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COMMUNICATIONS

Rational Growth of Bi_2S_3 Nanotubes from Quasi-two-dimensional Precursors

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The discovery of carbon nanotubes has attracted enormous attention over the past decade due largely to their potential significance in research on low-dimensional physics such as thermal- and electrical-transport characteristics and applications in nanodevices such as field emission and magnetic wave detection devices.[1] Tenne has predicted inorganic fullerene-like (IF) structures for a variety of compounds in his seminal article,[2] and many of these IF structures (nanotubes, onions) have indeed been synthesized in laboratory (including MX_2 [M: Mo or W, X: S or Se],[3] BN,[4] $NiCl_2$,[5] vanadium oxide,[6] and InS[7]). Recently, Rao et al. have stated they prepared multiwalled NbS_2 and TaS_2 nanotubes by hydrogen reduction of NbS_3 and TaS_3, respectively.[8] Li et al. have reported the synthesis of bismuth nanotubes by hydrothermal reduction of bismuth nitrite in the presence of hydrazine[9] and WS_2 nanotubes by direct pyrolysis of WS_4^{2-} precursors in a surfactant.[10] What is worth noting is that all the above-mentioned nanotubes have been derived from precursors of layered structures, the so-called two-dimensional (2-D) structures. However, as for those quasi-2-D structures such as Bi_2S_3, Sb_2S_3 and so forth, the evidence of the existence of the tubular form is still lacking.

In this communication, we report on the synthesis of Bi_2S_3 nanotubes by adopting the conventional evaporation method using nanometer-sized Bi_2S_3 powders as starting material. Although it has been well-developed, the evaporation approach has exhibited many intriguing outcomes recently.[11] Bismuth (III) sulfide is a semiconducting material with a direct band gap ranging from 1.3 to 1.7 eV.[12] Thin films of Bi_2S_3 have been used as promising candidates in the field of optoelectronic devices such as photodiode arrays and photovoltaics due to the ability of band gap tuning with varying size of the subcomponent. They also find applications in thermoelectric cooling devices.[13] Since Bi_2S_3 crystallizes to form layered networks, the possibility for it to form cylindrical shapes and its intrinsic anisotropic quantum transport deserve our special research efforts.[13]

Homemade Bi_2S_3 particles (ca. 50 nm) were used as starting materials. The preparation of Bi_2S_3 nanotubes was carried out in a ceramic tube (i.d. = 4 cm) which was placed in a horizontal tube furnace. The as-prepared Bi_2S_3 powder and pure sulfur powder (in molar ratio 1:1) were loaded in a ceramic boat and put in the middle (~640 °C) and upstream side (~300 °C) of the ceramic tube, respectively; a polished silicon wafer was placed at the downstream side in the ceramic tube as the deposition substrate. The tube furnace was purged with high-purity argon for 3 h prior to heating to remove any oxygen in the furnace. The furnace was heated to 640 °C in 3 min and kept at this temperature for 2 h with Ar both as protecting medium and as carrying gas. During the heating process, the Ar flow rate was kept at 60 sccm (standard cubic centimeter per minute). Ar was run for 2 h after the heating process to avoid oxidation of the prepared sulfide products before completely cooling of the furnace. Yellow-brown fluffy products were observed on the silicon wafer and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

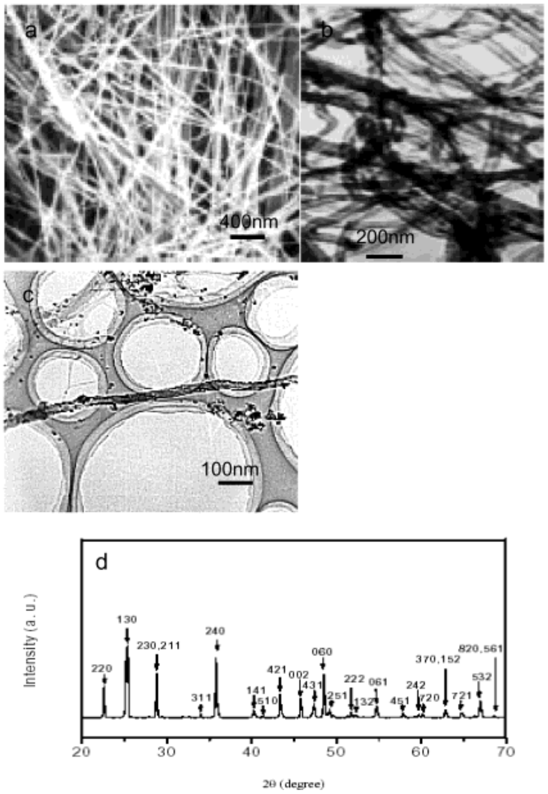

Figure 1. (a) SEM image of Bi_2S_3 nanotubes. (b) TEM images of Bi_2S_3 nanotubes. (c) TEM image of a Bi_2S_3 nanotube with outer diameter of 35 nm and wall thickness of 8 nm. (d) XRD pattern of the product.

The morphologies of the products are demonstrated in the SEM and TEM images (Figure 1a,b). The as-synthesized Bi_2S_3 nanotubes have diameters in the range 20−70 nm and lengths up to tens of micrometers. In Figure 1c a Bi_2S_3 nanotube 35 nm in outer diameter and 8 nm in wall thickness is displayed. We find that slow evaporation and vapor transport favor tubule formation, whereas rapid evaporation and vapor transport generally lead to multiple nucleation and whisker growth. Evaporation at a moderately lower temperature and for a relatively longer time also facilitates tubular structure formation. Platelets and particles have also been observed as dominant morphologies for the as-prepared materials on some particular regions on the silicon substrate, and their growth mechanism will be presented in another report . In the specific growth region where tubules are the dominant morphology, at least ca. 70% of the products are tubules. To further examine the composition and phase purity of the products, XRD was carried out (Figure 1d). All the diffraction peaks can be readily indexed to the orthorhombic phase

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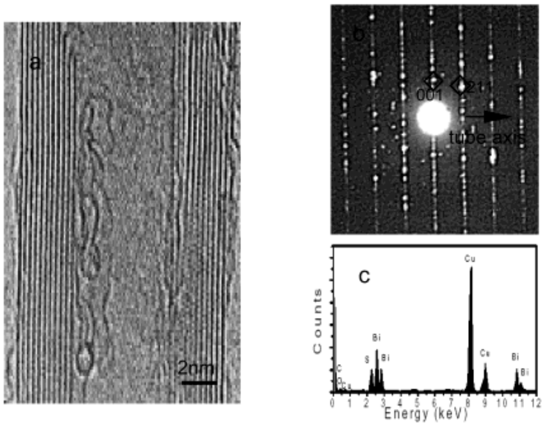

Figure 2. (a) HREM image of a nanotube with the multiwalled structure. (b) SAED pattern of the nanotube taken along [1$\bar{2}$0] zone axis. (c) Corresponding EDX spectrum taken on a single nanotube reveals the presence of Bi and S.

of Bi_2S_3 compatible with the standard values (JCPDS 17-0320). A high-resolution electron microscopy (HREM) image of a Bi_2S_3 nanotube (Figure 2a) shows clearly the multiwalled structure. The interlayer spacing is ca. 0.323 nm (approximately the separation between (001) planes) and agrees well with that calculated from SAED pattern (0.334 nm).[14] We expected that the Bi_2S_3 nanotubes would have high defect density due to the high stress and strain withstood by the tubules taking the strong interlayer interaction into consideration. However, to our surprise, the as-synthesized Bi_2S_3 nanotubules are not as defective as previously thought. As revealed by the HREM fringes, the walls of the nanotube are composed of regularly ordered molecular layers and include a low density of defects, such as stacking faults and missing layers. The composition of the nanotubes as extracted from the energy dispersive spectroscopy (EDX) spectrum (Figure 2c) give a Bi:S atomic ratio of 1:1.35. The deficiency of S with respect to stoichiometry in the nanotubes can be attributed to the vapor pressure of S higher than that of Bi. Little evidence of O was detected in this spectrum.

The chemical reactions we employed in the synthesis of the Bi_2S_3 nanotubes could be described as follows.

At the hot zone of the ceramic tube, Bi_2S_3 nanopowder reacts with S vapor to create BiS_2 vapor according to[15]

$$Bi_2S_3\,(s) + S\,(v) \rightarrow 2BiS_2\,(v) \tag{1}$$

When the BiS_2 gas is transported to the cold zone in the ceramic tube, BiS_2 decomposes to form Bi_2S_3 and S as

$$BiS_2\,(v) \rightarrow Bi_2S_3\,(s) + S\,(v) \tag{2}$$

Subsequently, Bi_2S_3 nucleates and grows on the substrate, and S vapor is further transported away. Although the exact growth processes of the tubular products at the atomic scale have not been completely resolved at this stage, an analogy could be drawn between the growth processes of other tubular materials (see, e.g., 1−10) and the present growth of Bi_2S_3 nanotubes. On account of formation mechanisms for carbon, BN, MoS_2, and WS_2 nanotubes, curving followed by seaming of molecular layers was proposed to be responsible for the tube-formation process. Remskar and coworkers did obtain direct evidence for derivation of tubules from bending of platelets.[16] Li[10,17] also suggested a rolling of layered structures to achieve nanotubes and nanowires and provided strong evidence for their model. In addition, Mallouk[18] and Domen[19] also provided clear evidence of chemical transformation of lamellar oxides into tubular structures, and interpreted the layering of structures as a rolling process. Recently, we have successfully synthesized Sb_2O_3 tubules and provided definite clues to support the above rolling model.[20] We postulate that the formation mechanism of Bi_2S_3 nanotubes might also involve rolling from its quasi-layered structure.

In summary, we have described a rational synthetic approach to obtain Bi_2S_3 nanotubes without the introduction of reducing gases of H_2 or H_2S, which is advantageous over most previously reported approaches in synthesis of other sulfide nanotubes where these dangerous gases were generally involved. Therefore, this work presents an extension of the nanotubular structures to a new compound. Bi_2S_3 crystallizes in an orthorhombic space group (P_{bnm}), which is common also to Sb_2S_3 and Sb_2Se_3. These materials are not characterized by a stacking of infinite 2-D planes of the kind found for example in MoS_2, WS_2, graphite, and so forth. This synthetic strategy might be extendible to these materials which are potentially important for thermoelectric devices.

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(14) The small contraction of the *c*-axis for the tubule against the bulk is different from how WS_2 and MoS_2 nanotubes behave, where expansion of several percent of the *c*-axis has been observed and explained as stress release. However, *c*-axis contraction has also been observed for the $Cu_{5.5}FeS_{6.5}$ nanotubes (*New J. Chem.* **2001**, *25*, 1359−1361) by Qian et al., although it has not been accounted for. We surmise that the different interaction between adjacent layers for Bi_2S_3 compared with WS_2 and MoS_2 may contribute to the abnormality.

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