Growth of Sb_2O_3 Nanotubes via a Simple Surfactant-assisted Solvothermal Process

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Sb_2O_3 nanotubes were successfully prepared via a simple surfactant-assisted solvothermal method. The nanotubes have an orthorhombic structure with outer diameter range from 40 to 150 nm, the wall thickness of 10 to 40 nm and a length of up to several micrometers. The formation of nanotubes followed a rolling-up mechanism.

Since Iijima discovered carbon nanotubes in 1991,[1] nanotubes materials have attracted much attention in both fundamental and industrial studies owing to their unique structural and physical characteristics: extraordinary mechanical properties, electrical properties, unusual adsorption, and advanced catalysis, etc.[2] These properties render nanotubes very promising candidates for the realization of highly functional, effective, and resource-saving nanodevices, e.g., single electron transistors, sensor capacitors, or storage and release systems.[3] Nanotubes of different composition have been synthesized in an attempt to create tubular structures with novel and tailored properties. Most inorganic oxide nanotubes have been prepared by using an anodic alumina template method and sol–gel processing, e.g. titania nanotubes by chemical processing,[4] silica nanotubes by an anodic alumina template method[5] and vanadium oxide nanotubes by a sol–gel reaction following hydrothermal treatment.[6] It is a challenge to find new synthesis routes to other oxide tubular structures.

Antimony oxide is a very attractive material because of its interesting applications as catalysts and gas sensors.[7,8] In addition, Sb_2O_3 is very useful as a high-efficiency flame-retardant synergist in plastics, paints, adhesives, and textile back coatings.[9] Nevertheless, there are few reports about the growth of Sb_2O_3 nanotubes. Recently, Ye et al. reported the synthesis of Sb_2O_3 fibrils and tubules by a vapor–solid route.[10] In this work, we have synthesized of Sb_2O_3 nanotubes by a surfactant-assisted solvothermal method.

All the reagents were of analytical grade and were used without further purification. A typical preparation procedure of Sb_2O_3 nanotubes is as follows: 0.04 mol $SbCl_3$, 0.032 mol CTAB (cetyltrimethylammonium bromide), 0.028 mol $NaBH_4$, and 40 mL ethanol were added to a 50-mL flask. And then the mixtures were stirred in a magnetic stirrer for 30 min before being transferred to a Teflon-lined autoclave. The autoclave was kept at 150 °C for 30 h and then cooled to room temperature on standing. More interestingly, the samples in the autoclave were automatically separated into two layers. The above layer was white powder (about 80%) and the below one was black (about 20%). The two layer samples were carefully collected, washed with distilled water and absolute alcohol for several times, and then dried at 80 °C for 8 h.

The XRD patterns of the as-prepared samples with different color are shown in Figure 1. Figure. 1a is a XRD pattern of the white products in the above layer, in which all the peaks can be indexed to the orthorhombic structure of Sb_2O_3 (JCPDS 11-689). Figure. 1b is a XRD pattern of the black products deposited in the bottom of the autoclave, in which almost all the peaks can be indexed to the hexagonal structure of Sb (JCPDS 85-1324). And no characteristic peaks of impurities were appeared in both patterns, which substantiates that the as-prepared products are very pure. These results also indicate that Sb_2O_3 products can be easily separated from Sb.

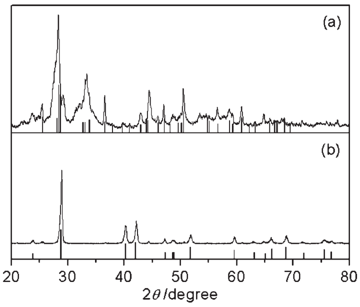

Figure 1. XRD pattern of as-prepared samples. (a) Sb_2O_3 nanotubes in the above layer; (b) Sb materials in the below layer.

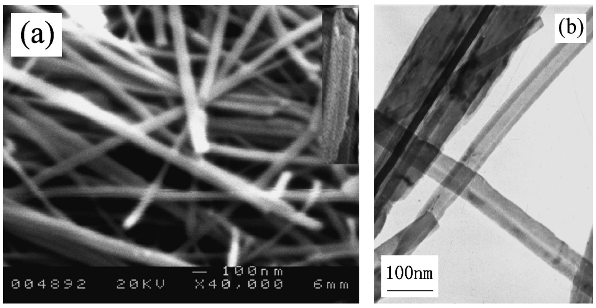

Figure 2. (a) SEM and (b) TEM images of as-prepared samples.

The SEM image shows that the as-prepared products are very copious (shown in Figure 2a). Figure 2b is a typical TEM image of the Sb_2O_3 nanotubes. It can be seen that the Sb_2O_3 nanotubes are basically straight and have outer diameters range from 40 to 150 nm with the wall thickness of 10 to 40 nm and the length of up to several micrometers. In addition, the walls of some nanotubes do not have the equal thickness. Remškar et al. also observed the phenomenon of unequal thickness of the WS_2 nanotubes and ascribed them to the strain of the inner molecular layers of nanotubes.[11]

Figure 3a is a TEM image of an individual nanotube and selected area electron diffraction [the inset in Figure 3a] substantiated that the nanotubes we obtained are of single crystals. Figure 3b shows a typical HRTEM image of a single nanotube and the inset is the magnified image of the rectanglar region. As can be seen from the high-resolution fringes, the walls of the nanotube are composed of regularly ordered molecular layers and contain few defects such as stacking faults. The dark lines, 0.625 nm apart, are the images of the basal (121) planes.

During the solvothermal synthesis, the reaction path is very sensitive to the applied experimental conditions, e.g., temperature, pH value, and duration of the solvothermal treatment. Sever-

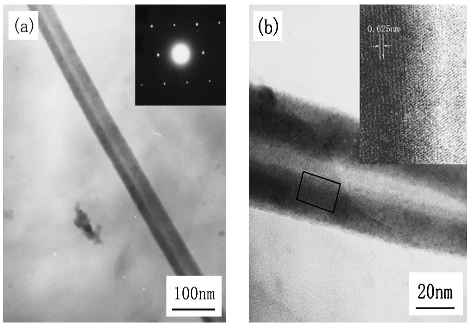

Figure 3. (a) TEM image of a single Sb_2O_3 nanotube; The inset shows SAED of the nanotube. (b) A HRTEM image of the nanotube. (c) A partially magnified image of the rectanglar region in (b).

al experiments were performed to investigate the effect of temperature and duration on the morphology of the final products. In both cases, the concentration and amount of the reactants remained unchanged. As a result, only nanorods were obtained at lower synthesis temperatures (e.g. at 90 °C), or only sheet-like structures and a small amount of nanotubes were formed for shorter periods of solvothermal treatment at 120 °C. The optimal growth condition for Sb_2O_3 nanotubes is a period of 30 h at 150 °C. This suggests that higher temperature or thermal stress might activate the layered structures link together into tubules. Beside the influence of the temperature and reaction time, it was found that the concentration or the amount of CTAB in the system is also a very important factor in the formation of the Sb_2O_3 nanotubes. Only nanorods were obtained without addition of CTAB. In the present experiment, it is obvious that CTAB played a role of the soft template in the formation of Sb_2O_3 nanotubes.

It is well known that the formation mechanism is a very important for exploring synthetic methods of the nanotubes. Mallouk and co-workers did a series of significant works on lamellar structures, in which lamellar sheets, tabular structures, and rolling phenomena were observed.[12–14] Li et al.[15] and Chen et al.[16] synthesized WS_2 and vanadium oxide nanotubes respectively, and provided strong evidence for their rolling model of layered structures. To investigate the growth mechanism, we performed several experiments through intercepting the intermediates at different time. Under shorter reaction time, a large amount of plate structures and a small part of nanotubes were obtained. A more direct evidence for the rolling mechanism is a half-tube or half-plate structure, as shown in Figure 4, and these sheets were transformed to nanotubes after treating again under the same condition of nanotube formation. The partly rolling sheet structure confirmed that Sb_2O_3 nanotube is formed by a rolling process.

Figure 5 shows room-temperature photoluminescence and excitation spectra of the Sb_2O_3 nanotubes at different excitation wavelengths together with that of Sb_2O_3 powders. Obviously, the PL intensity of nanotubes is very stronger than that of powders, and the optimal excitation wavelength for Sb_2O_3 nanotubes is 470 nm, the PL intensity greatly decreases at other excitation wavelength (e.g. 455 and 485 nm). The PL intensity of Sb_2O_3 nanotubes is higher than that of Sb_2O_3 powders under all the circumstance, which indicates that the nanotubes might have higher activity than powders. Since the PL peak shape and position of Sb_2O_3 nanotubes and powders are basically identical under the same excitation wavelength, which indicates that the PL mechanism of Sb_2O_3 nanotubes might be the same as that of Sb_2O_3 powders. We speculated that the PL of Sb_2O_3 nanotubes might originate from the oxygen vacancies.

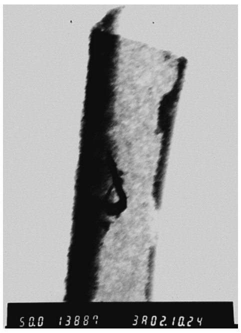

Figure 4. A typical TEM image of the intermediate for shorter reaction time, which shows the rolling of the sheet-structures.

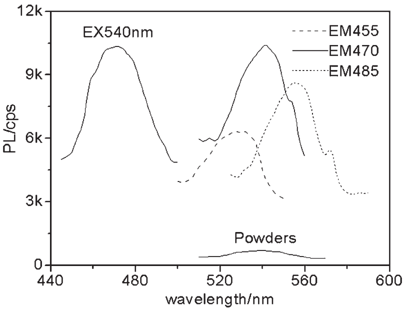

Figure 5. Photoluminescence and excitation spectra of the Sb_2O_3 nanotubes and powders.

In summary, a simple surfactant-assisted solvothermal process has been developed to synthesize Sb_2O_3 nanotubes by using $SbCl_3$, $NaBH_4$, and CTAB as raw materials at 150 °C. Careful control of the reaction factors is indispensable for morphological control of the products. It is expected that the surfactant-assisted solvothermal method of nanotubes growth can be extended to the synthesis of other oxide nanotubes. The formation mechanism of Sb_2O_3 nanotubes follows the rolling-up model.

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