows the main functionalities that a modern warrior should exploit where nanotechnology can be involved.

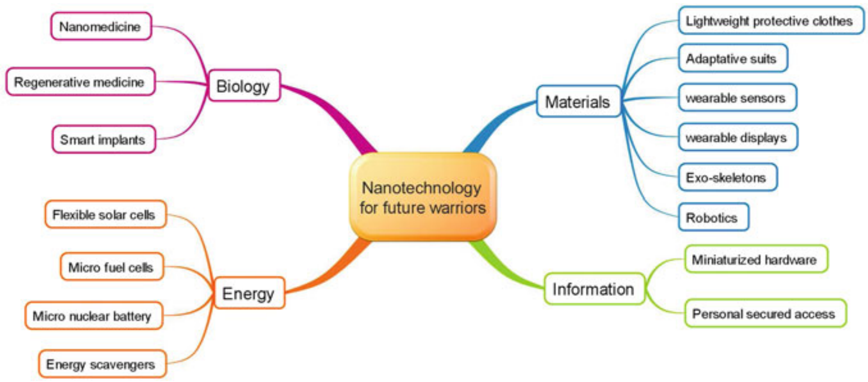


Fig. 25.14 Areas where nanotechnology can play a significant role in the equipment of future warriors. Built from data of Simonis and Schilthuizen

Fig. 25.15 Nanotechnology is involved in many of the components of the equipment of the warrior of the future

The future warrior should be equipped with different systems communicating with each other: he is a wireless soldier with the ability to interact in real time with other soldiers, logistics, and various weapons. The abilities require micro- and nanotechnology systems enabling lightweight equipment that is still highly sophisticated. For safety, communications have to be encrypted which requires powerful portable data processing units.

The equipment of a soldier is increasingly sophisticated (Fig. 25.15). There is the helmet incorporating several functions such as wireless communication, GPS, wide angle camera, vision display, infrared vision, and visor display. It should be able to filter the air. It is coupled to a personal digital assistant (PDA) to get additional information, and to a watch which could also be used for health monitoring and drug delivery. The uniform is multifunctional and should protect against chemical, biological, or radiological agents in addition to having anti-ballistic properties against bullets and fragments of grenades, mines, or bombs. Furthermore, the soldier should feel comfortable. Ventilation and insulation are therefore necessary.

On top of that soldiers carry sophisticated weapons. The whole equipment of the modern warrior needs energy to function. Lightweight energy sources are required and harvesting waste energy such as vibrations or low temperature heat is an

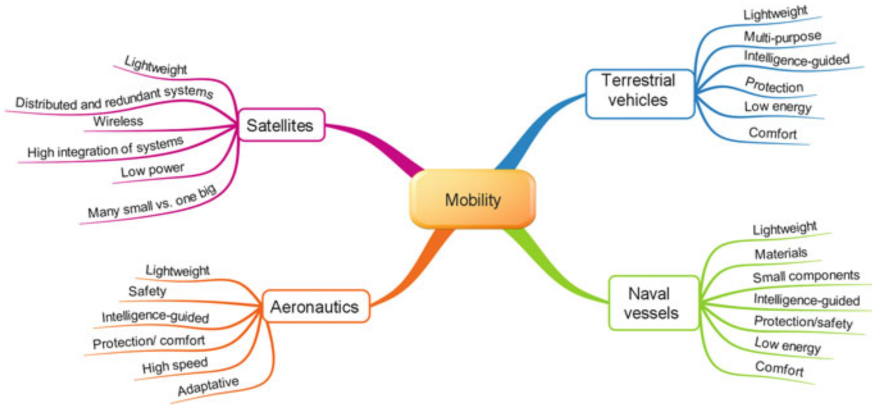


Fig. 25.16 Different aspects of mobility for the military. Built from data of Simonis and Schilthuizen

important issue to decrease the weight of power sources. Collecting solar energy in flexible cells is of course of great interest.

Nanotechnology helps to reduce the weight and volume of the soldier's equipment. It also helps to reduce energy consumption and enhances the characteristics of energy sources such as batteries or microfuel cells.

25.4.3 Mobility

Mobility is essential for the military. The sectors concerned with nanotechnology are shown in Fig. 25.16.

A common keyword is "lightweight." Replacing metal by high strength nanocomposite plastics is worthwhile. Another benefit of doing that is to reduce the radar signature of the vehicles. Information and communication technologies also rely heavily on nanotechnology.

Power is a real issue and nanotechnology permits enhanced performance of energy sources and decreases the energy consumption of components.

In aeronautics, stealth with radar absorption coatings or thermal camouflage, and high-energetic propellants such as nano-dispersed aluminum are interesting applications of nanotechnology. There is also an evolution toward remote and unmanned guidance. Satellites are more and more used for observation, collecting information, and telecommunications. In this sector, the payload is an important parameter. There is a now a tendency toward orbiting networks of small satellites rather than a single large one. The classification of satellites is shown in Fig. 25.17 in order to give orders of magnitude.

Fig. 25.17 Classification of satellites. The picture shown corresponds to the minisatellite SMOS (Soil Moisture and Ocean Salinity). SMOS mission is a joint ESA/CNES/CDTI Earth observation programme

25.4.4 Weapons

New weapons are developed in two opposite directions: lethal and nonlethal. For lethal weapons, the goal is to make them even more lethal. They are an evolution of conventional weapons including better precision, targeting, and intelligence. Nonlethal weapons are developing to temporarily neutralize an enemy. They are interesting for the police and security services. Many of them are based on energy waves. Some of the areas of weapons where nanotechnology can be used are shown in Fig. 25.18.

25.5 Conclusion

To summarize, for military capabilities, the driving force of nanotechnology is summarized in Fig. 25.19: smaller, lighter, faster, and cheaper.

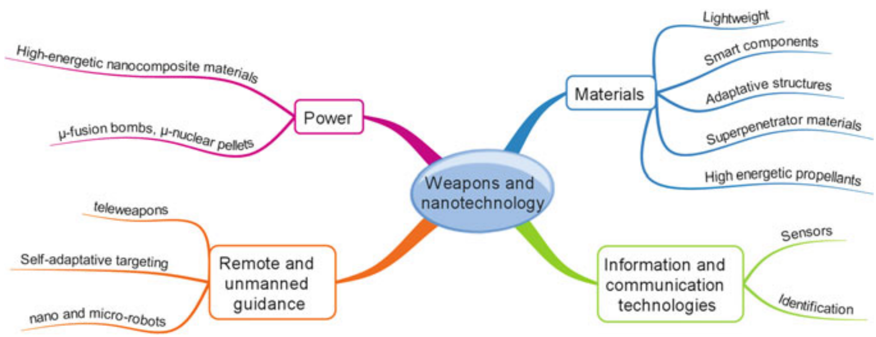


Fig. 25.18 Some areas where nanotechnology can improve weapons

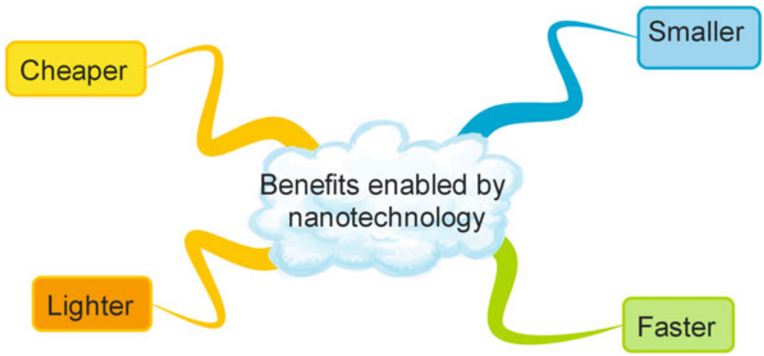


Fig. 25.19 Benefits enabled by nanotechnology in the military domain

Several technologies can be applied both to the civilian and military domains (dual-use technologies). This allows cutting down the costs and being more efficient. Defense and security is a domain which should not be underestimated by society as everything should be done to protect our citizens while keeping the freedom of expression.

Part VIII
Nanotechnology in Industry, Defense, and Security

Conclusion

Nanotechnology has spread to virtually all industrial sectors and provides an asset to those industries using its possibilities to improve existing products and services and to develop new one. Nanotechnology will be the engine of development of this whole century. It will bring benefits but also potential drawbacks which have to be seriously assessed.

Nanotechnology is now at the heart of industry development. It will improve existing products and create innovative new ones. In Fig. VIII.1 we show some of the industrial sectors impacted by nanotechnology.

For instance, many processes and chemical reactions would not exist without catalysis. Nanomaterials pave the way for nanocatalysis to make catalysis more efficient, more selective, less energy consuming, and more stable. Made from

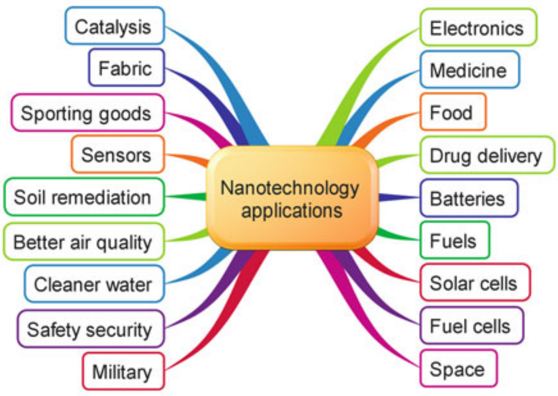


Fig. VIII.1 Some sectors where there are industrial application of nanotechnology. Of course there are others

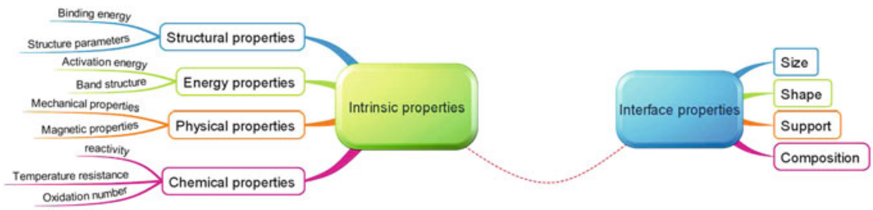


Fig. VIII.2 Some intrinsic properties of catalysts and the effect of interface properties on their efficiency

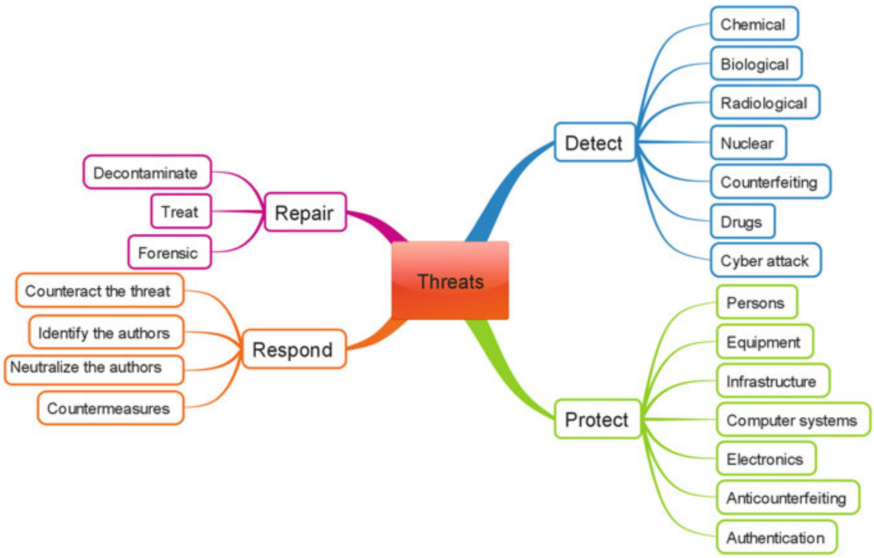


Fig. VIII.3 Management of different threats

molecules or nanomaterials, a catalyst has intrinsic properties (Fig. VIII.2). Its structural and physical properties and its band structure are important for some crystalline nanomaterials, etc. The nanomaterial is prepared in such a way that it becomes an efficient nanocatalyst. This is done by changing the nature of the interfaces with the reactants: shape, surface, size of the nanoparticles, etc., to produce a very reactive material which is able to catalyze chemical reactions.

In a broader context, there are today numerous threats to society.

Information is quickly available around the world, so while personal safety is much improved compared to 100–200 years ago, the publicity of any negative event is highly publicized and terribly amplified. Furthermore, people want a zero-risk environment which is very difficult to obtain in some sectors such as road transport.

New threats have emerged in society with the associated problem that the threat can affect anyone. Figure VIII.3summarizes the different aspects to be taken into account when faced with a threat. The threat has to be detected, people and equipment have to be protected, a response should be formulated, and repairs have to be done afterward.

Part IX
Nanotechnology: Opportunities and Risks for Society

Introduction

Structuring materials at the nanoscale level allows improvements in their bulk or surface properties, leading to innovations in product functionality. Combinations of nanotechnologies will contribute to novel systems for energy storage and conversion, such as nanorechargeable batteries, solar cells, and hydrogen production; smart coatings for buildings, nanofilters for diesel engines, low energy lighting, and new textiles. Nanotechnology will be a major contributor to reductions in carbon emissions and the drive toward sustainable development.

A *nanomaterial*[1] can be formally defined as a natural or manufactured material containing particles, in an unbound state or as an aggregate, where, for at least a proportion of the particles, (named nanoparticles), one or more external dimensions is in the size range 1–100 nm. Fullerenes, graphene flakes, and single-wall carbon nanotubes all be considered as nanomaterials. Figure IX.1 represents the scale from human cells to manufactured components from meters to nanometers.

Nanomaterials and nanotechnologies are poised to become extremely valuable commodities in the near future. Many segments of industry will have to exploit them to succeed and there will be knock on benefits for impact on society. The revolutionary development of the nanofield will demand special attention to safeguard the environment and the health of the general public.

[1] European Commission guidelines dated 2012 identify various risks from exposure to nanomaterials: Environmental risks: release of nanoparticles into the environment, soil, water, or air Risks in nanomedical treatments. Waste management and end-of-life reclamation and recycling.

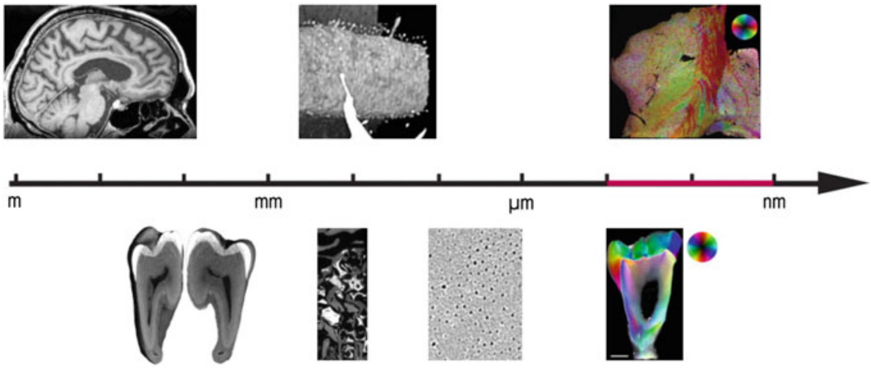


Fig. IX.1 Scale effect of components from meter to nanometer Image courtesy of University Basel

There are uncertainties about possible toxic effects of at least some types of nanoparticles. Since these materials could be used by all consumers, through medical, transportation, clothing, construction, and food applications, the health and environmental consequences cannot be neglected. Safe processes for post-consumer disposal and recycling must be developed.

Chapter 26
Risks and Toxicity of Nanoparticles

Risks of nanotechnologies cover a large spectrum of possible types of exposure, such as in the home and office environment from cosmetics, medicines, foodstuffs, and cleaning products: or, risks to workers exposed to nanoparticles and nanomaterials during manufacturing and production processes. In addition, accidental release of nanoparticles from commercial products during manufacturing or assembly may be highly undesirable.

26.1 Risks and Hazards

It must be stressed that humans have always lived in an environment filled with nanoparticles: natural aerosol particles from dust storms, from volcanic eruptions or forest fires; or those produced as side effects of human industrial activity such as the use of fossil fuels, the combustion of vegetation to clear agricultural land, and ultrafine-nanoparticle emissions in automobile traffic. In large cities, the air may contain a few hundred thousand nanoparticles per cubic centimeter. Smoke from cigarettes also contains nanoparticles.

Risk and hazard

A hazard is a source of potential damage such as an adverse health effect or harm on a person. It can also damage equipment or an organization. For example, I can cut myself with a knife or I can get a mesothelioma if I am exposed for a long time to Asbestos. A risk is the probability that somebody is harmed or experiences an adverse health effect if exposed to a hazard. In the case of equipment or an organization, it is the probability that there is damage if exposed to a hazard.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,

DOI: 10.2991/978-94-6239-012-6_26,

Fig. 26.1 Loosely speaking the risk is the product of the danger and the hazard

Risk and hazard

For example, there is a hazard associated with rock climbing but no risk if you never undertake this activity. Similarly, the risk of dying from lung cancer is larger if you smoke 30 cigarettes per day compared to the situation where you are a nonsmoker. For a given hazard, the risk depends on the exposure to the hazard. The exposure itself depends on many conditions: to how much and for how long a person is exposed? This means that the risk is, loosely speaking, the product of the hazard with the "exposure" (Fig. 26.1). To reduce the risk one can play both on the hazard and on the exposure. For example, with dangerous nanoparticles, the best is to prevent any exposure to them. This can be done during manufacturing and easily monitored.

At present, there is only minimal exposure to nanomaterials originating from industrial manufacturing, with some exceptions for workers in the chemical or related industries, who may experience dermal exposure through filling, pouring, cleaning or powder handling, or where ingestion via hand-to-mouth contact can occur if precautions are not followed.

The widespread use of nanoelectronic and nanomechanical components or NEMS and other nanosensor devices causes little or no exposure to populations outside the workplace. This situation may change as more and more companies become involved in nanotechnologies, with corresponding growth in production volumes and product ranges, leading to the possibility of higher level exposures. A knowledge base must be developed to allow a partition between potentially dangerous and safe products and applications. Care must be taken in applying processes such as cutting and machining of materials containing nanocomponents.

Figure 26.2 shows the possible interactions between people (workers or consumers) which can lead to contamination by nanoparticles. A risk can exist for workers in the production, transport, storage, and waste stages. There can be a risk for the consumer during the use of the product. Consumers can themselves eventually create a risk when they get rid of the object. These risks are direct risks. At all stages of the product lifetime, there can be a risk of an environmental pollution. This can be considered as an indirect risk through the air, the water, and the food which can be polluted with nanoparticles and reach people.

The unique characteristics of nanoparticles mean that current health and safety guidelines for well-established chemical and engineering products and processes may have to be adjusted. The same properties of small size, large surface area,

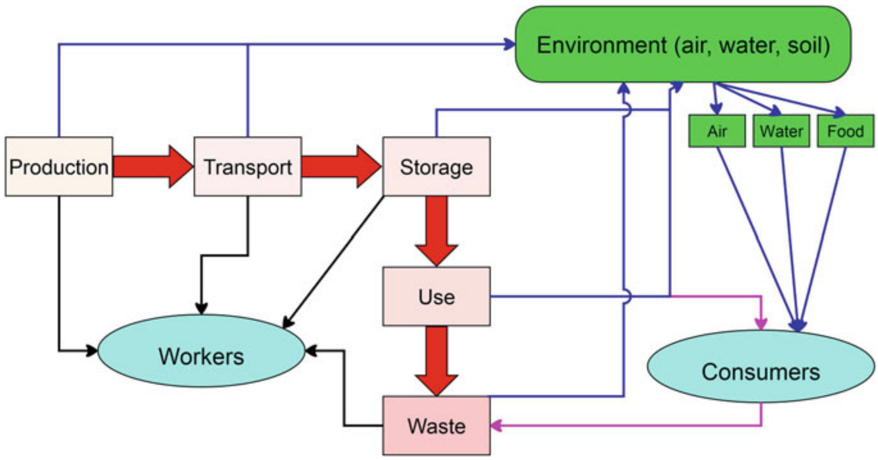


Fig. 26.2 Different interactions of workers and users with pollution due to nanoparticles

and increased chemical reactivity that make nanomaterials beneficial may cause damaging effects once they have entered the human body.

The assessment of immune safety of nanomaterials is of the greatest importance in the context of human health protection. The human immune system is the defender of our body's health and thus it is of the utmost importance that contact with foreign nanoparticles does not affect the immune system. In essence, the effect of nanomaterials on the immune system should be the starting point in defining safety criteria and operating restrictions for nanomaterials. Standard safety devices should be developed to monitor and protect human safety.

It is important to note that there are already nanomaterial systems in batteries, fuel cells, and catalyst and filter systems to reduce pollution in cars and airplanes which present no health hazard for humans. Nanotechnology hazards are mainly limited to "free" nanoparticles and not to nanomaterials embedded into a material, component, or consumer product. Nanomaterials in foodstuffs and nanomedicines or pharmaceutical treatments may require special attention. It is unlikely that engineered nanoparticles that are bound in a matrix or somehow fixed in a product (nanocomposites) will be released subsequently due to burning, grinding, or machining operations. The problem may arise in nanocomposites with biodegradable matrices (bio-nanocomposites) as the nanoparticles can be liberated in the environment during the slow biodegradation process unless they are also biocompatible (biodegradable or biocompatible nanoparticles).

In order to avoid health problems and to guarantee the successful development of nanoscience and technology, it is of the utmost importance to define the boundaries between safety and danger for health and the environment. Therefore, appropriate actions, both for regulations and technologies, should be undertaken by governments, nationally, European and internationally and the nanoindustry.

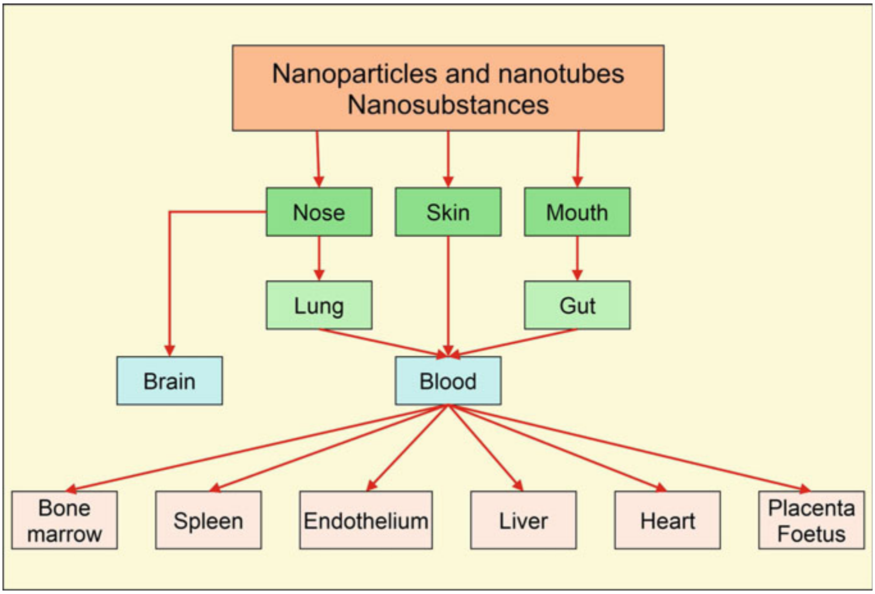


Fig. 26.3 Risks roadmap of nanoparticles

26.2 Engineered Nanoparticles and Human Health

"Free" nanoparticles can enter the human body via inhalation, ingestion or through the skin. They can be dispersed deliberately or accidentally into the environment, be present in foodstuffs, in medical treatments, or in personal care products such as cosmetics or hair coloring. Once in the body, the pathways taken by nanoparticles are unpredictable and strongly dependent on the nanomaterial in question: its composition, size, crystalline structure, and surface characteristics. It is therefore important to investigate their implications for human health and the environment more broadly (Fig. 26.3).

To study the risks of nanotechnologies, traditional physical, chemical, and biochemical measurement techniques for safety assessments of toxicity cannot be simply extrapolated to determine the behavior of the nanosubstance: one has to address the particular characteristics of the material in the nanostructured form. Nanoparticles tend to be chemically much more reactive than microparticles. A typical example of increased reactivity due to this size effect is seen for the metal gold: it is inerted in bulk form but chemically reactive as a catalyst in the form of gold nanopowders.

Nanosized particles could enter the lungs via the mouth and nose and induce toxic effects: inflammation in the respiratory tract, pulmonary dysfunction, or transport through the blood stream to other organs or tissues of the body (Fig. 26.4). Inhalation studies in rats have shown that exposure to various nanoparticles leads to them being trapped or immobilized by immune cells in the lung. Low particle concentrations

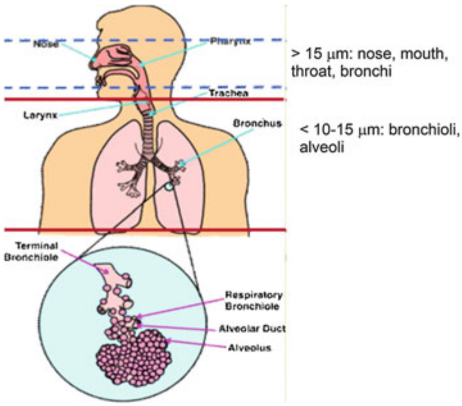


Fig. 26.4 Inhalation exposure of nanoparticles—risk assessment. Image courtesy of VUB, Brussels

have no or little effect, but at higher concentrations, inflammation of the lung occurs. However, some nanoparticles are more aggressive: for example, multiwall carbon nanotubes caused significant effects after inhalation as pulmonary granulomas were found in the lung which may develop into tumors.

The exposure of consumers to nanoproducts used in the food and drink industry can occur through ingestion. This includes additives carefully tested for safety, but in addition materials that are not intended to be ingested such as packaging can still be taken in accidentally and lead to internal damage.

Nanoparticles may penetrate the skin or produce reactive molecules that could lead to skin cell damage. Nanotechnologies used in products such as cosmetics, toothpaste, or medical wound dressings are designed to bring nanoparticles into contact with the body for beneficial effects. Dermal penetration studies on human skin *in vitro* indicate that TiO_2 and ZnO nanoparticles do not pass through healthy skin, but there are concerns that small wounds or damage from sunburn or eczema could allow the materials to penetrate to the bloodstream with unforeseen effects.

Nanoparticles which reach the inside of the body may not necessarily cause damage; but once durable, biopersistent nanoparticles have been accumulated in a sufficiently high concentration for a long time in sensitive areas such as in the lungs, brain, or liver, then they might induce damage or create oxidative stress effects. There is a lack of toxicological understanding of the long-term effects that nanoparticles may have. Nanoparticles have not been found to lead to genetic damage, however.

The effects of nanomaterials in the wider environment must also be established. The aquatic toxicity of nanoscale TiO_2 and ZnO was found to be low in tests: the chronic toxicity did not differ essentially from that of non-nanoscale materials. Indeed it could be associated with release of ions which can occur independent of size, it should taken into account that ions and molecules are almost always even smaller than nanoparticles.

Although the study of toxicology of nanoparticles is still in its infancy, it is evident that the interaction of nanosubstances with the human body may lead to damage.

The possibility and extent will depend on various parameters such as chemical properties, size, and shape, and whether or not the particles dissolve or agglomerate (both of which makes them safe), or remain as free particles and cause irritation and damage to the immune response. This in turn is a function of their chemical properties, morphology, and size.

Industry, governments, and regulators must perform robust life cycle assessments and demonstrate the safety of nanotechnologies to the public, to the workers, and to all involved with nanoparticles usage and applications. Open communication and interaction between all stakeholders is necessary to ensure transparency of the scientific results and to generate a feeling of trust toward nanotechnologies.

26.3 Toxicity and Risks

The development and the application of nanomaterials and nanotechnologies have been a subject of media concern and there has often been adverse publicity without real evidence. Nanoparticles are too small to be visually observed, so they are considered as an unseen hazard like ionizing radiation, and the effects on health and the environment are perhaps wrongly assumed to be significant and potentially of high risk.

It is not appreciated by society that nanoparticles are already used widely in consumer products, and have been for many years in some applications such as cosmetics. Sun creams, for example, are more transparent when applied to the skin because the size of the (nano)particles used in the emulsion has decreased. The nanoparticles of titanium dioxide that are incorporated in cosmetic products are effectively immobilized by the binder material that minimizes any toxicity, so they are safe to be used. The product is not labeled as containing nanoparticles, so the technology is unseen by the consumer.

Release of engineered nanoparticles to the environment—air, water, or soil may occur deliberately or accidentally. Products such as agricultural fertilizers and pesticides will be deliberately used in the open, as will nanosensor arrays for environmental monitoring and products for clean-up of pollution. Then there may be permitted or accidental release of nanoparticles from industrial processes. Accidental releases could occur by leakage during production or use of a product, or of a container during transport, or through discharge of waste products containing nanomaterials.

A new generation of environmental remediation technologies based on nanoparticles would lead to the deliberate introduction of nanoparticles into the environment. Nanoscale iron particles, for example, can transform and detoxify environmental contaminants like PCBs or cadmium owing to their high reactivity and large surface area. It is important to know whether nano-iron particles remain reactive in the environment after release; whether they may be transported by water or through the air; and then whether they may be absorbed if they come into contact with humans, plants, or animals. The same properties that make nanoparticles highly effective in industrial processes and in the treatment of pollution also make them potentially toxic if they are absorbed in the body. It is thus necessary to investigate whether the unique chemical and physical properties of new nanoparticles result in specific toxicological hazards. As well as direct absorption of nanoparticles by the body, there is the possibility that nanosubstances may accumulate in the food chain. Heavy metals such as mercury, released through industrial pollution, can already be found in large concentrations in seas and oceans and are cause for concern, for example in large fish. If nanoparticles of various types become prevalent in the seas, they also may accumulate in marine life and so enter the food chain. A similar effect may also happen with nano-enhanced fertilizers and pesticides passing in the food chain directly or through cattle or other food animals. One promising path to prevent potential health hazards is to make the nanoparticles biodegradable (bionanoparticles) by water or enzymes so that they do not persist.

Ideally, the toxicological risk parameters of nanomaterials should be characterized for the whole product life cycle, accounting for changes in the material over its lifetime because of ageing and contamination effects. There are various degrees of risk. Of low concern and risk are nanosystems that will dissolve in bodily fluids and then be excreted. Likewise, particles that agglomerate within the body, for example in contact with nasal mucus or sweat on the skin are unlikely to give problems. Higher risks are posed by nanoparticles that enter the bloodstream through the skin or via the lungs, and potentially accumulate in the organs or fatty tissues. The body's natural immune defense system may not be able to neutralize and eliminate such nanosubstances, or may be disrupted by them.

New ways to evaluate the potential toxic effects and risks of nanoparticles and nanomaterials systems are essential for the scientific and medical communities. This is the concern of nanotoxicology (Fig. 26.5). Detailed biological *in vitro* and *in vivo* investigation of nanoparticles, nanofilms, and other nanoscale elements and products are required. Understanding of the mechanisms of particle pathways within the body should be obtained, investigating the links between the physical characteristics of nanoparticles and their interactions with cells and intracellular components of the body. All nanoparticles entering the human body must be carefully evaluated, but significant risks to health may be posed by fiber and needle type nanomaterials structures similar to the well-known example of asbestos and its associated problems and those merit very detailed investigations. Complete understanding may reveal ways to "engineer out" the capacity for widespread distribution and subsequent toxicity of nanomaterials within the body through modification of surface texture, use of coatings or altering other aspects of the nanoparticles. Such studies require new tools for in situ characterization of nanoparticles, standardized protocols for nanoparticle characterization, efficient analytical methods for body and excreted fluids, and cross-disciplinary communication between scientific and engineering disciplines to assure consistency of results across laboratories.

In-depth understanding of nanoparticle toxicology requires chemists and physicists skilled in characterization of nanomaterials and toxicologists, pharmacologists, and biologists able to identify mechanisms for toxicity. Development of toxicity models demands investigations that accurately track the passage of a nanomaterial through the body from its initial introduction through to eventual deposition or

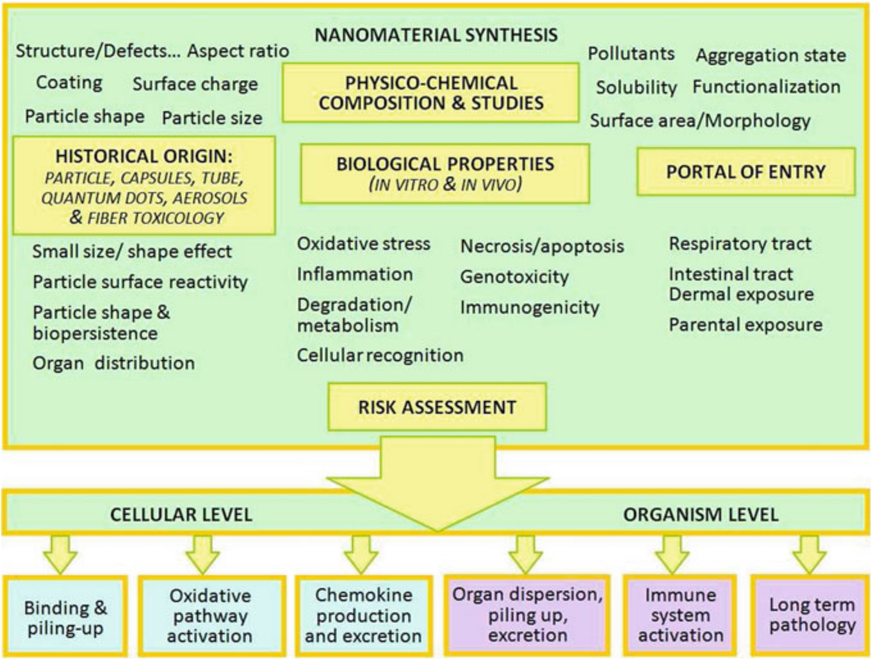


Fig. 26.5 Nanotoxicology: an overview of the principal components of nanotoxicology, from synthesis, thorough physicochemical characterization of particles, to biological testing of particles using *in vitro* and *in vivo* model systems, to risk assessment and regulatory/legislative issues

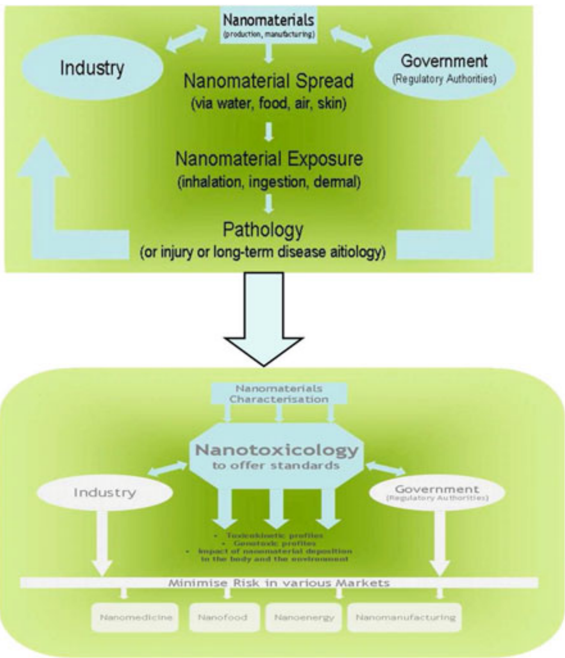
excretion. It has been shown that nanoparticles when initially absorbed may not result in any symptoms—the body may show no irritation in the form of inflammation, for example—but they can still cause stress within the organs following exposure, so their effects can be unpredictable. There is also the issue as to whether a nanoparticle, after absorption, accumulates in the body or whether the concentration gradually reduces with time.

The main criteria affecting the risks of nanosubstances on human health and the environment are therefore their toxicity, persistence and bioaccumulation. Substances that can cause direct damage to organisms (high toxicity), that decay very slowly in the environment (high persistence) and that concentrate in fatty tissues (high bioaccumulation) are of particular concern. The long-term risks of chronic/cumulative exposure and interactions with the immune system for people with impaired immune response (sick people, the elderly, or children) need to be carefully addressed.

It is of vital importance to have a good understanding of nanoparticle toxicity mechanisms in order to robustly define the safety criteria for nanomaterials and to avoid future health scares, adverse publicity, and irreparable damage to the entire nanomaterials domain.

A service to governments and industries has to be established in order to categorize nanomaterials based on standardized methods that will indicate the hazards for any

Fig. 26.6 NanoToxicology: industry—government standardization procedure



nanomaterial at what dose it will pose risks, and how such risks can be alleviated and treated (see Fig. 26.6). In principle, a worldwide standardized database is necessary for safety standards spanning nations and continents but it is also important for the welfare of the nanomaterials and technology markets, worldwide. This will cut across industrial sectors including foodstuffs, energy, medicine, and nanomanufacturing.

Guidelines are required for a safe handling of nanomaterials in the workplace. Companies have a responsibility for their employees regarding the toxicological properties and of nanosafety risks, to make sure that the workplace is safe, measurements of exposure levels are performed and all protective measures are taken similar to practices taken in other potentially hazardous working places such as in nuclear installations.

26.4 Conclusion

Nanotoxicology is a real concern to people. Several tens thousands of tons of silica, alumina, carbon black, titanium dioxide, and nanoclays are produced each year. Hundreds of tons of metals, rare earth, carbon nanotubes, and ceramic metals are yearly produced globally.

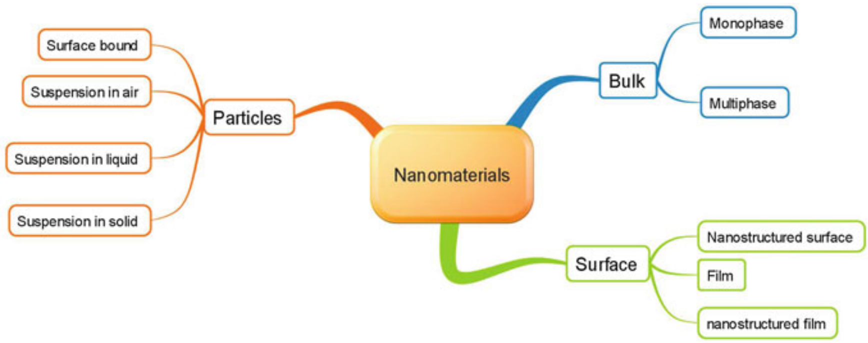


Fig. 26.7 Classification of nanomaterial according to their location in the object

The most common nanoparticles which are used in food or packaging are metallic oxides (titanium dioxide, silicon dioxide, antimony pentoxide), metal nanoparticles (silver, magnesium, zinc), and carbon nanotubes.

Nanoparticles of SiO_2 and TiO_2 are widely used in thickeners and preservatives. In 2007, more than 300 nanofoods were commercially available and nanoparticles are present in more than a hundred packaging materials. Their aim is to modify color, taste, smell, texture, fluidity, and conservation of food. They are also used for tracking and recycling packaging. Nanoadditives are also used to mask undesirable flavors.

Nanomaterials can be classified according to the way they are incorporated in the bulk or surface of a material and according to the way nanoparticles are distributed in the object or in the environment. Figure 26.7 summarizes this classification.

Two separate situations have to be considered while looking at toxicity of nanoparticles:

The first corresponds to the case where an object is manufactured using nanotechnology components. In this case the dangerous step is during manufacturing, but it is easy to take measures to prevent any direct contact between the nanoparticles and the workers. There still remains one step where some risk is present: when the object becomes useless and is thrown away to the refuse. If nanosized dust is produced by operations such as cutting or machining, there is some risk of inhalation of these nanoparticles.

The second corresponds to the case where free nanoparticles are voluntarily incorporated into a product such as a foodstuff or cosmetic. Usually, this incorporation is done in such a way that the nanoparticles are prevented from sticking together. In this case, there can be a potential risk and studies are required to ensure that they are harmless.

Chapter 27
Protection of Society and Economical Aspects

We have seen, in the preceding chapter, the risks of nanotechnology. As with any technology, there are positive and negative aspects. The decision to use a technology or to reject it relies on a cost-benefit assessment, as well as on public acceptance which is a more subjective concern. In this chapter, we shall briefly cover some aspects of nanotechnology related to safety and security of people as well as to economic development.

27.1 Nanomaterials Technology: Safety and Security for the Protection of Society

In everyday life, we take for granted our personal environment and the infrastructures that support our lives: the power in our homes, the food in the supermarkets, and the transport systems that take us to work. Disruption of our critical infrastructures, by natural disasters like floods or earthquakes, or human causes like major road accidents, have very great effects that can be extremely costly to mitigate. Safety, security, and environmental protection are very high priorities for the foreseeable future, and there are areas where the application and commercialization of nanomaterials can have great impact.

27.1.1 Nanosafety Applications

The scope of nanosafety applications focused on the human being can span protection against terrorism, murder, and violence. Security has to do with malicious attacks against the human being, and preventing and protecting against crime in all forms (see Chap. 25). Safety has to do with protection against accidental risks to the person. Security and safety also encompasses critical installations that support our

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_27, © Atlantis Press and the authors 2014

quality of life such as power plants, petroleum installations, and transport installations. The 2003 North–East Blackout that occurred throughout parts of the United States and Canada affected 50 million people. The effect of this blackout on Internet and telephone networks was enormous, with much loss of data by companies and the corresponding impact on economic activity.

Quality of the environment is a factor that can improve or decrease quality of life, so it is linked to safety. Our environment can be effected by both human and artificial causes.

Nano-enabled technologies will ensure a safe world, with personal protection, enhanced public security, secure communications, and more secure infrastructures. Nanoelectronics offers wireless devices that will lead to more efficient, highly networked security systems. Improved information access will enable security systems that automatically monitor and give warning of external threats: for example potentially dangerous baggage left unattended in airports can be identified via nano-enabled automatic security systems.

Our complex modern world demands an enormous computational resource to organize and monitor the data generated by our evolving information society. Nanoelectronics is the future here, providing effective environmental monitoring methods, better distributed healthcare, efficient safety and security systems, and reduced energy consumption, all via nanotechnological developments. One of the most critical factors in scaling down for nanodevices is the heat generation by the circuits, and the smaller the size the more difficult it is to keep the temperature of the circuit at an acceptable level: hence a new nanoelectronic approach, in the future, will be both welcome and necessary.

In some ways, nanotechnology can be seen as the further miniaturization of traditional microelectronics technology, adding additional functionalities to the processing and communicating capabilities of integrated circuits. These include sensing, actuating, power, and interfacing. By contrast, the bottom-up structuring of matter at the nanoscale level can provide new, unforeseen functions; or the realization of previously existing functions at a dramatically decreased cost, allowing the large-scale implementation which is critical for commercial success (Fig. 4.4).

An important field of technology convergence is that of Nano, Bio, Information, and Cognition technologies (NBIC). An example which illustrates this convergence is nanosecurity: the development of nanodevices to play a role in protecting persons and critical infrastructure from human threats. Efforts to contain such threats, known as CBRN/E threats (Chemical, Biological, Radiological, Nuclear, and Explosive), will benefit from the merging of nanoscience and biological disciplines. For instance, the use of specific antibodies encapsulated in nanodevices opens new routes to the multiplex detection of chemical, biological, or explosive agents. Nanoscale encapsulation allows fast and easy deployment over large volumes while maintaining sensitivity: such functions can be only achieved through the combined usage of nanotechnologies.

27.1.2 Protection Technologies

The advantage offered by nanotechnologies for protection systems is that developments will make them responsive to multiple hazards, and they will be able to change their response with time (Fig. 27.1). The hazard from an event such as fire, chemical attack, or bodily injury can change as time elapses from initiation of the incident: fires cause smoke, then high heat, then toxic gases as materials combust and decompose. Nanotechnologies also offer fast response times in identifying toxins and pathogens, without the need for offsite, possibly slow, laboratory analysis. Thus, for major incidents, information can be acquired by embedded sensors worn by first responders, allowing the level of protection to be more precisely adapted to the event. This requires embedded communication technologies and also the ability to reconfigure the properties of protection suits and secondary protection devices.

Decontamination and remediation technologies play a major role in crisis management. Aerogels with nanodesign cages can be used to capture toxins so that further contamination can be avoided: a "smart" film can decontaminate a victim's skin and make it easy to clean wounds by peeling from the surface. Nanofilms can intelligently sort or filter substances, so that for example, toxins are stopped but air can pass through for respiration.

Anti-counterfeiting and authentication technologies can be applied to ensure that a physical product is genuine. Nanotechnology-based approaches to this include laser surface authentication and magnetically patterned tags, which are unique and provide a solution at acceptable cost.

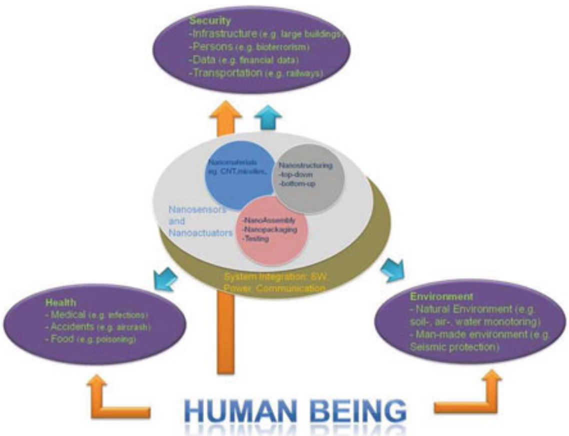


Fig. 27.1 Nanosystems for the safety, security, and environmental protection of the human being Image courtesy of CSEM—International Conference on Mechatronics and Automation (ICMA), Beijing (CN), 15th August 201

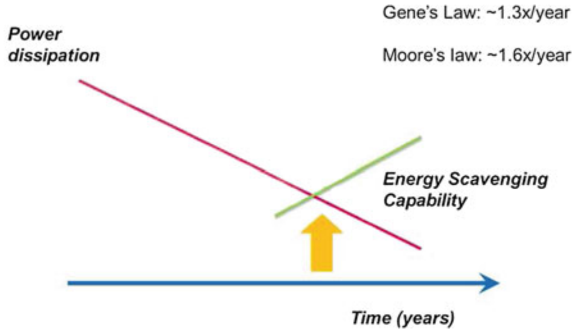


Fig. 27.2 Continuous decrease of power needs per circuit and the increase of scavenging allow micro and nanodevice operation without batteries, Image courtesy of CSEM S.A., Neuchatel (CH)

27.1.3 Nanoelectronics: Energy Source

Depending on their application, nanodevices may draw power from a wired source, from an internal "microsource," or from a chemical or biological reaction. The wide spectrum of energy scavenging devices is outlined in Fig. 27.2. The development of power sources for nanodevices is a critical area of development to ensure the success of these technologies. The continuous trend toward decreased energy usage in combination with energy scavenging (Fig. 27.2) will soon allow us to overcome the usage of batteries, which is a major environmental issue when thousands of nanosystems are predicted to be deployed.

Finally, there are issues to be addressed in the social acceptance of nanotechnologies. Society must demonstrate good risk management in deployment of nanotechnologies, particularly around issues of potential toxicity, and sound ethics over their widespread use in monitoring applications.

27.1.4 Industrial Challenges

Assembling of nanodevices at a small scale is highly challenging, as is quality assurance and the development of test techniques. The power needed to operate smaller and smaller devices decreases with the cost (Fig. 27.3). There are also issues to be considered in disposal and recycling of devices, which first require methods for the retrieval of devices that may have been released in a fairly uncontrolled manner: for example, by airborne dispersal to monitor contamination over a large area following a chemical or radioactive release.

The development of nanomaterials for security, safety, and environmental protection will of necessity span industrial sectors, as the manufacturing facilities and expertise will not all be available within a single company or industry. There will have to be active engagement across industry, if the realization of this new generation of technologies is to be a success. Nanotechnology concepts, in order to be

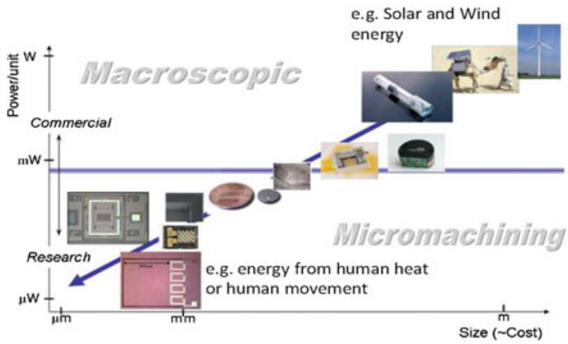


Fig. 27.3 Source: MEDEA + report on Energy Autonomous Systems: Future Trends in Devices, Technology and Systems, 2008

realized as commercial products, must overcome basic hurdles in manufacturing and packaging, as well as in training of users.

Integrating actuators and sensors based on nanomaterials device into existing control environments creates great demands on nanoelectronics. Nanodevices will not be used in isolation, but in systems of networks that may encompass tens of thousands of individual devices. The systems science alone in making such networks achievable is a challenge in itself, but there are also practical problems of energy supply and the dissipation of waste heat from nanodevice networks, as well as in the communications bandwidth required between thousands of networked devices. Large nanodevice networks will need to be self-organizing, managing their activity and communications to best effect and optimal energy consumption, without outside control and intervention. Failure mechanisms of the nanomaterials themselves will have to be understood, and condition monitoring methods implemented so that device failure can be predicted and accounted for.

The requirements for developments of nanotechnologies for security and safety applications span the whole chain from fundamental, basic research, through to applied research, development, production, and use. At present, the phases of development and industrialization have not yet really begun, because efforts on the laboratory scale must be made first on the basic principles, proofs of concept, and prototypes. The life cycles of products have to be mapped out, including their degradability and recyclability.

The technological goals for many applications are already defined: for example, having chemical detection built-in to surfaces that react to toxins in the atmosphere. Labs-on-chips are the next stage, providing specific information on a toxin threat so that the appropriate response can be prepared. Finally, systems are envisaged for the remediation and clean-up of toxic chemicals or residues.

The obstacles for introducing nanotechnology are: technological immaturity; the high price arising from initial production costs of low quantities; low market demands for nanodevices; and the environmental, health, and societal aspects. More efficient nanodevices and nanosystems may increase productivity and automation, and thus bring the threat of increased unemployment. However, the emergence of new nanotechnology will shake the markets and that opens possibilities for existing and new companies and the creation of new, high-value jobs.

27.2 Business Aspects and Marketing of Nanotechnologies

Nanomaterials are central to future breakthroughs within all industrial sectors, including the chemical and petrochemical industries, pharmaceutical and medical companies, energy and transport sectors, information technology, and personal security, Fig. 27.4. As a result, nanotechnology is becoming one of the world's fastest growing, highest impact industries. It is a productivity-enhancing technology that will drive growth in established industries and lead to the formation of new products and applications. Like information technology, nanotechnology has the potential to impact virtually every product, from automotive and energy to healthcare and food technology and to the home of the future.

The great potential of nanomaterials and nanotechnology is to revitalize the competitiveness of our industries via the development of novel materials, systems, and technologies, and to achieve the goal of sustainable development in Europe. It will help in solving current problems in our society such as energy and raw materials supply, climate change, and terrorism. It will also help in the efficient development of the emerging global economies.

Political priorities are shifting from military security, and it associated technologies, to economic and social well-being and health. This, in turn, creates changing demands on materials science and engineering and a need for better education

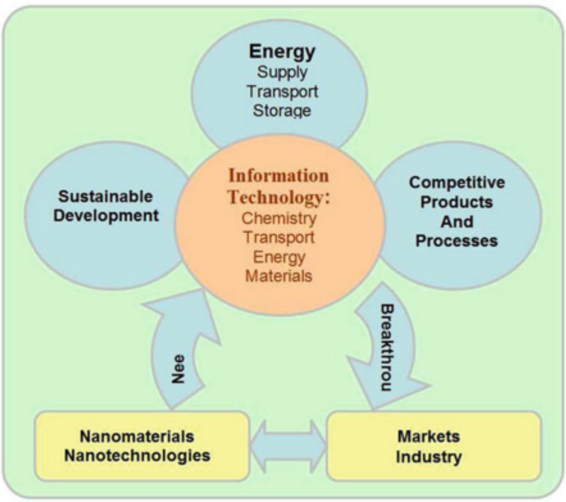


Fig. 27.4 Nanobusiness spectrum

of scientists and engineers in nanomaterials for today's employment market, and improvements in industrial competitiveness and strength.

The value, volume, and impact of manufactured nanomaterials is rapidly growing, with an increasing variety of brands applying nanotechnology. By 2025, annual growth of the markets for nanomaterials will be considerable, driven by expectations for improved quality of life (healthcare, healthy living, and accessible sport facilities), environmental concerns, security in cities with reduced crime rates, and lower energy consumption and cost. Indeed, it will be extremely difficult for companies to survive in the year 2025 without being actively involved in the development or deployment of nanotechnology in some form. Exposure to selected nanotechnology stocks on a medium- to long-term basis will be advisable for investors aware of the risks. Nanomaterials science and technology is still in its infancy but it is predicted to become one of the most important themes of the twenty-first century. There is already a range of start-up companies in the nanotechnology sector, demonstrating a spectrum of innovations. The chemical industry, a very large employer, is a major player in nanotechnology. The volume of the global nanotechnology market may reach 700 billion € by 2015.[1]

Nanotechnology has progressed rapidly from an aspirational research area to a reality where products are available that have been actively designed for nanostructure and the exploitation of nanoscale mechanisms and effects. It is no longer just a "buzzword" that will never deliver benefits or profits: it is a truly innovative technological approach to the development of materials and products that spans sectors and offers genuine solutions to industries looking to expand and maximize their returns.

Nanotechnology is not just another step toward miniaturization. At the nanoscale, material properties depend not just on composition but also on size and shape, and differ significantly from the same properties in the bulk: nanotechnology seeks to develop materials that exhibit improved or novel properties and functions exploiting these effects. Nanotechnologies will be truly disruptive, and will profoundly change major industries through visionary new product concepts. In addition to applications within Europe, nanotechnologies have the potential to provide benefits to the developing world to fulfill the needs of a growing population without compromising principles of sustainable development and increasing carbon generation. European companies will be able to take advantage of a global market with enormous growth opportunities in this decade and the next. However, there are also threats for companies that are not engaging with research in nanotechnologies, as they risk seeing their existing products displaced by competitors. There is therefore a need for education in European industry of what are the capabilities and possibilities of nanotechnology in enhancing existing products, developing entirely new products, and in the redefinition of market sectors through the merging of functionalities that have historically rested in different commercial domains. An example is the possibility of innovative textiles, leading to applications such as clothing that releases medication in response to chemical sensing on the skin.

[1] DE-Report 2011: http://www.bmbf.de/pub/nanoDE-Report_2011.pdf.

Fig. 27.5 Modern vehicle with imbedded nanotechnology

The synergies offered by the "multiple functions" available by exploiting nanotechnology are revolutionary. For example, in an electric car one can combine functions across nanoelectronics, photonics, advanced nanomaterials structures, biotechnology, and,nanobatteries (Fig. 27.5).

To meet the global challenges of the future, we need technological progress to guarantee economic stability, but this cannot be realized without the acceptance of society. In order for Europe to remain a successful industrial continent, it must create a social climate in which new ideas and processes can flourish.

Besides the chemical industry, information and communication, energy, construction engineering, healthcare/pharmaceuticals, and the service sectors are key players in the exploitation of nanotechnologies. Nanotechnology brings benefits to: the construction, automotive, and electronics industries; energy efficiency; water purification and treatment; efficient and environment-friendly aircraft; batteries, super capacitors and fuel cell technologies; healthcare, drugs, medical devices, and cancer treatment and cosmetics.

27.3 Conclusion

The impact of nanomaterials and nanotechnologies on safety, security, and environmental protection will be truly revolutionary. The new capabilities will surpass what is currently achievable and will be as far in advance of current technology as existing methane sensors in mining are in advance of canaries. The importance of nanodevices for safety and security are a consequence of a number of features such as their small volumes that allow large-scale deployment without their being noticed. Devices and networks built from them can be highly robust and reliable, meaning that they do not require specialist technical knowledge to operate. They can be extremely sensitive, which is ideal for the detection of many threats: the detection of the first molecule/particle/pathogen is crucial in case of a crisis to determine as soon as possible the nature of the alarm, so that prevention/protection means can be deployed efficiently.

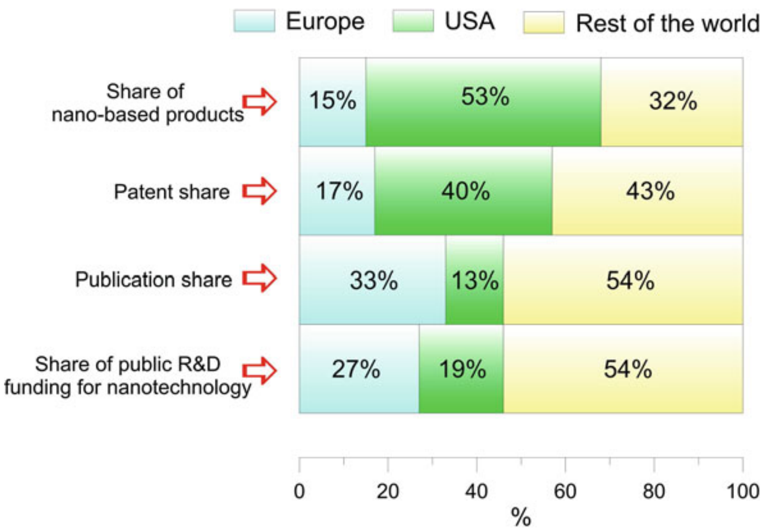


Fig. 27.6 Publications, patents, and public R&D funding share in Europe, the United States, and the rest of the world. From the report High-level Expert Group on key Enabling Technologies, final report 2011. Reference of the data can be found in this report

Patents and Nanotechnology

According to studies carried out by statnano.com, 27,350 nanotechnology patents had been published by the end of December 2012 in USPTO, among which 57 % were published by the United States, making the US ranked N^o.1 *followed by Japan, Republic of Korea, and Taiwan. The Republics of Korea and Taiwan showed a one-step increase in the ranking, while Germany fell one step, becoming fifth in the rankings. According to the table, Far East and Asian countries have paid special attention to American nanotechnology markets. In 2012, more than 13,350 nanotechnology patents were granted, which equaled 5.7 % of the total patents in the same year. In this ranking, the United States, Japan, Republic of Korea, and Taiwan hold the first to fourth rank, respectively. The share of efforts in the nanotechnology domain is different around the world. Figure* 27.6 *gives a summary of the situation as far as publications, patents and public R&D funding are concerned. Europe provides 27 % of the global funding in nanotechnology and produces 33 % of the global publications in this domain. However, it contributes to only 17 % of the patents and 15 % of the nanobased products. It turns out that the rest of the world, especially China, Japan, and South Korea and much more adept in exploiting the results and commercializing products.*

The development of innovative nanomaterials and technologies is rapidly progressing, and the variety of advanced commercial products on the market or in development is increasing rapidly. Nanotechnologies offer great potential for wealth generation, job creation, and improvements in quality of life. The importance of nanotechnology as an innovative force lies in its varied applications across many industries. Nanotechnology's impact in helping companies to enter new markets is beginning to be realized. There is a relatively short window of opportunity for organizations to invest and adapt to the potential of nanotechnologies to revolutionize their sectors, if they are not to be overtaken by competitors.

A crucial step for the development of innovative products at the nanometer scale is the integration of known production processes and their adaptation to the fabrication and processing of nanomaterials. Crucial aspects that go beyond the scalability of production processes are the synthesis and processing of ultrapure materials. Here it is important to ensure the formation of materials and functionalization of nanomaterials in bulk quantities and the reliability of these processes should be at the level of, or better than, today's electronic manufacturing standards.

Chapter 28
Social Impact of Nanoscience and Nanotechnology: A Perspective

Nanomaterials offer a new frontier across all industrial applications and consumer products. By exploiting nanoscale phenomena where properties of materials change significantly compared to the macroscale, new levels of performance can be achieved. As the size of material elements falls below 100 nm, novel effects occur as the quantity of interfaces and surfaces rises greatly. Nanomaterials technologies that change the design, production and application of structures, devices, and systems by controlling material shape and size at the nanometre scale will be the next revolution in processing. Some nanotechnologies will be evolutions from existing materials and technologies. This includes technologies that have gradually shrunk to the nanometre scale, or improvements of existing products with nanomaterials. Examples are the incremental reductions in size of semiconductor devices, and the use of nanoparticles in cosmetics products.

In contrast, there will be revolutionary nanomaterials science and technology, based on the discovery and innovation of new nanometre scale products and technologies, e.g., the discovery of carbon nanotubes with the nanotube transistor as a result.

The role of nanomaterials science and technology is often invisible: products may contain nano-enabled components without advertising it as such; cosmetics companies speak of "innovative molecules" when marketing their nanotechnologies. Many applications are still science fiction, but their embedding and impact are science fact for the next two decades.

Nanosubstances are not a new phenomenon. Naturally occurring ultrafine particles, include viruses (20–300 nm), bacteria (300 nm and larger), and dust from desert storms ($\approx$ 100 nm). In the environment, ultrafine particles from technological processes include combustion soot (10–80 nm), paint pigments (80–100 nm), welding fumes (10–50 nm), diesel exhaust particles (7–40 nm), and carbon black for photocopier toner (10–400 nm). Engineered nanoscale materials have similar dimensions: fullerenes or buckyballs (1 nm), nanotubes (1–5 nm $\times$ 10 μm), quantum dots (5–20 nm), and so on.

C. Ngô and M. Van de Voorde, *Nanotechnology in a Nutshell*,
DOI: 10.2991/978-94-6239-012-6_28,

28.1 Great Challenges, Promises, and Benefits of Nanomaterials Science and Technology

The US National Nanotechnology Initiative, launched in 2000, has been at the forefront of large research and development (R&D) efforts in nanotechnology in the US and around the world. Sustained R&D programs at the national level by the European Union, China, Japan, Korea, and Taiwan have also been launched followed closely by other countries such as Russia, India, Brazil, etc.

The European nanomaterials science and technology initiative aims to fully realize the promise of nanotechnologies. It will translate that promise into improvements in Europe's economy, security, safety, and quality of life, while protecting public health and the environment.

Nanotechnology will create new products and processes, and will impact on the whole spectrum of industrial sectors and social activity, from communications to health, leisure, transport, and environmental engineering. Nanotechnology will allow for cleaner energy generation and more efficient utilization of resources: transforming dangerous substances and creating better materials processes such as through the use of less energy or removing toxic consumables and by-products. Nanomaterials and nanotechnologies offer great potential for the development of new products and innovations.

In the short term, innovations with nanotechnologies are seen as a way to reinforce competitiveness of industry by putting more "intelligence" in materials, along the line of the knowledge society concept which is the guideline for European development. This "intelligence" could be in the form of smart materials or materials with embedded intelligence through sensors and microchips. Environmental questions are presently directed toward energy consumption and CO_2 emission reductions: energy-efficient products will be more attractive, there is a positive image for consumers, and sometimes there is also a gain in safety. There is already a strong development activity in materials for energy, with transportation being a particular target sector through fuel cells and high-capacity batteries. Other applications like antimicrobial surface coatings and catalytic systems for pollution reduction could develop if there is a sound basis to prove that their large-scale use is harmless for the environment. There is presently some controversy about the scalability of some current technologies applying materials such as titanium dioxide and silver.

In the longer term, novel materials can be more aggressively targeted toward sustainable development. Due to limited resources for energy and materials, to supply the increase of global population (10 billion inhabitants expected in 2,050), more and more technologies must evolve toward closed loops, supported by renewable energy. This will lead to a modified economic model such as that now applied for cars, which have to be recycled at end-of-life. Nanotechnology can greatly help in recyclability of waste and packaging, and the development of materials which can be assimilated by the environment such as in the development of degradable plastic bags made from corn.

Nanotechnology already provides positive impact on the environment and human health. However, since the properties and effects of all nanomaterials and nanoproducts on the human body are not sufficiently understood, their future success will be challenged by consumer acceptance of nanomaterials, the ethical and social implications of nanomaterials, the health and safety considerations of nanotechnology and finally the impact of nanomaterials on the wider environment. Therefore, it is a necessity to inform and educate the public and the consumer; to investigate and manage the potential risks associated with the development and deployment of nanotechnology; and to correctly and openly disseminate all information about nanotechnologies to ensure the general public's acceptance of nanotechnology.

28.2 Positive Effects and Social Benefits of Micro and Nanotechnologies

In the future, the development of nanotechnology will be revolutionary, with a large spectrum of consumer products with better performance, higher quality, longer lifetime, and lower cost; but where the use of nanomaterials may be effectively 'hidden,' not necessarily intentionally, from the end user. Improved diagnostics and potential disease identification, new and improved medical treatments, optimum carriers for targeted drug delivery, and new techniques for continuous monitoring of patients with chronic diseases will be based on and depend on nanotechnology discoveries and developments. Ultraprecise and sensitive detection and monitoring of toxic substances will benefit personal and environmental medicine and protect food safety. The next generation of computer processors, storage, and displays will be based on nanotechnological advances. Products and methods for CO_2 emission reduction, carbon sequestration, waste reduction, low-impact pesticides, and environmental remediation and clean-up of air and water will be able to take advantage of nanoinnovations.

The rate of extracting materials (metals, oil, and coal) must decrease. It is already expected that some elements will not be available in a few tens of years: materials used as catalysts (platinum), rare earths used in displays (terbium, europium), lithium for batteries (estimated reserve 11,000,000 tons to be deployed in billions of cars), hafnium used in transistors. This will compel researchers and industry to find solutions with a restricted range of elements, replacing rare elements by common ones. This can be done by nanostructuring allowing modified properties.

At present, nanoparticles originating from industrial production have little exposure to populations outside the manufacturing workplace. The situation may change in future since it is expected that an increasing number of companies will become involved in nanotechnologies, that the growth in production volumes will be significant, and the product range will extend over all possible industrial sectors. The risk can vary with exposure: so the risks will be different for workers in nanomanufacturing plants compared to the general public. The perceived hazard may also be different: the public may accept a risk associated with a life-saving medical treatment, but reject any risks associated with nanofoods, even if they cannot be explicitly identified.

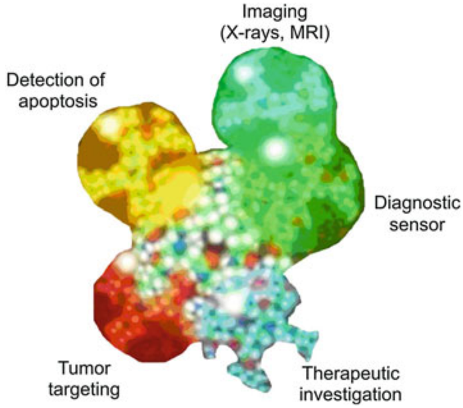


Fig. 28.1 Nanomedicine applications: diagnostics techniques to early target cancers. (MRI stands for Magnetic resonance Imaging)

A specific example of the potential use of nanosubstances is the following: sick rooms and corridors in hospitals have to be disinfected daily by law. Although conventional disinfectants destroy germs, the potency of the disinfectants lasts only for a few minutes. After that the germs can multiply again. A disinfectant exists which exhibits a long-term germ-killing activity for up to 10 days. On the disinfected surface a very thin sponge-like film forms, in which clinically authorized germ-killing components are intercalated. These biocides are released in the presence of bacteria and fungi and kill them efficiently.

Another example is the use of gold nanoshells for cancer therapy: they are biocompatible, recognize cancer cells, and are small enough to pass through the circulatory system: see Fig. 28.1. With nanotechnology it is possible to give billions clean water to drink; wipe out toxins that have plagued us for thousands of years; give a better life to our children and our grandchildren.

A balanced assessment of the potential of new nanomaterials and technologies must weigh the risks against the potential benefits. The basic innovations that come from nanotechnologies have the potential to contribute to human health, environmental safety, and the economy in many ways (Fig. 28.2). The existing database for properties of the bulk material is not sufficient to classify the environmental risk of engineered nanoparticles of the same material and the risks associated with free nanoparticles on ecosystems are not well understood. Therefore, something has to be done.

28.3 Societal Acceptance of Micro and Nanotechnology Innovation

Worldwide there is increasing investment in the private and public sectors in technology-driven innovations such as nanotechnology. The key question about the development and use of nanotechnology is whether the unpredictable risks of

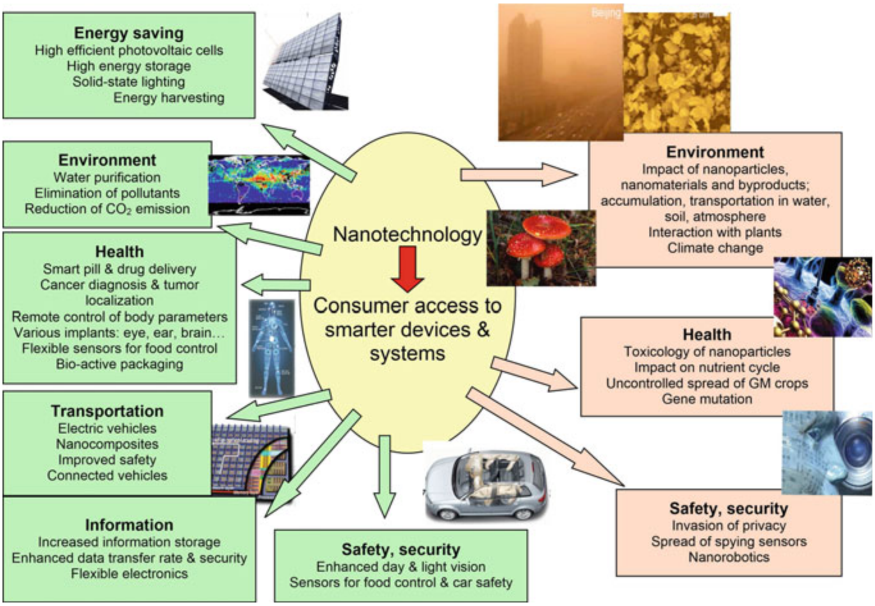


Fig. 28.2 Benefits of nanotechnology

engineered nanoparticles and nanotechnology-enabled products, in particular their health and environment impact, outweigh their established benefits. The lack of transparent, reliable, and accurate technical data on the risks associated with nanomaterials fuels arguments between nanotechnology proponents and skeptics and leads to public rejection.

Successful implementation and commercialization of emerging (nano)technologies depends on societal acceptance of nanotechnology overall. Consumer responses to different applications of nanotechnology may vary: consumers are more negative toward nanoagrifoods compared to applications in medicine or nanoelectronics. Despite this, public awareness of many innovations in nanotechnology is presently rather low, although this is likely to change as more diverse products become available and public attitudes crystallize. Societal and consumer acceptance may be influenced by low levels of public confidence in technological innovation and regulatory systems. Identification of potential ethical issues (for example, relating to health and environmental toxicology) must occur, and be incorporated into regulatory and communication practices if these raise specific concerns. The assessment, management and communication of potential risks, and benefits associated with emerging applications of nanotechnology must be both transparent and societally inclusive: any real and perceived lack of transparency in risk analysis systems and decision-making practices are not helpful in reassuring the public.

To be successful, public engagement exercises need to be proactive and have policy impact. Willingness to respecify the direction and goals of research and development based on the outcomes is essential. If this is not done, the reasons why not need to be made transparent.

Order of entry into the market place is important: first-generation products with tangible and desirable consumer benefits will facilitate positive societal attitudes toward nanotechnology applications more generally.

28.4 Uncertainties, Risks, Incidental Concerns, and Societal Implications of Nanomaterials

28.4.1 Uncertainties

For new sciences and technologies from trains in the 19th, synthetic chemicals and civil nuclear power in the 20th, to biotech and genomics in the late twentieth century, it is virtually impossible to prove that something is absolutely safe. The food and agri-industries are enthusiastic about nanotech's promises but are also very nervous: their successes or failures could affect the future commercialization of nanomaterials technology products in all industries.

An unacceptable risk would be to utilize nanomaterials without evaluating the consequences: the widespread introduction of nanoparticulates into the ecosphere when their toxicological impact is not known. We should avoid what occurred in the 1950–1960s for new molecules. No currently available measurement method for nanomaterials can be universally used for determining whether recommended safe requirements can be fulfilled. In addition, there is also a lack of correlation between *in vitro* and in *in vivo* toxicology results. A proper combination of measurement methods is required which remain to be checked and validated.

28.4.2 Relevant Existing Regulatory Standards for Safety

Research in national and European nanomaterials laboratories, private industry, and academia is now in progress to determine how nanotechnology-based materials may differ from conventional ones in their implications for public health and the environment. Existing European and national regularity mechanisms are in place for assessing and regulating workplace, environmental, and health risks of new materials. Efforts are underway to ensure that these regulatory mechanisms or appropriately amended ones provide proper coverage of nanotechnology-based materials.

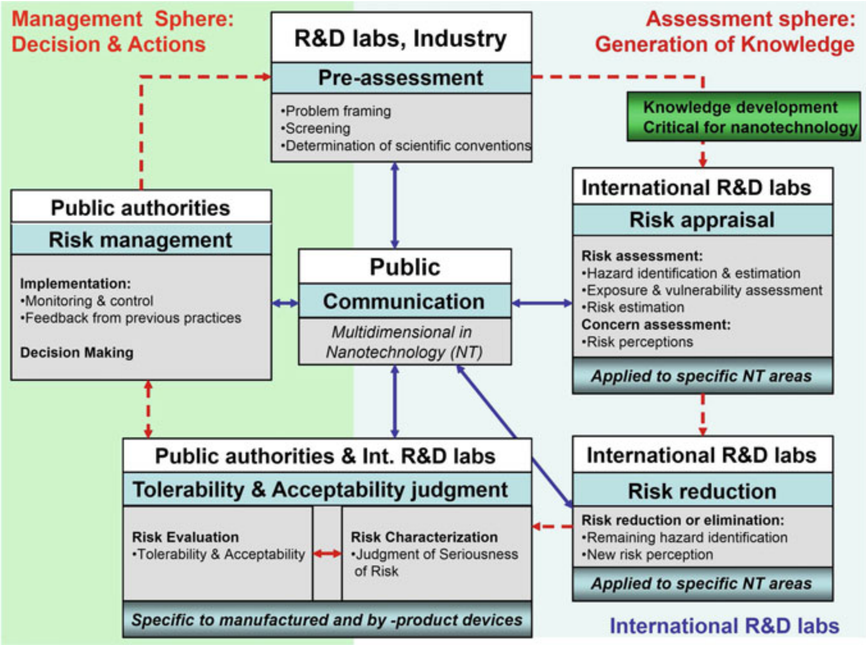


Fig. 28.3 *Risk assessment and management framework for nanotechnology*

28.5 Strategies for Improving Governance Practices Associated with Nanotechnologies

Many important emerging issues are linked to the development of effective governance practices. A global effort toward understanding of nanotechnology-specific risks and benefits is a fundamental requirement if large and small industries are to operate on a level playing field and developing economies are not to be denied essential information about safe nanotechnologies. It is the role of governments in collaboration with industry to provide the necessary rules.

Companies already have the experience to help in the development of guidelines for working with nanoparticles and nanotechnology. Companies have a special responsibility toward their employees, customers, suppliers, and society, and also toward future generations.

Developing robust ways of evaluating the potential impact—good or bad—of a nanotechnology-enabled product from its initial manufacture through its use to its ultimate disposal must engage both the scientific and policy communities (Fig. 28.3). Communicating research results on the assessment, minimization, and prevention of nanotechnology risks outside the scientific community is challenging, but it is essential in order to prevent any misrepresentation or stifling of the nanotechnology industry. Education needs to be embedded from primary education through to University. Teaching children accurately and truthfully about nanotechnology is an excellent tool to indirectly inform the general public as well. Dissemination of information to the public must be transparent, reliable, and performed by all stakeholders, including public interest groups, the scientific community, social science experts, nanotechnology manufacturers, and government (Fig. 28.3).

Furthermore, risk management of nanomaterials and nano-enabled products is challenged by the broad range of technology and products encompassed by the term "nanotechnology," which can include existing metal alloys, new drugs, and electronics. Thus, the regulatory standards for safety, and the regulatory mechanisms for assessing and regulating the workplace, and for quantifying the environmental and health risks of new engineered materials must be tuned and improved to cope with the wide range of nanotechnology-enabled products.

28.6 Conclusion

Every product or technology can have positive and negative impacts. A knife is very useful to cut meat during meals but can also be a dangerous weapon and kill people. Products enabled by nanotechnology will be more easily accepted if their toxicity properties or safety are understood on a firm scientific basis. Furthermore, if the products containing nanoparticles are very useful or necessary in daily life and bring many advantages to consumers, they will be more ready to accept the risk, especially if it is low.

The issue concerning risk is that it is relatively easy to discover a product is toxic. It is far more difficult to show that it is harmless. The reason for that is the time scale under consideration. For example, even if we know that a product is harmless after a feedback of 10 or 20 years, there will be always somebody to argue that you do not know if the product is not dangerous in 30 or 50 years from now. Another issue is the low doses problem where it is very difficult to know if any positive or negative effect occurs. This requires a good scientific understanding of the mechanisms coming into play when nanoparticles are absorbed.

Part IX
Nanotechnology: Opportunities and Risks for Society

Conclusion

The development of nanotechnologies will be highly beneficial for our society, but at present, public awareness about nanotechnology is limited. The word “nano” in itself indicates nothing about potential risk or hazard. However, misappreciation of nanotechnology may create a general fear that nanomaterials and nano-enabled products are toxic, and this must be investigated and addressed.

With the production of engineered nanoparticles, we are confronted with a new class of materials that have novel properties compared to bulk material. Clear identification of the risks and hazards of nanoparticles is needed in order to understand and implement measures to reduce or avoid health issues for humans. The uncertainties involved in nanomaterials toxicity have to be seen against the background of the benefits of nanomaterials and nanodevices, balanced by the increasing potential for exposure as the quantity and types of nanoparticles used in society grow.

A transparent discussion of benefits and risks will help people reach a considered, balanced view. This will enable a greater public acceptance, which, in turn, will enable society as a whole to profit from these fundamental technological developments, while at the same time, being assured that the risks are kept under control.

A responsible and successful development of nanomaterials and nanotechnology requires the following criteria Fig. IX.1:

- to protect workers manufacturing nanomaterials or nano-objects;
- to develop excellent detection techniques. At present, it is not acceptable that only a few methods are available for detecting, for example, silver nanoparticles in complex matrices. Silver nanoparticles are increasingly used in consumer products and food contact materials. It is timely for National and Regional Governments and the European Union to take urgent action to assure safety, while recognizing that companies and manufacturers are taking this matter seriously and devote much attention to safeguarding the consumer;

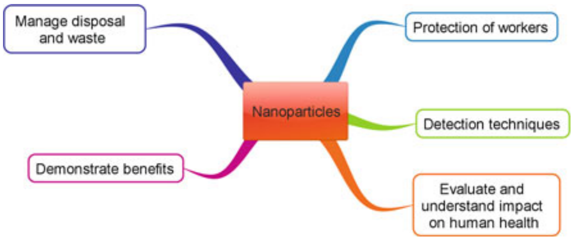


Fig. IX.1 Important criteria for a successful development of nanoparticles and nanotechnology

- to understand fully the effect of nanoparticles on human health and the environment in ensuring the protection of people, and preventing illnesses and health problems;
- to demonstrate the benefits of nanosubstances to consumers, reduction of pollution through improved products, better food packaging materials, and disease treatments and cures;
- to consider possible problems during postconsumer disposal.

The impact of nanotechnology on the environment is very important for the welfare of a modern, cost effective, and sustainable economy and society. For example, global energy generation and consumption involves high economical and environmental costs and this offers challenges for energy and environment friendly nanosystems.

This risk identification process is a task for all parties involved and it should remain a dynamic process which always takes into account new scientific, technological, societal, and legal trends.

Further developments in nanomaterials for security and safety applications depend on advancements expected in other nano-related technologies such as electronics, biology, physics, and cognition, targeted toward systems which are capable of self-powering, with local intelligence, and a combination of selectivity, versatility, and sensitivity in their response.

Concerning the integration, testing, and design of nanosystems at an industrial level, we are still navigating in uncharter waters due to the lack of precedents. The extremely high number of potential systems indicates that there is a strong need for global co-operation which, in the precompetitive phase, shall enable the creation of knowledge that will then be adapted to specific applications. For Europe to be at the forefront of nanotechnology development and application, a joint strategy for research, development, and innovation is required by European countries, governments, and industries. The early involvement of industry, through dedicated incentives for participation in research and development efforts that lead to commercial products, is vital in the exploitation of the knowledge and methods that have been generated so far for nanomaterials and nanodevices. Industrial-scale production and exploitation can be hampered by fragmentation of application fields and the range of companies involved.

For businesses, there are commercial risks in nanotechnology investments, with concerns over the costly developments of new products and processes. There are

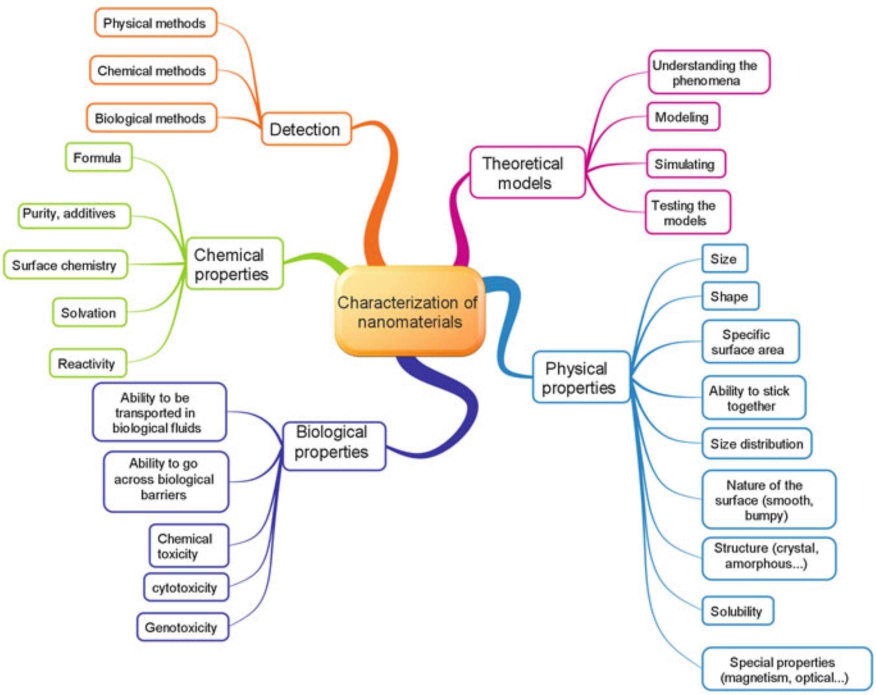


Fig. IX.2 Main items which have to be investigated to understand the properties and risks of nanoparticles

also political risks around the export and acceptance of products based on nanotechnologies. It is critical that there is early dialog on the commercial, legislation, and social aspects of application and trade of nanomaterials and nanotechnologies, including open debate on the assessment and mitigation of perceived risks and hazards. The potential value of the nanotechnologies runs into tens of billions of Euros, so the rewards greatly merit early engagement and investment with the possibilities for new products, processes, and profit lines.

The societal acceptance of nanomaterials and their commercialization is dependent on:

- effective governance;
- tangible societal and consumer benefits;
- societal inclusivity in regulation and product development.

The main difficulty of public acceptance is that it is not a rational approach to the problem but an emotional one. Furthermore, some groups will actively amplify any possible negative effect. On the other hand some industrials have a tendency to minimize the risk to maximize their profit. It is very hard for nonspecialists to separate the wheat from the chaff. It is often a question of communication and the best publicity often wins over the truth, especially when the aim is to scare people. Essential items have a greater chance to be accepted because the people really want and need them.

Nanoparticles show different properties than macroparticles and deserve special and complete studies. The main items that should be investigated are displayed in Fig. IX.2. It is necessary to detect the nanoparticles with a good accuracy. Modeling and simulation will be important to reduce the number of experimentations but they should be closely coupled and tested with experimental results. Physical and chemical properties have to be precisely measured in order to see the influence of the different parameters on the possible hazards of nanoparticles. As far as biological properties are concerned, there is a demand to know the ability for the nanoparticles to spread in the human body and to quantitatively evaluate their different toxicities.

Taking advantage of the special properties of nanomaterials, a wide spectrum of companies are being founded and developed, and innovative products are already generating significant profits for them. There is a range of research challenges that must be addressed by science and innovation, directed toward economic success. Sustainable nanomanufacturing will create the industries of the future, ensure job creation, and move nanotechnology to the market!

Part X
Outlook

Chapter 29
Outlook

In this book we tried to provide a comprehensive overview of nanotechnology. The field of nanotechnology will impact on almost every manufactured product, from clothing to electronics, from cement to aircraft. We have reviewed the many different potential applications of nanotechnology, from products that have been on the market for some time, to development ideas that may not be realized for several decades. The needs for robust safety assessment and processes have been explained.

Nanotechnology is a new branch of science and technology which is able to create innovation and improve existing technologies in numerous sectors. Some of them are listed in Fig. 29.1 but others exist today and will certainly appear tomorrow.

Because of the broad possibilities offered by nanotechnology, it is a generic domain which will be the source of multiple applications during this century. It is the essence of a new revolution which will extend over the whole century and beyond. It will have a great impact on our daily life and in all industry sectors. Because of the strong economic implications of nanotechnology, any developed country should invest in this field, both at the basic research level but also in applied research and the promotion of entrepreneurship. It offers a unique chance for creating wealth and jobs. Countries which do not invest in this field will stagnate and see other countries reap the economic benefits.

Nanotechnology can have applications in many important domains for the society such as medicine, pharmaceuticals, information and communication technologies, materials, energy, and food. Nanotechnology is already used in commercial products which can be found today: in March 2011, more than 1,300 commercial products were available. The website http://www.nanotechproject.org/inventories/consumer/ gives a real-time inventory of nanotechnology-based consumer products. It is interesting to have a closer look at this evolution. Figure 29.2 shows the data between 2005 and 2010, and we see a huge increase in the available products.

A distribution into different categories has been done by http://www.nanotechproject.org. Figure 29.3 shows the share among these categories.

It is interesting to go a little bit further and see which markets are contained in the different categories. This is shown in Fig. 29.4. For health and fitness, which is

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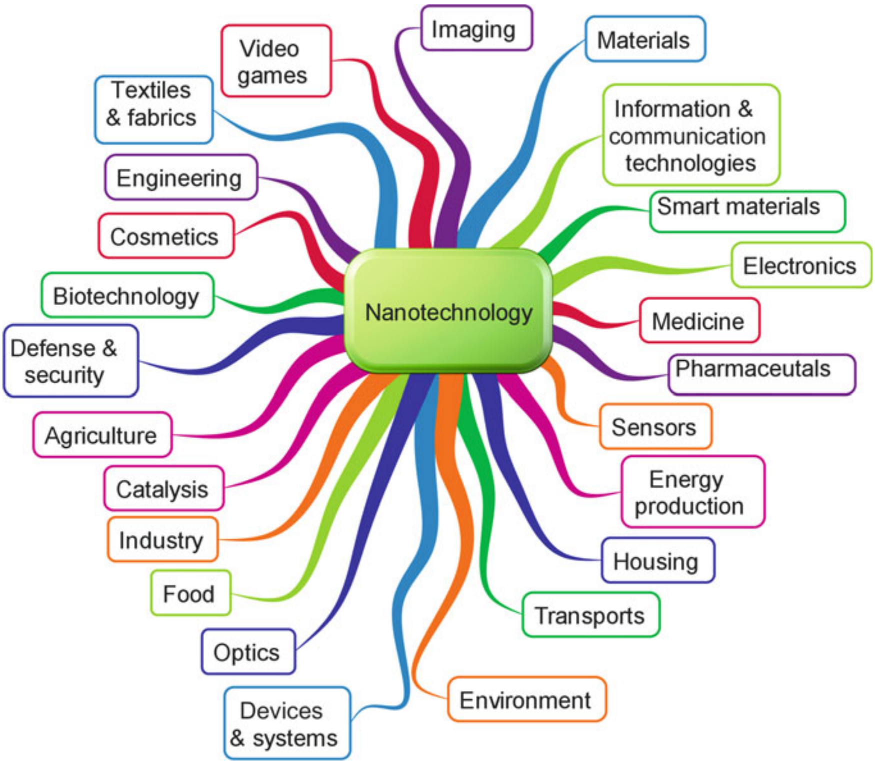

Fig. 29.1 Many sectors will be impacted by nanotechnology. Some of them are shown in the figure

the largest market where nanotechnology is involved, the share between the different subcategories is also shown.

29.1 Nano-Objects

Nanoparticles are extensively used in nanotechnology, as well as nanostructures of one dimension (nanowires, for example) or two dimensions (nanofilms, for example). These nanoscale objects can be made either by a top-down approach or a bottom-up approach.

The top-down approach consists of starting from a large piece of material and carving it using mechanical, physical, or chemical methods. This is typically what is done in integrated circuits manufacturing in the electronics industry.

The bottom-up approach is still in infancy. It consists of starting from atoms or molecules and putting them together using self-assembly or directed assembly. This

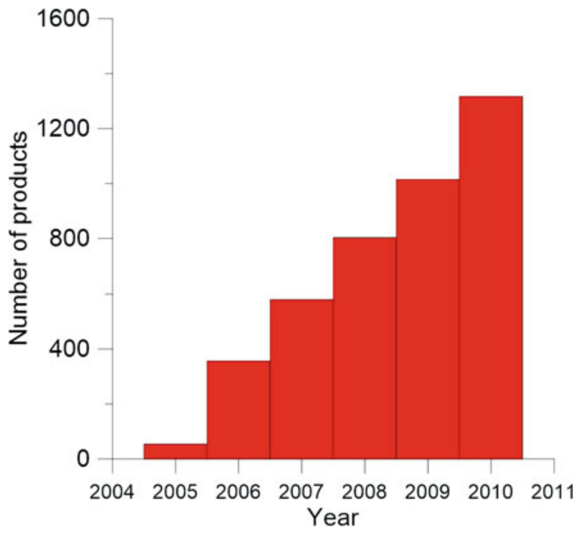

Fig. 29.2 Evolution of the number of commercial products based on nanotechnology between 2005 and 2010. Data from http://www.nanotechproject.org/inventories/consumer/

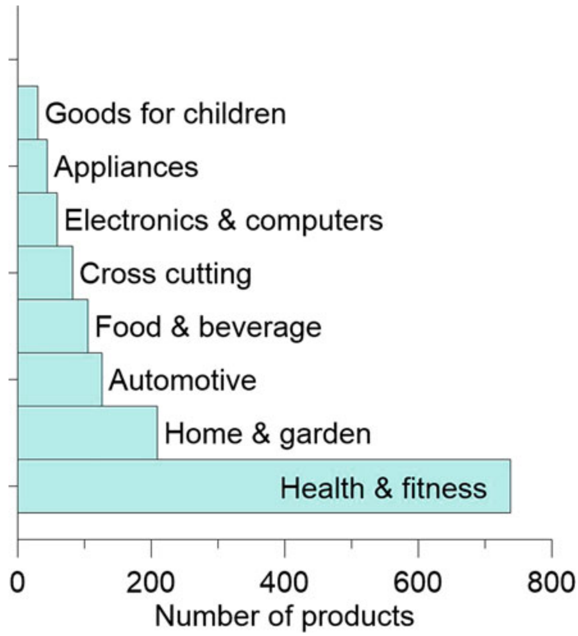

Fig. 29.3 Share of the products based on nanotechnology, classified in categories as defined in http://www.nanotechproject.org/inventories/consumer/

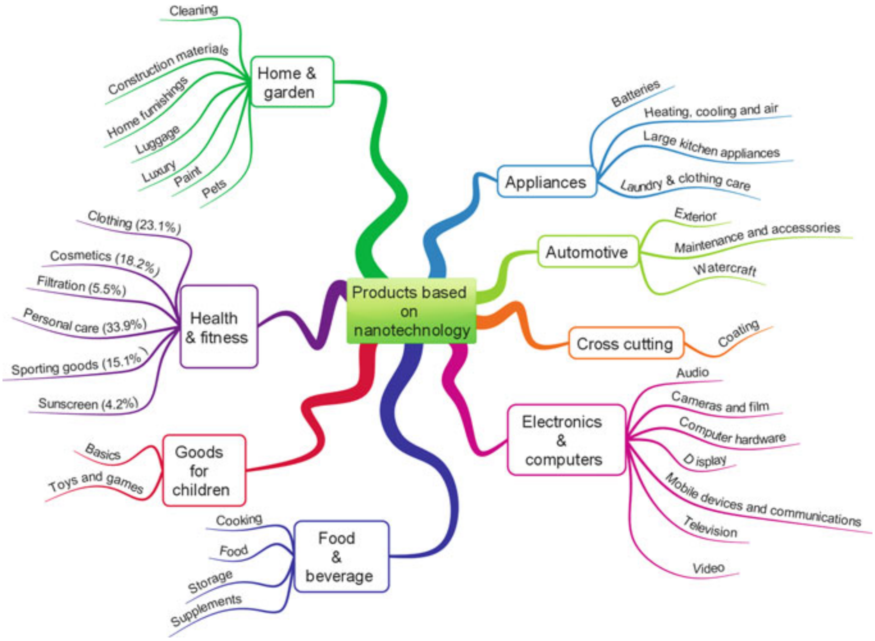

Fig. 29.4 Categories and subcategories of market with commercial products based on nanotechnology. Figure built from the results of http://www.nanotechproject.org

approach has a great potential and epitomizes nanotechnology in the narrow sense of the term.

Different classifications of nanoscale objects can be made depending upon the goal of interest (Obervatorynano project). This is summarized in Fig. 29.5. One may be interested by the dimensionality of the nano-object (1-dimension, 2-dimensions, or 3-dimensions).

One can also be interested on the nature of the phase where nano-objects are involved: single solid phase, solid multicomponent, or mixed multiphase systems. Finally, one may classify according to the fabrication process used.

29.2 Nanomaterials

Nanomaterials designed and engineered at the atomic scale will provide novel solutions to energy, water, food, raw materials, and other resource-based challenges; including breakthrough technologies that turn carbon dioxide from a global liability to a valuable resource. Nanotechnologies can provide wireless power, high energy density power systems, and personalized medicine and nutrition. Opportunities lie in all parts of the healthcare cycle from screening and early diagnosis to treatment,

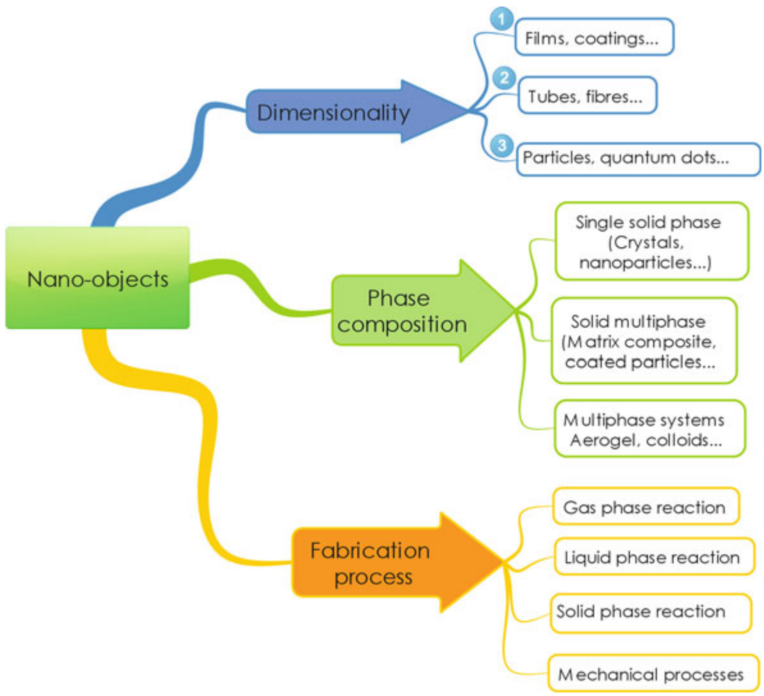

Fig. 29.5 Different possible classification of nano-objects according to the Obervatorynano project

therapy monitoring, and aftercare (including the long-term management of chronic diseases such as heart failure, diabetes, and arthritis). Innovation in these areas has the ability both to improve patient outcomes and contain healthcare costs.

To realize these ambitions, integration of the following background elements is required (Fig. 29.6).

There is a wide variety of nanomaterials. It is possible to classify them into broad families as shown in Fig. 29.7 built from the studies of the Obervatorynano project.

Carbon-based nanomaterials have pure carbon nanoscale components in the bulk material. This includes for example fullerenes, carbon nanotubes, and porous carbon materials. However polymers, which contain other atoms than carbon, do not belong to this family.

Nanocomposites are materials reinforced by nanoparticles or nanoscale structures dispersed inside the bulk material.

Nanostructured metals and alloys contain a metal or alloys nanoparticles, nanocrystals, amorphous, or polycrystalized nanopowders. TiO_2 nanoparticle coatings or gold nanoparticles for sensing belong to this family.

Nanopolymers are polymers with a nanostructure, inducing a change in the properties of the material. Dendrimers belong for instance to this family.

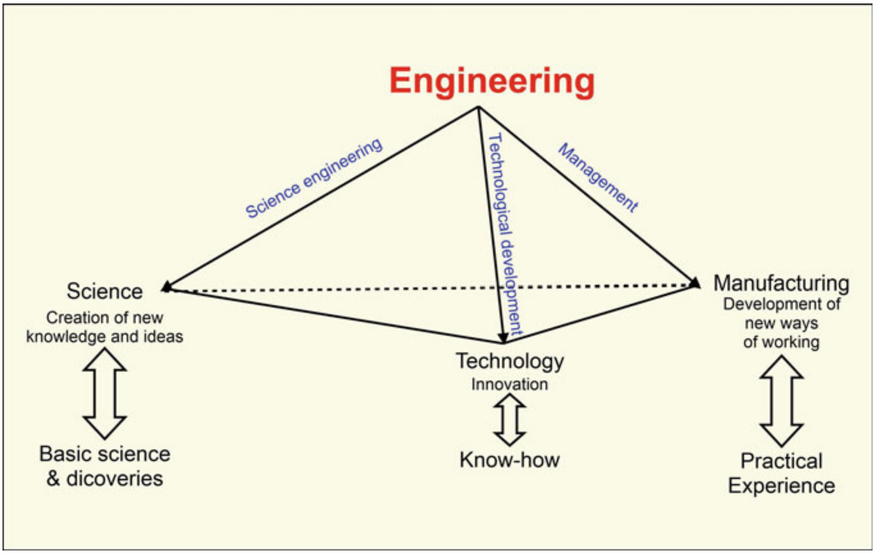

Fig. 29.6 Nanoworld twenty-first century: nanomaterials engineering base

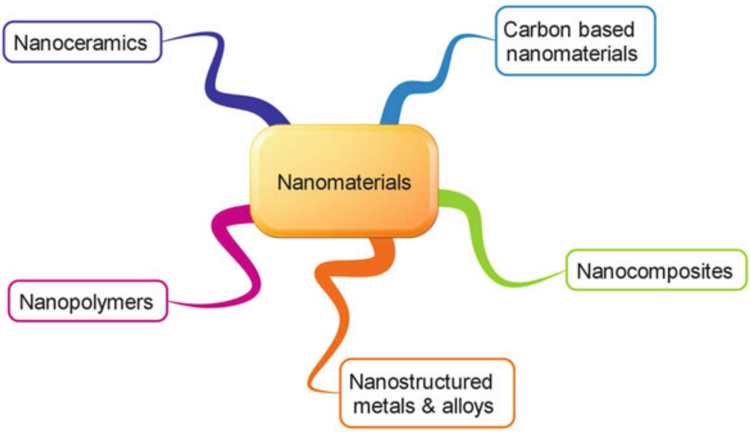

Fig. 29.7 Families of nanomaterials according to the Obervatorynano project

Nanoceramics are ceramic materials containing nanoparticles or nanoscale structures. Oxide materials, nitrides, and carbides belong to this family.

29.3 Nanotechnology in the Home

The nanotechnologies of the future will find applications in daily life of which nanotechnology in the house of the future is a typical example, Figs. 21.9 and 29.8.

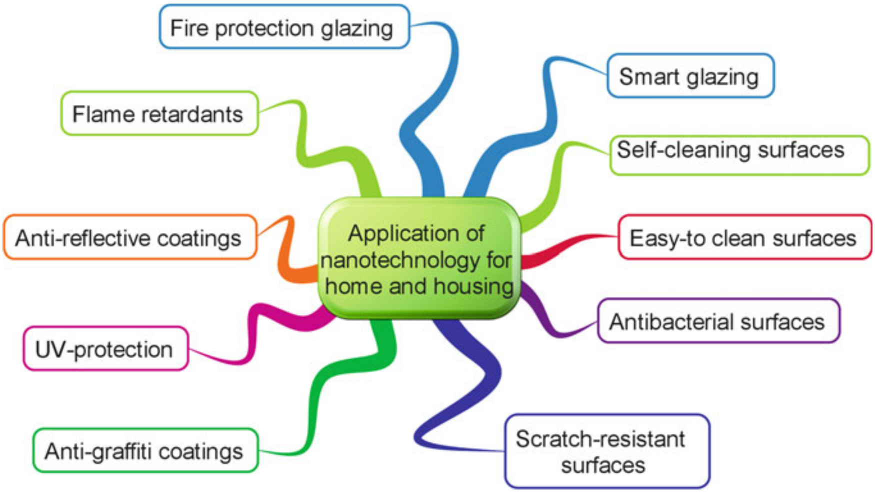

Fig. 29.8 Some present or potential application of nanotechnology at home and for housing

Nanotechnologies will provide a revolution in household goods and quality of life. Surfaces, textiles, and clothing will require less frequent cleaning because of inbuilt dirt and dust repellence. New nanosensors, integrated with actuation and control systems, will allow for better environmental control, reducing heating costs by optimizing temperatures based on where people are in the house, and using passive heating and cooling through adjustment of the heat loss or transmission through windows. Sensors in food packaging will allow monitoring of when foods need to be reordered automatically from the supermarket, and will give automatic programming of the cooker for food preparation.

There are plenty of applications of nanotechnology (present and future) to homes and buildings. Some of them are recalled in Fig. 29.8.

29.4 Nanotechnology in the Industry

Industry and the economy will greatly profit from these new technologies and daily life will be markedly changed. Nanotechnologies can provide wireless power, upgrade parts of the healthcare cycle, optimize nutrition, provide a greener transport system, assure a safe and secure society, with excellent communication facilities such as the wireless telephone, Fig. 29.9.

The increasing demand on natural resources requires unprecedented gains in efficiency. Nanostructured materials with tailored properties, designed and engineered at the atomic scale, give novel and unique features that will usher in the next clean energy revolution, reduce our dependence on depleting natural resources, and increase atom-efficiency manufacturing and processing.

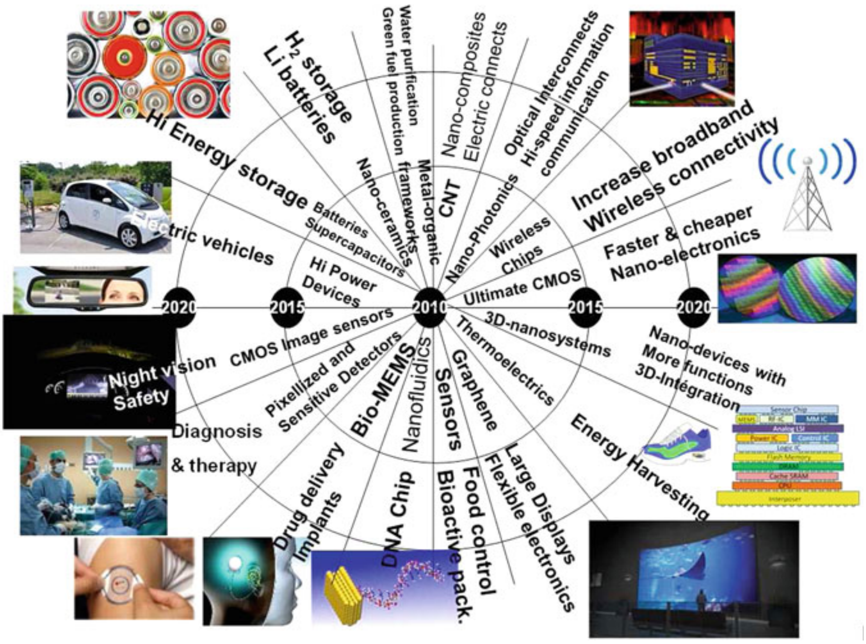

Fig. 29.9 Spectrum of nanotechnology applications in energy, environment electronics, and materials

29.5 Nanoelectronics

Nanoscience and nanotechnology have made the greatest impacts in nanoelectronics. The evolution of electronics during recent decades relies on applications of new nanotechnologies. The increasing density of devices on a chip is now at the point where the complexity is equivalent to the brain power of simple insects, and if the trend continues they will reval the human brain with three decades.

The impacts of nanoelectronics in industry and society are schematically represented in Fig. 29.10. Electronics does not only have impact in computers and mobile phones, but also in medicine, transport, and energy.

In applications such as computing, communication, and integrated circuits, nanotechnology can provide systems which are faster, smaller, and cheaper while storing more information. This includes nanotransistors, magnetic random access memories, flash memories, displays with OLEDs, and so on.

For example, the trend is toward nanotransistors which are faster, more powerful, more energy efficient, and cheaper than larger transistors because a smaller number of electrons are involved in their operation. For magnetic random access memories, the goal is that they can store a tremendous amount of data while being able to quickly save data safely and securely if an accidental shut down of the device occurs.

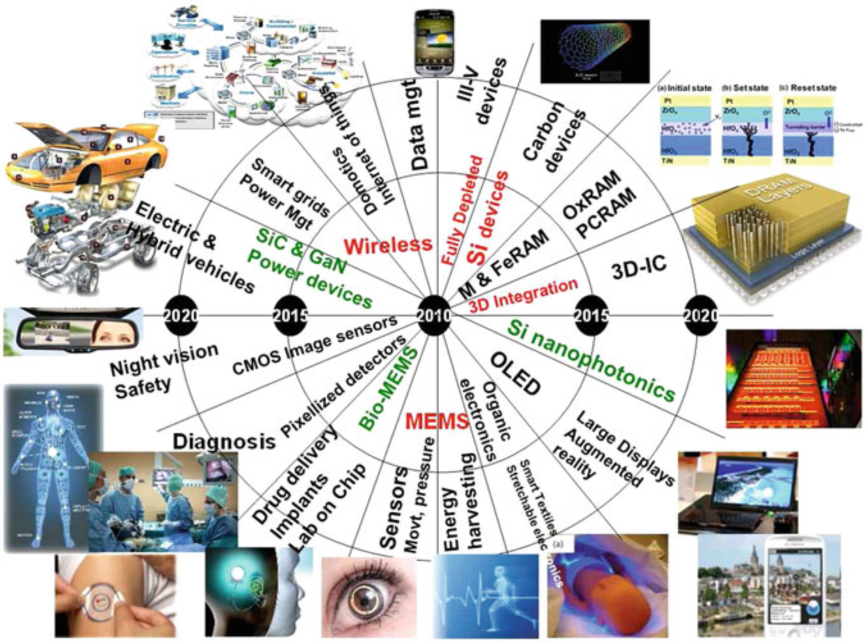

Fig. 29.10 Applications of nanoelectronics for technologies, spanning human health, society, and well-being

In addition to nanoelectronics, Fig. 29.11 shows the importance and the multiple applications of:

- piezotronics which is the coupling between piezoelectricity and semiconductor technologies;
- piezophotonics which couples piezo-electrics and photoexcitation effects;
- optoelectronics which has a coupling between photoexcitation and semiconductors;
- and finally the three-way coupling between piezotronics, and piezophotonics, and optoelectronics, leading to piezophototronics.

The linking of different existing functions into single devices through nanotechnology has incredible potential, from better touch interfaces to active implanted devices to improve quality of life.

More generally, nanotechnology comes into play in many areas of the communication and information technologies. The areas where it is fundamentally involved are shown in Fig. 29.12.

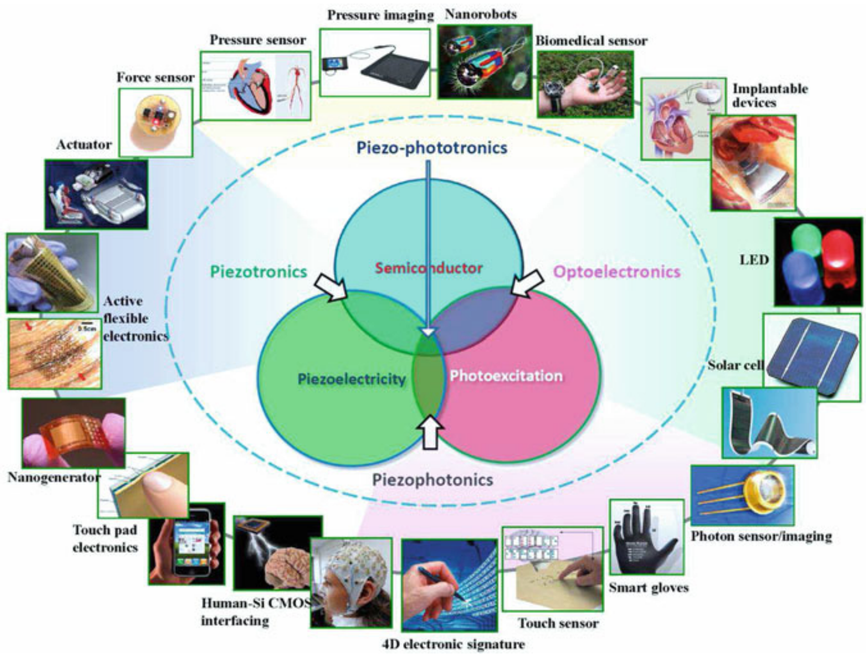

Fig. 29.11 Three-way coupling among piezoelectricity, photoexcitation, and semiconductor with multiple potential applications. Image courtesy Zhong Wang, MRS Bulletin, volume 37, 9, pp. 814–827 (2012), Cambridge University Press

Fig. 29.12 Areas of information and communications where nanotechnology can play a role

29.6 Human Health and Aging

Meeting the health and well-being needs of an aging society poses immense challenges, but at the same time it also offers valuable opportunities to exploit strengths in technology innovation. Nanotechnology plays a role in all healthcare domains going from prevention to follow-up of patients as summarized in Fig. 29.13.

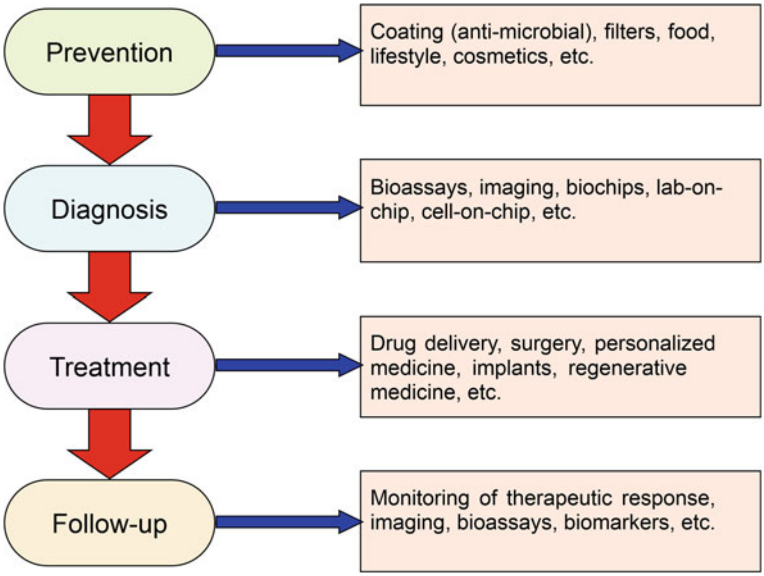

Fig. 29.13 Fields in medicine where nanotechnology plays a role

The goal of nanotechnology in this sector, as well as in others, is to develop cheaper, safer, portable, and easier-to-use systems. Quantum dots can be useful in medical imaging and provide an optical detection sensitivity which can be about three orders of magnitude better than conventional dyes. Gold particles can be used to detect Alzheimer's disease at an early stage.

Nanotechnologies will play a crucial role in the medical revolution that will solve the looming problems in healthcare. They will enable the development of ultrasensitive DNA/protein tests that can be used for highly personalized (genome-based) risk assessment, diagnosis, therapy selection, and treatment monitoring, and which can be used at a patient's bedside to rapidly identify infections and select the appropriate drug with a personalized dose. Nanotechnologies will also facilitate advancements in molecular imaging, layering quantitative functional information onto anatomical data to assist in the early detection and treatment of disease and speed up the (pre-) clinical testing of new drugs. It is quite important to be able to detect the tiny molecular signals associated with the early stages of cancer.

Telemonitoring networks that employ unobtrusive sensors to monitor vital body signs will allow patients to return home sooner, freeing up valuable hospital resources and making healthcare more affordable. Nanotechnology-based prosthetics will restore sight to the blind, hearing to the deaf and will automatically administer drugs in the right dose and with better dose rates than is achieved with conventional technology.

Achieving these objectives will involve the development of nanoelectronic devices such as sensors that interact with molecules and living cells in real time. Achieving the required biocompatibility, ultra-low power consumption, device miniaturization, and safety-critical reliability will pose major challenges.

Multifunctional therapeutics based on nanoparticles will be used to target cancer cells and deliver the proper treatment at the precise location. This will reduce the collateral effects on healthy tissues.

Studies are currently underway both in vitro and in vivo on animals to use nanotechnology to spur the growth of nerve cells or to use nanofibers to regenerate damaged spinal nerves. This is highly worthwhile since it could be used to repair damaged spinal cord or brain cells.

29.7 Food Security and Sustainable Agriculture

Nanotechnology has the potential to improve the quality, safety, and availability of the food that we eat. Nanosensors similar to those developed for healthcare applications that can respond to specific genes or proteins will enable the development of plant strains that are resistant to disease and adverse climatic-conditions. In this sense, biomaterials, medicine, dentistry, pharmaceuticals, and food and agriculture have links between each other as far as nanotechnology is concerned and belong to the field of nanobiotechnology (Fig. 29.14).

Embedded into packaging and labeling, nanosensors will provide consumers with an immediate indication of a food's suitability for human consumption. Embedded into production processes, they will ensure the quality, reliability, and traceability of food processing operations.

Opportunities also exist in the agrochemical industry. For example, nanobased sensors, with very high sensitivity and fast response time, will allow detection of the

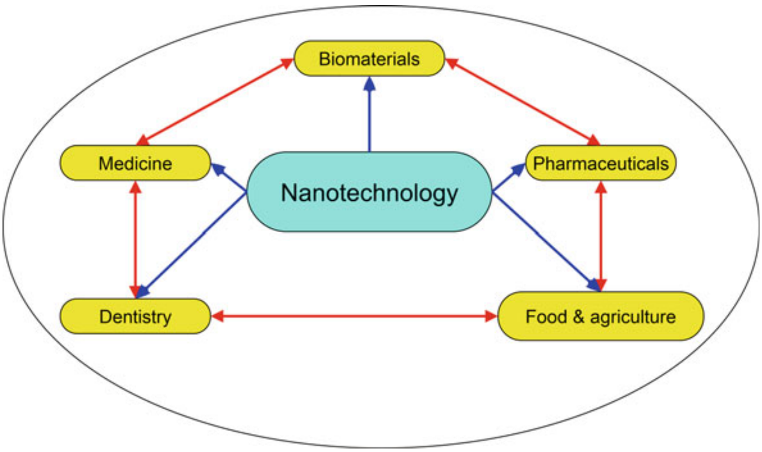

Fig. 29.14 Overview of nanobiotechnology branches

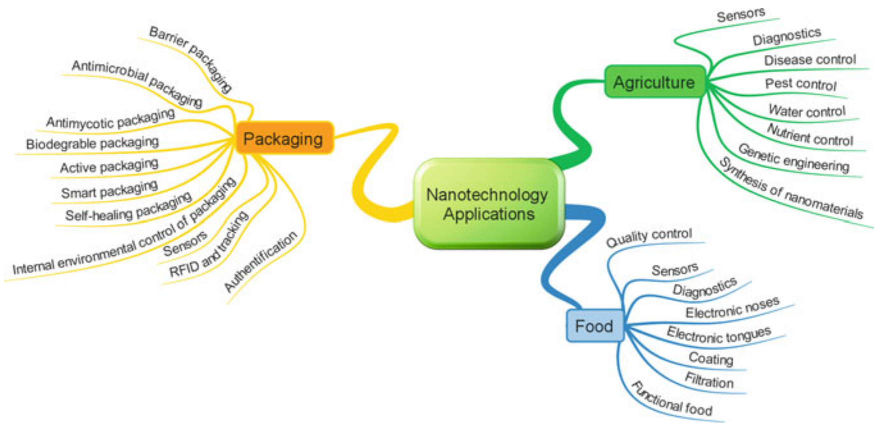

Fig. 29.15 Areas where nanotechnology is involved in agriculture, food, and packaging domains

presence of pesticides, herbicides, and fertilizers, so that they do not enter the food chain or adversely affect biodiversity and the wider environment.

Developing and implementing such applications will involve the design and fabrication of biologically sensitive nanosensors for the detection of specific chemical/biochemical signals, and micro /nanoelectromechanical actuators that can response to those signals to provide an appropriate response.

The main areas concerned by nanotechnology are shown in Fig. 29.15 for agriculture, food processing and functional food, and food packaging and distribution (see the Obervatorynano project for details).

29.8 Secure, Clean, and Efficient Energy

By the end of the twenty-first century, a large part of the world's energy requirements will need to come from CO_2-free energy sources such as renewables or nuclear energy. The reason is that the use of fossil fuels leads to CO_2 emissions together with other pollutants and oil and natural gas are likely to be much more expensive than today. Nanotechnology has the potential to address the challenge from both ends, by helping to minimize the world's energy consumption and by making renewable energy sources more affordable.

As shown in Fig. 29.16, nanotechnology plays a role in several areas of the energy domain: production, transport and storage, and in energy use.

Through the relentless pursuit of nanoscale miniaturization, the semiconductor industry will be able to continue to deliver lower cost higher performance chips that consume less energy. These nanoelectronic microchips will help to reduce power consumption in many other sectors as well: for example, by bringing greater intelligence to energy distribution (smart grid), public and private spaces (smart lighting, smart buildings), and industrial automation. Nanofabricated devices that convert heat or

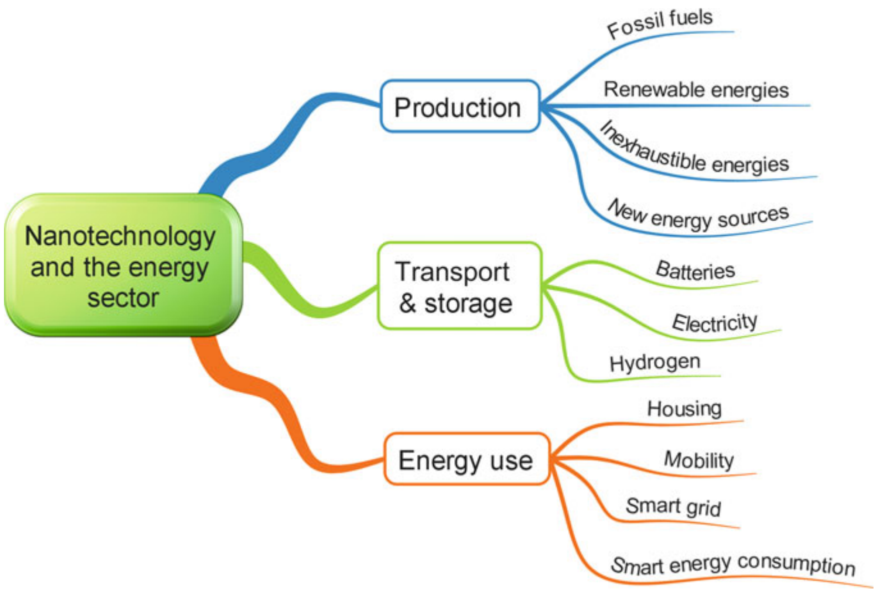

Fig. 29.16 Main areas where nanotechnology is important in the energy sector

motion into electrical energy will allow novel solutions to scavenge power to operate from their surroundings. At the same time, nanotechnological advances will reduce the cost of renewable energy sources such as solar power, and increase the viability of clean fuels such as hydrogen (the basis of the so-called hydrogen economy), particularly in automotive applications. They will be at the heart of the energy management systems needed to utilize these new and diversified energy sources.

29.9 Smart, Green, and Integrated Transport

An integrated transport infrastructure that encompasses all modes of transport (air, rail, road, and water) is vital to ensuring economic prosperity and social cohesion.

As the volume of traffic on Europe's roads continues to increase, there will be an ever-increasing demand for drive-by-wire systems that outperform humans in terms of speed control, fuel efficiency, and collision avoidance. More information will need to be transferred to, from, and between moving vehicles; not only for driver information, navigation, and entertainment purposes, but also for vehicle tracking and road toll applications. Nanotechnology will contribute in many sectors such as those presented in Fig. 29.17.

Greater fuel efficiency will be required from gasoline/diesel powered vehicles. Cleaner alternatives such as electric (battery powered) vehicles, hybrid vehicles, plug-in hybrid vehicles, and fuel-cell powered vehicles will need to be developed well beyond their current state-of-the-art.

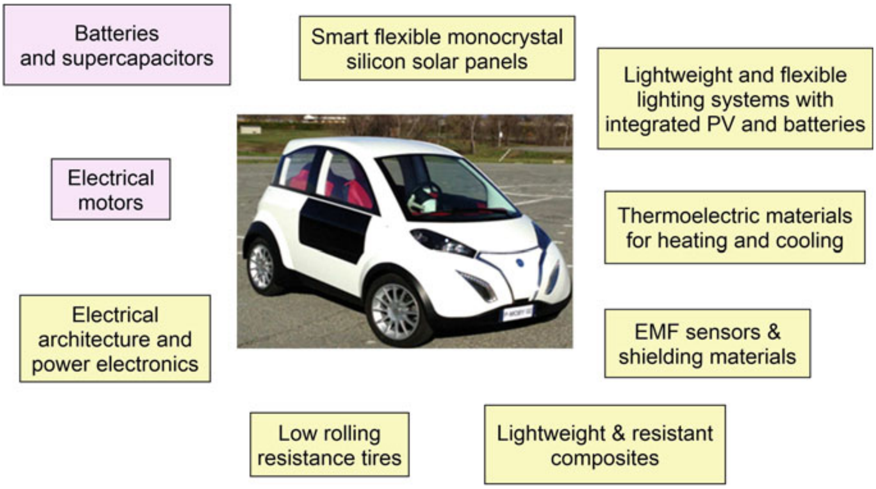

Fig. 29.17 Nanotechnologies enabling clean, safe, and efficient electric mobility. Image courtesy of P. Perlo Torino e-district, IFEVS

29.10 Resource Efficiency and Climate Change Action

Environment protection and sustainable development are now an important challenge to industrialized societies. Humans are in constant interaction with air, water, and soil that they can pollute. Figure 29.18 shows the important concerns about environment protection.

Europe has particular strengths in environmental (green) technology and eco-innovation (the development of products and processes that contribute to sustainable development). It already accounts for approximately one-third of the global market in these high growth domains. The range of applications in which innovation opportunities exist is very broad, ranging from energy generation and energy efficiency

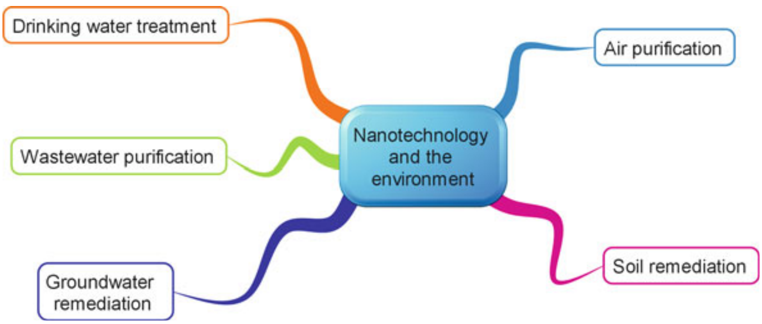

Fig. 29.18 Important areas for environmental protection

to conservation, recycling, waste reduction, emissions control, and environmental management. Virtually all of these are important in strategic sectors such as construction, transport, and agriculture.

A current example where rapid developments in nanotechnology, notably nanoelectronics, is making rapid advances is in LED lighting, providing very large energy savings and cost reductions. New semiconductor materials (such as SiC and GaN) will provide large efficiency gains in energy conversion for a multitude of applications. Environmental monitoring and control using smart sensor networks is another potential high-volume market for nanoelectronics-based solutions.

29.11 Inclusive, Innovative, and Secure Societies

Feeling safe and secure, putting the world around us into context and communicating with friends and loved ones are all basic human needs that technological breakthroughs such as mobile telephony, the internet, and smartcard technology have done a great deal to address. Yet these remains a paradox: the more in formation we can access about the world we live in, especially in relation to issues such as crime and terrorism, the less secure we feel. The more data we generate, the less comfortable we are about our privacy being respected. "Cybercrime" and "cyber terrorism" now figure in our vocabulary as much as their physical counterparts. Next-generation information, security, and communication systems will need to overcome this paradox by embracing a paradigm shift to "ambient intelligence": systems that are capable of recognizing individuals and responding to their individual needs in highly personalized ways.

In modern societies a number of threat exist and the most important ones are shown in Fig. 29.19. Nanotechnology can be involved in devices aiming to detect, treat, cure and respond to the threats, and mitigate effects.

Nanotechnology, through its ability to provide the necessary sensors, actuators, and computing power at an affordable cost level, will be the single most important enabler of ambient intelligence. For example, it will enable security systems that use multifaceted biometrics to identify individual users, communication systems that tunnel data from source to destination without relying on dedicated network infrastructures, and home environments that automatically respond to people's needs in ways that make them feel safe and secure.

29.12 Cleaning and Purification

Nanomaterials can play a role in novel cleaning and purification solutions. Membranes that use nanotechnology for filtration can be used in both domestic and industrial applications. In the home, they can provide cleaning of drinking water—particularly in countries where control of central supply quality is variable—and filtration after cleaning of clothes and crockery. In industry, membranes can be used in wastewater treatment, in the remediation of pollution, and in purification for high-quality process control. Nanostructured membranes have also a potential in the oil and gas industry.

29.13 Summary

In terms of the technological developments over the next two decades, nanomaterials will be the most important area of activity. Microelectronics has already moved to systems embedding nanotechnologies and most integrated circuits and memories are manufactured today at dimensions in the nanoscale range. Nanotechnologies will be transformative, and this will be true in the home as much as in industry. From clothing to computers, from cars to chemicals, from water to policing, nanotechnologies will change the way that products and processes are developed and used.

The impact will go far beyond “things” such as products and brands, as communications will change, becoming more ubiquitous and real-time. The amount of data available to an individual about their contacts, their surroundings, and their state of health, will be greatly enhanced compared to today, yet the systems providing the information will be almost unseen. The same applies for monitoring systems in the global environment, providing safety in cities and pollution control in the countryside.

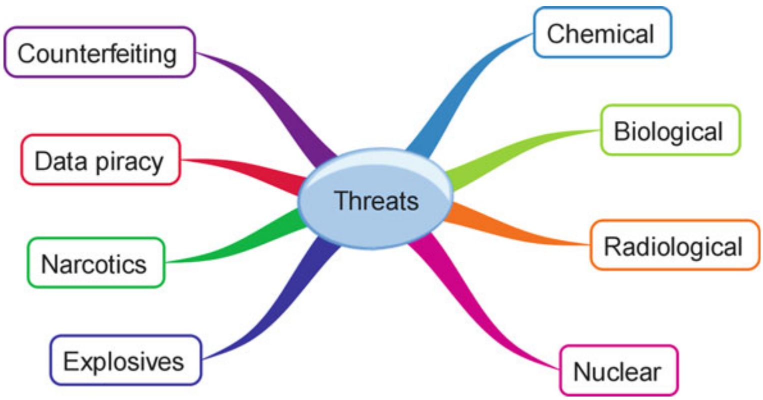

Fig. 29.19 Different threats in modern societies

Nanotechnology may help solutions to problems that are current unsurmountable: damage from earthquakes and tsunamis; cheap space travel; 100 % safe round transportation; the zero energy homes.

Nanotechnology will be a great driving force for economic growth, providing new means for countries to exploit their local resources, and generate high-technology products that can be marketed around the world. It will therefore promote prosperity and the creation of new jobs.

As a consequence, nanotechnology will contribute to have a better interaction between societies around the world; making people more interdependent on one another. Because of that, it may help to create world which we hope will be more stable and peaceful.

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