14 Ultra-small Single-walled Carbon Nanotubes and their Novel Properties

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1. INTRODUCTION

Carbon nanotubes (Iijima, 1991) are currently being intensively investigated because of their remarkable electronic and mechanical properties. A multi-walled nanotubes can be thought of as graphite sheets wrapped into a coaxial seamless cylinder. In 1993, Iijima's group as well as Bethune's group found that the use of transition-metal catalysts could lead to nanotubes with only a single wall (Iijima, 1993; Bethune, 1993). The diameter of each freestanding single-walled carbon nanotube (SWNT) ranges from 0.7 nm to a few tens nanometers with a maximum length of about 1 µm. Although theoretical calculations have predicted the stability of a SWNT with diameter as small as 0.4 nm (Sawada, 1992), the existence of free-standing SWNTs with a diameter smaller than that of C_{60} fullerene (0.7 nm) has been in doubt for quite a while (Ajayan, 1992) because of the extreme curvature and reactivity of these structures. Smaller carbon nanotubes can exist, however, in a spatially confined environment. Carbon nanotubes with diameters of as small as 0.5 nm (Sun, 2000) and 0.4 nm (Qin, 2000) have been observed existing in the centre of multi-walled carbon nanotubes. It is still not clear, however, that whether these small nanotubes are stable in free space. Recently, we have shown that 0.4 nm-sized SWNTs can be produced by means of pyrolysing hydrocarbon molecules in 1 nm-sized channels of $AlPO_4$-5 (AFI) single crystals (Tang, 1989; Wang, 2000). These 0.4 nm-sized SWNTs have the same size of the smallest possible fullerene C_{20} (Prinzbach, 2000). They are stable inside the AFI channels but not very stable when they are in free standing.

Within the band-folding scheme, the diameter and the chirality of a SWNT are believed to determine whether the nanotube is metallic or semiconducting (Blasé, 1994; Dresselhaus, 1996; Saito, 1998). Their electronic density-of-states (DOS) have van-Hove singularities, which have been directly observed by scanning tunnelling spectroscopy (Wildoer, 1998). Optical transitions between the van-Hove singularities have also been observed in absorption spectra of SWNT bundles and nanotube thin films (Ichida, 1999; Kataura, 1999). Due to the fact that even weak Coulomb interaction can cause strong perturbations in a one-dimensional (1D) system, bundles of SWNTs may exhibit Luttinger-liquid behaviour (Bockrath, 1999). In very small SWNTs, σ^*-π^* hybridizations can be introduced by strong curvature effect (Blasé, 1994). Thus, the electronic

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properties of a small-sized SWNT can depart from the prediction of the band-folding theory for large-sized SWNTs (Zhao, 2001). The induced curvature opens new electron-phonon scattering channels that increases the electron-phonon coupling and makes the small tubes superconducting (Benedict, 1995). Experimentally, superconductivity has really been observed in ropes of SWNTs (1.4 nm diameter) at temperature below 0.55 K (Kociak, 2001), and in 0.4 nm sized SWNTs at a mean-field superconducting temperature of as high as 15 K (Tang, 2001).

In this paper, we report the detailed fabrication process of ultra-small SWNTs accommodated in the 1 nm-sized channels of microporous aluminaphosphate $AlPO_4$-5 (AFI) single crystals. These nanotubes have been observed directly by transmission electron microscopy (Wang, 2000; Wang, 2001), and indirectly by X-ray diffuse scattering (Launois, 2000) as well as by micro-Raman measurements of the nanotube breathing mode (Sun, 1999a; Sun, 1999b). The data consistently indicate a nanotube diameter of 0.4 nm, probably at or close to the theoretical limit. The system of the mono-sized SWNTs stabilized in the zeolite channels brings the experimental results much closer to the real of theoretical predictability. It constitutes the best example of 1D quantum wires, and would have extremely interesting physical properties, which are not predicted in SWNTs of larger diameter.

2. EXPERIMENTAL

The SWNTs were produced in the channels of micro-porous aluminophosphate $Al_{12}P_{12}O_{48}$ (AFI) single crystals. Its framework consists of strictly alternative tetrahedra of $(AlO_2)^-$ and $(PO_2)^+$. They form parallel opened one-dimensional channels arrayed in a hexagonal structure. The inner diameter of the channels is 0.73 nm, and the distance between two neighbouring channels is 1.37 nm. Fig. 1(a) shows the framework structure viewed along [001] direction of the crystal. In the figure, the carbon nanotubes are also schematically shown inside the channels. The starting material used for the synthesis of the SWNTs is tripropylamine (TPA) molecules, which were introduced into the channels as templates during the growth of AFI single crystals. The AFI single crystals were grown by hydrothermal synthesis in Teflon-lined autoclaves (Qiu, 1989). The reactants were 85% H_3PO_4, aluminium isopropoxide, and hydrofluoric acid. The aluminium isopropoxide was first hydrolysed in water, and then H_3PO_4,TPA, and HF acid were added under vigorous stirring. After keeping this mixed gel in the autoclave at 175 °C for 10-24 hours, optically transparent single crystals with a beautiful hexagonal shape were obtained. An optical microscopy image of the as-grown AFI single crystals is shown in Fig. 1(b). The typical size of the obtained AFI single crystals is about $100\times100\times500$ μm^3. SWNTs were produced by pyrolysis of the TPA molecules in the channels in a vacuum of about 10^{-3} Torr at temperature 500-600 °C. After carbon nanotubes are formed in the channels, the tube-contained AFI crystal behaves as a good polarizer with high absorption for the light polarized parallel to the channel direction (*E//c*) and high transparency

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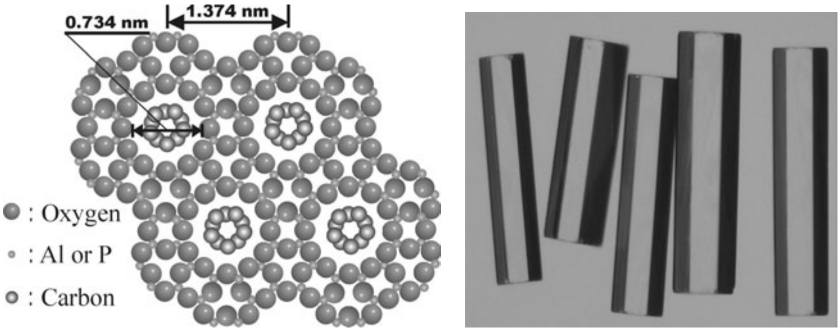

(a) (b)

Figure 1 (a) The framework structure of the crystal viewed along [001] direction. The carbon nanotubes are also schematically shown in the figure. (b) Photograph of as-grown AFI single crystals.

for the light polarized perpendicular to the *c*-axis ($E\perp c$), which is consistent with the one-dimensional character of the nanotubes.

Raman spectra were measured using a Renishaw 3000 Micro-Raman system equipped with a single monochromator and a microscope. Samples were excited using the 514.5 nm line of a Ar^+ laser with a spot size of ~2 μm. Signals were collected in a back scattering configuration at room temperature and detected by an electrical-cooled charge-coupled-device (CCD) camera. The spectra resolution of the optical system is about 1 cm^{-1}.

3. RESULT AND DISCUSSION

3.1. TEM Observation

Fig. 2 is a high-resolution transmission electron microscope (HRTEM) image (JEOL2010 electron microscope, operating at 200 kV) of the nanotubes. The AFI framework was removed using hydrochloric acid before the TEM observation (Wang, 2001). The contrast of the SWNTs is very weak due to their small dimensions compared to the thickness of the supporting amorphous carbon film (~ 10 nm). However, it can be recognized that the typical SWNT contrast consist of paired dark fringes. Such contrast becomes more obvious when the picture is

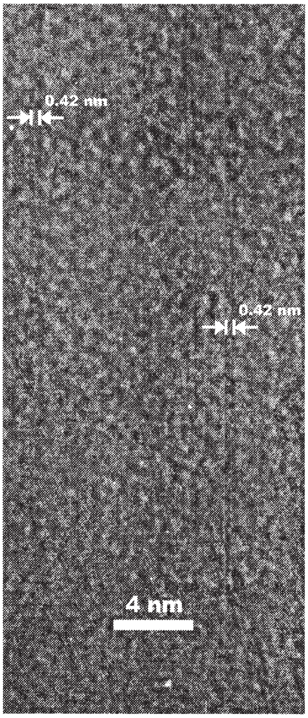

Figure 2 High-resolution TEM image of the SWNTs. The nanotubes were moved out from the AFI channels and dispersed on a carbon lacy film for the TEM observation.

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looked along the tube axes. Most SWNTs are straight and around 10-15 nm long. They are not stable under electron beam radiation in TEM. During observation, the SWNTs faded away in 10-15 s while graphite with raft-like layers in the view field persisted (not shown in Fig. 2). The diameter of the SWNTs is determined to be 0.4 nm, which is in consistent with the result obtained from the X-ray diffuse diffraction measurement (Launois, 2000). There are only three limited possible structures for the 0.4 nm sized SWNT, they are the zigzag (5,0), armchair (3,3) and chiral (4,2) tubules whose diameters are, respectively, 0.40 nm, 0.41 nm and 0.42 nm. The system energies of these nanotubes are similar to each other, with only a slight difference in the order $E_{(4,2)} \leq E_{(3,3)} \leq E_{(5,0)}$ for the free-standing tubes. However, the abundance of these tubes are not necessarily governed by this order since the stereo constraint of the limited channel space may favour the smaller (5,0) tube; and in addition, the kinetics of the formation process would be an important factor to consider.

3.2. Raman Spectra

The unpolarized Raman spectra are shown in Fig. 3. In general, the Raman spectrum exhibits three main zones at low (400-800 cm^{-1}), intermediate (1,000-1,500 cm^{-1}) and high (1,500-1,620 cm^{-1}) frequencies. In high frequency region, there is a graphite-like tangential Raman mode at 1615 cm^{-1} with a shoulder around 1585 cm^{-1}. The Raman signals observed in the intermediate frequency region (1000-1500 cm^{-1}) are associated with the presence of D-band or finite-size

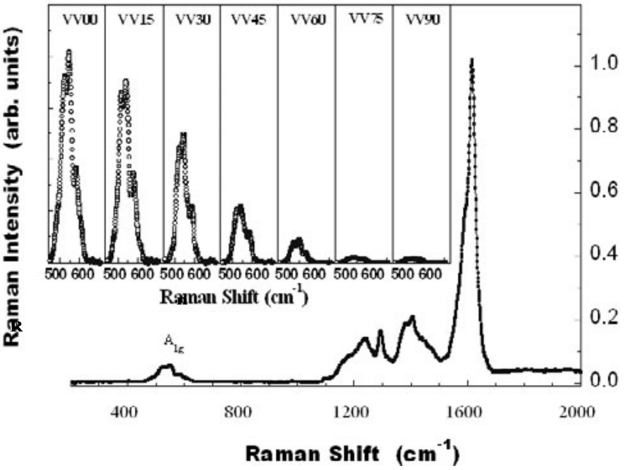

Figure 3 Raman Spectra of the SWNTs excited using 514.5 nm line of an Ar^{+} laser. The inset is the Raman signal in RBM region under the polarization configuration from VV00 (the excitation laser light and the scattered Raman light polarized parallel to the tube direction) to VV90 (polarized perpendicular to the tube direction).

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effects in sp^2 carbons. Detailed analysis and assignments of the Raman bands in the high-frequency region have been given elsewhere (Sun, 1999a; Sun, 1999b). The low-frequency modes are silent for all other carbon specimens. The Raman signals in this region is due to the radial breathing mode (RBM) vibration which is not sensitive to nanotube structure but to the nanotube radius. There are three fine structures in the RBM region. The peak positions of the three RBM Raman lines are at 523 cm^{-1}, 545 cm^{-1}, and 584 cm^{-1}, respectively. The magnified spectra are shown in the inset (see the inset VV00). Three RBM peaks indicate that there exist three different diameters for the SWNTs in the AFI channels. Using an elastic force-constant model (Dresselhaus, 2000; Jorio, 2001), the tube diameter can be calculated from the RBM frequency using $d = \alpha/\omega$, here ω is the vibration frequency of the RBM, and α is the proportional constant. From the well-established data for (10, 10) armchair nanotubes (Rao, 1997), α can be estimated to be 224 $nm\cdot cm^{-1}$. Thus, the three RBM Raman frequencies of 523, 545, and 584 cm^{-1} are assigned to three different diameters of the SWNTs: 0.43, 0.41 and 0.38 nm, respectively, which is in excellent agreement with the diameters of three possible structures of (5,0), (4,2) and (3,3) of SWNTs. The Intensity of the RBM Raman signals are strongly polarization dependent. As shown in the inset, in the VV polarization configuration (vertical polarization both for the excitation laser light and for the back-scattering Raman signal), the magnitude of the RBM Raman signal is monotonically decreasing with the increase of the polarization angle (VV00: the excitation laser light and the scattered Raman light polarized parallel to the tube direction; VV90: lights polarized perpendicular to the tube direction). This polarization behaviour indicates that the RBM has characteristic of A_{1g} symmetry.

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