6 Solvothermal Synthesis of Non-oxides Nanomaterials

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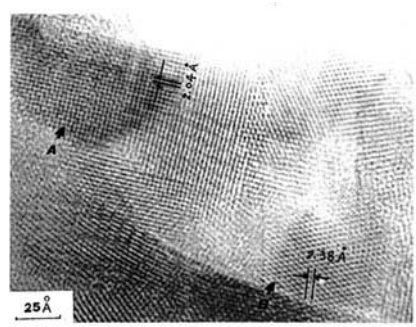
Non-oxides are traditionally prepared by solid state reactions of elements at high temperature, which is difficult for preparing nanomaterials; the pyrolysis of organometallic precursors containing M-N bonds sometimes give amorphous products. It is necessary to post-treatment at high temperature for their crystallization, which, however, results in the growth of particles and the particle sizes beyond the nanometer scale.

Solvothermal synthesis is analogous to hydrothermal synthesis, except that the organic solvents replace the water as the reaction medium. This method is effective in avoiding the oxidation, hydrolysis and volatilization of non-oxides and their reactants, and favorable for reaction and crystallization of products due to the sealed reaction condition in autoclave.



We developed the solvothermal synthesis into an important solid state synthetic method, by which non-oxides nanomaterials including III-V group (BN, GaN, InAs and InP) and II-VI group (CdE, ZnE, HgE, E = S, Se, Te) semiconductors, diamond, carbon nanotubes were prepared. SiC nanowires, BN and Si_3N_4 nanoparticles and nanorods are also synthesized by this method. The synthetic temperature and pressure of non-oxides nanocrystallites are obvious lower than

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those of traditional methods. Nanocrystalline GaN nanocrystals are benzene-thermally synthesized (Xie, 1996) at 280 °C through the exchange reaction of $GaCl_3$ and Li_3N (Fig. 1). InAs nanocrystallites are synthesized in toluene at 160 °C through the co-reduction of $InCl_3$ and $AsCl_3$ by metal zinc. Nonstoichiomtric phase Co_9S_8 are also obtained by this method.

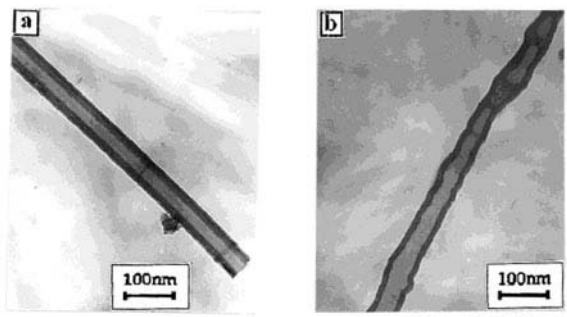

Fig. 2 TEM images of multiwall carbon nanotubes.

Metastable structure is one of the important research directions in current physics, chemistry, materials and earth science fields. At the benzene-thermal conditions the ultrahigh pressure rocksalt type GaN metastable phase (previous exist at 37Gpa) are found at ambient condition (Fig. 1). Diamond crystallites are found (Li, 1998) through the Na-reduction of CCl_4 in autoclave at 700 °C. With a similar process, multiwalled carbon tubes were also synthesized (Jiang, 2000) at 350 °C (Fig. 2). Cubic BN, AlN and Si_3N_4 nanocrystallites are also prepared at 500~700 °C. All these reaction conditions are milder than those of tradition methods, which show that solvothermal synthesis have good prospects in research of metastable structures.

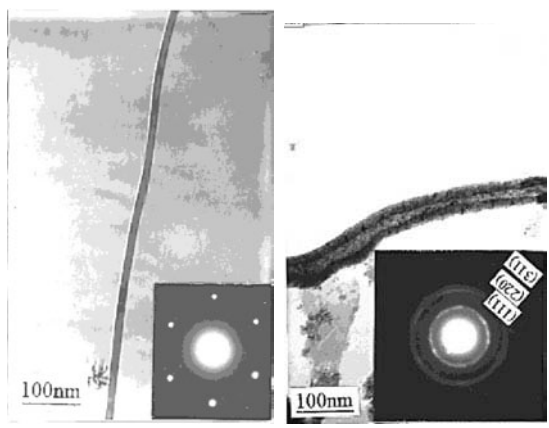

Fig. 3 TEM images of SiC nanowire (left) and tubular structure (right).

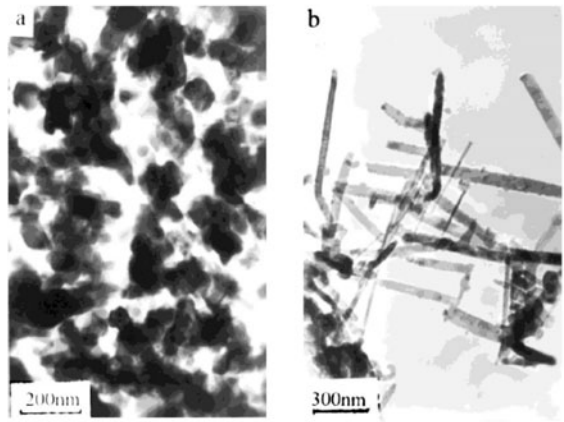

Fig. 4 TEM images of Si_3N_4 nanoparticles (left) and nanorods (right).

A series of non-oxides one-dimension nanocrystallites such as carbon nanotube, $Cu_{2-x}Se$ nanocubes, carbide, nitride and chalcogenide nanorods. SiC nanowires are synthesized at 350~400 °C by the reaction of CCl_4 and $SiCl_4$ using metallic Na as the reductant. SiC nanowire with tubular structure was also observed (Hu, 2000) in the sample (Fig. 3). By the reaction of $SiCl_4$ and NaN_3 at 670 °C Si_3N_4 nanoparticles and nanorods were fabricated (Fig. 4) (Tang, 1999). Microtubes and balls of phosphorus nitride imide (HPN_2) were synthesized by benzene-thermal method (Meng, 2001) at temperatures lower than 250 °C (Fig. 5). Very long CdS nanowires (100 μm × 40 nm) were synthesized using polymer-controlled growth (Zhan, 2000) in ethylenediamine at 170 °C (Fig. 6). Cadmium sulfide with different morphologies were synthesized (Yu, 1998) using solvothermal route (Fig. 7). Metal selenides nanorods (CdSe, PbSe, SnSe, Bi_2Se_3) are obtained at room temperature. This method has also applied into the preparation of ternary metal chalcogenides such as $CuInE_2$ (E = S, Se), $CuMS_4$ (M = Fe, Ga, Sb), $AgMS_2$ (M = Ga, In). CdS with hollow sphere and peanut-like structures were synthesized by an *in-situ* source-template-interface reaction (Huang, 2000) in organic solvents (Fig. 8).

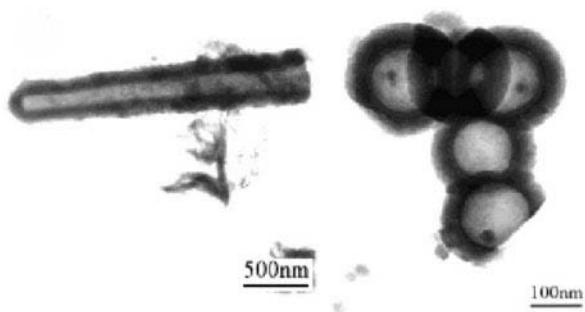

Fig. 5 TEM images of tubular (left) and sphere (right) structure HPN_2.

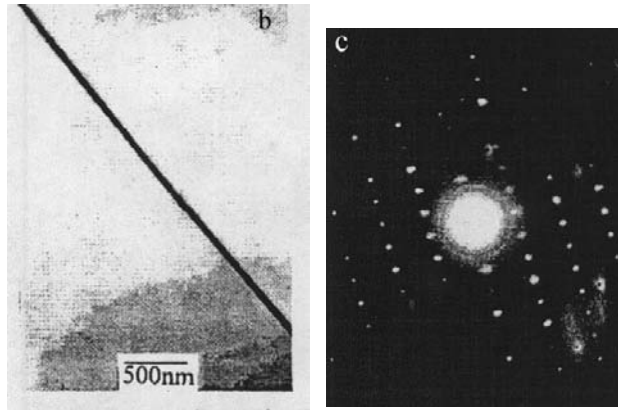

Fig. 6 TEM image (left) and SAED pattern (right) of CdS nanowire.

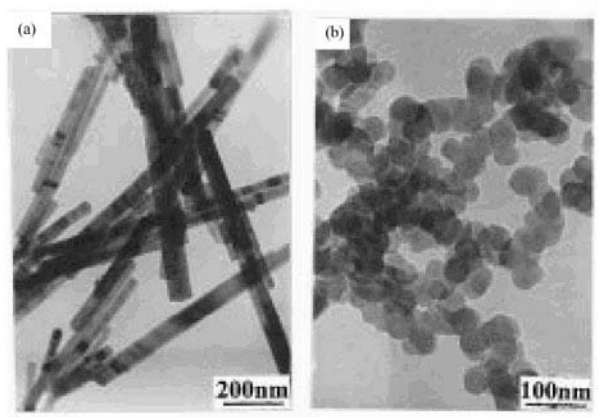

Fig. 7 TEM images of CdS nanorods in ethylenediamine (left) and CdS nanoparticles in pyridine (right).

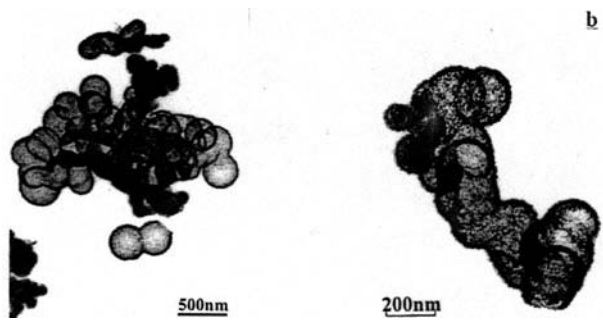

Fig. 8 Hollow spheres of CdS.

As a comparison, hydrothermal method is also applied to synthesize novel structured materials. A series of tubular structured inorganic materials and inorganic/polymer composites were fabricated by the method. Millimeter-sized tubular crystals of Ag_2Se are successfully grown for the first time *via* a hydrothermal reaction route (Hu, 2000) from AgCl, Se and NaOH at 155 °C (Fig. 9).

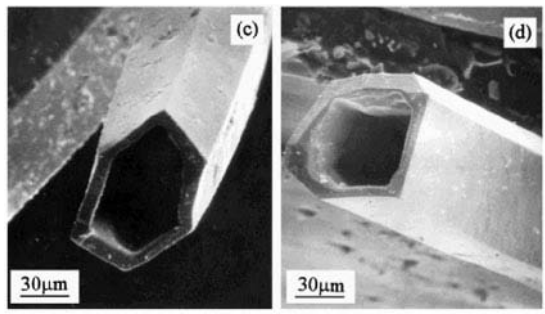

Fig. 9 SEM photos of tubular Ag_2Se.

REFERENCE

Xie, Y., *et al.*, 1996, A benzene-thermal synthestic route to nanocrystalline GaN. *Science*, **272**, pp. 1926-1927.

Li, Y. D., *et al.*, 1998, A reduction-pyrolysis-catalysis synthesis of diamond. *Science*, **281**, pp. 246-247.

Jiang, Y., *et al.*, 2000, A catalytic-assembly solvothermal route to multiwall carbon nanotubes at a moderate temperature. *J. Am. Chem. Soc.*, **122**, pp. 12383-12384.

Hu, J. Q., *et al.*, 2000, Synthesis and characterization of SiC nanowires through a reduction-carburization route. *J. Phys. Chem. B*, **104**, pp. 5251-5254.

Tang, K. B., *et al.*, 1999, A novel low-temperature synthetic route to crystalline Si_3N_4. *Adv. Mater.*, **11**, pp. 653-655.

Meng, Z. Y., *et al.*, 2001, Microtubes and balls of amorphous phosphorus nitride imide (HPN_2) prepared by a benzene-thermal method. *Chem. Commun.*, pp. 469-470.

Zhan, J. H., *et al.*, 2000, Polymer-controlled growth of CdS nanowires. *Adv. Mater.*, **12**, pp. 1348-1351.

Yu, S. H., *et al.*, 1998, A novel solvothermal synthetic route to nanocrystalline CdE (E = S, Se, Te) and morphological control. *Chem. Mater.*, **10**, pp. 2309-2312.

Huang, J. X., *et al.*, 2000, An in-situ source-template-interface reaction route to semiconductor CdS submicro hollow spheres. *Adv. Mater.*, **12**, pp. 808-811.

Hu, J. Q., *et al.*, 2000, Growth of tubular-crystals β-Ag_2Se through a hydrothermal reaction route. *Chem. Commun.*, pp. 715-716.