Bismuth Nanotubes: A Rational Low-Temperature Synthetic Route

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The discovery of carbon nanotubes has initiated an exciting, intellectually challenging, and rapidly expanding research field for one-dimensional (1D) nanostructures.[1] Over the past several years, considerable efforts have been placed on the synthesis of nanotubes or nanowires. A particularly significant breakthrough in MX_2 (M: Mo or W, X: S or Se) nanotube synthesis was made by Tenne and co-workers.[2] Various approaches to other nanotubes, such as BN,[3] $B_xC_yN_z$,[4] $NiCl_2$,[5] vanadium oxide,[6] and InS[7] have also been reported, which implies that substances possessing layered structures might be able to form nanotubes under favorable conditions. Here we report the synthesis of bismuth metal nanotubes with diameters ∼5 nm and lengths ranging between 0.5−5 μm. A low-temperature hydrothermal reduction method with bismuth nitrate [$Bi(NO_3)_3$] and aqueous hydrazine solution ($N_2H_4{\cdot}H_2O$) at 120 °C has been successfully used to synthesize large quantities of nested bismuth nanotubes. The resulting Bi nanotubes were characterized by X-ray powder diffraction, transmission electron microscopy and composition analysis.

Metallic bismuth (α-Bi) (Figure 1a) has a pseudolayered structure very similar to that of rhombohedral graphite and black phosphorus.[8] In each layer, one Bi atom is connected with three other Bi atoms according to the 8-*N* rule and thus forms a trigonal pyramid. These pyramids further form a folded bismuth layer by vertex-sharing. The distances between one Bi atom and its three neighbors in the same layer and the neighboring layer are 3.072 and 3.529 Å, respectively, and the Bi−Bi−Bi bonding angle is 95.5°. The analogy between the layered structures of α-Bi (Figure 1a) and graphite/phosphorus suggests that the Bi nanotubes (Figure 1b) may also exist. In fact, theoretical simulation indeed

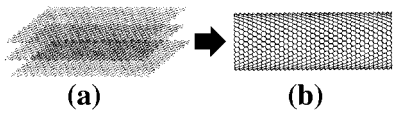

Figure 1. Three-dimensional models for bismuth nanotubes (b) formed from the layered structures α-bismuth (a).

indicates that phosphorus nanotubes are stable.[9] More recently, both theoretical and experimental studies have established the existence of multishell gold nanotubes.[10] Here, we report the synthesis of the Bi-nanotubes (NT) with uniform diameters of 5 nm and lengths ranging between 0.5−5 μm.

Bismuth's small effective mass (∼$0.001m_0$) and large mean free path (∼0.4 mm at 4 K) make Bi nanotube an interesting system for studying quantum confinement effects.[11] In addition, nanoscaled bismuth materials have recently been suggested to have enhanced thermoelectric properties at room temperature.[12] However, owing to the relatively low melting point of Bi (271.3 °C), the synthesis of Bi nanotubes is much more difficult than that for carbon or MX_2 analogies. Most of the existing high-temperature approaches, such as arc-discharge evaporation, laser ablation, or chemical vapor deposition are inappropriate for synthesis of Bi nanotubes. Hence, the investigations of rational synthesis, physical properties, and applications of the Bi nanotubes or nanowires remain as challenges to materials scientists.

We have developed a low-temperature controlled hydrothermal reduction method[13] to prepare Bi nanotubes. The chemical reaction we employed for synthesis of the Bi nanotubes can be formulated as

$$4Bi(NO_3)_3 + 3N_2H_4 + 12NH_3{\cdot}H_2O \rightleftharpoons 4Bi + 3N_2 + 12H_2O + 12NH_4NO_3 \quad (1)$$

The above reaction comprises two half reactions

$$N_2 + 4H_2O + 4e \rightarrow N_2H_4 + 4OH^- \quad (E^0 = -1.16V) \quad (2)$$

$$Bi(OH)_3 + 3e \rightarrow Bi + 3OH^- \quad (E^0 = -0.46V) \quad (3)$$

On the basis of the values of $E°$, the standard Gibbs free energy change $\Delta G°$ of reaction 1 could be estimated to be about −810 kJ mol^{-1}, which implies a very strong tendency for reaction 1 to progress toward the right-hand side.

Analytically pure bismuth nitrate [$Bi(NO_3)_3$, 0.01mol] and an excess amount of aqueous hydrazine solution ($N_2H_4{\cdot}H_2O$, 0.02mol) were put in distilled water at room temperature to form a mixture with insoluble precipitate. The pH value of the resulting solution was adjusted to the range of 12−12.5 by addition of aqueous $NH_3{\cdot}H_2O$. The mixture was stirred strongly for about 0.5 h and then transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120 °C for 12 h. After the reaction was completed, the resulting black solid product was filtered, washed with diluted hydrochloric acid (1 M) for several times to remove bismuth oxide or hydroxide possibly remnant in the final products and then saturated $NaBH_4$ solution to avoid

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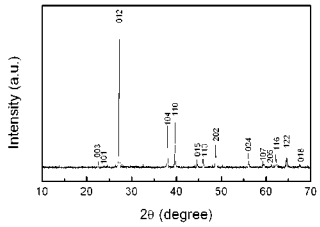

Figure 2. A typical XRD pattern of the obtained bismuth product.

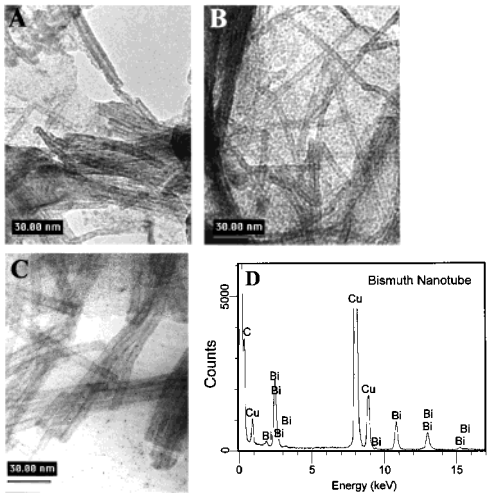

Figure 3. Representative TEM images (A−C) and EDX spectrum (D) of the bismuth nanotubes.

oxidation of the product, and finally dried in a vacuum at 60 °C for 4 h. The sample was then sealed in a glass tube under dry nitrogen to prevent it from being oxidized. In a typical synthesis, several grams of the product could be obtained.

The phase purity of the product was examined by X-ray diffraction (XRD) using a Bruker D8-advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). All of the reflections of the XRD pattern in Figure 2 can be readily indexed to a pure rhombohedral phase [space group: $R\bar{3}m(166)$] of Bi with lattice constants $a = 4.55$ Å, $c = 11.85$ Å, compatible with the literature values of $a = 4.546$ Å and $c = 11.860$ Å (JCPDS 05-0519). This XRD pattern indicates that the reduction of Bi^{3+} is complete under current synthetic conditions; consequently, pure metal Bi products were obtained.

The micro-/nanostructure of the Bi products was further examined with transmission electron microscopy (TEM). A significant portion (about 30%) of the sample dispersed on the TEM grids shows tubular structures, although other nano-sheets were also observed. The existence of the sheetlike structures, as well as the tubular structures, might be related to the layered feature in the crystal structure of rhombohedral Bi. Figure 3 shows several TEM images of a typical bismuth sample exhibiting tubular structures with uniform diameters of ∼5 nm and lengths of 0.5−5 μm. Energy-dispersive X-ray (EDX) analysis of these individual nanotubes, nanosheets, or the bundle structure showed that they are all pure bismuth (Figure 3d). Figure 4a shows a high-resolution image of an individual multiwalled Bi nanotube. The interlayer spacing is determined to be ∼6 Å, about half of the lattice constant along the *c*-axis of the Bi structure. Electron energy loss spectra (EELS) recorded on individual nanotubes

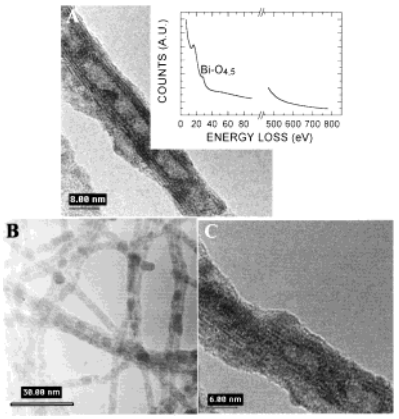

Figure 4. HRTEM image of an individual Bi nanotube (a). Inset in (a) shows an EELS spectra recorded on individual nanotubes. (b) Typical TEM images of the Bi nanotubes after electron beam irradiation. Note that all Bi nanotubes have transformed into polycrystalline nanowires. (c) HRTEM image of the same Bi nanotube as in (a) after beam irradiation.

show a peak corresponding to $Bi-O_{4,5}$, and no signals from oxygen at about 538 eV (O−K) could be observed (Figure 4a inset).

These Bi nanotubes are highly sensitive to beam irradiation during the TEM examinations, which is expected due to their low melting points (271.3 °C). It is observed that the nanotubes melt upon beam irradiation (Figure 4b). Figure 4c shows a high-resolution TEM image of the same individual Bi nanotube in Figure 4a after the beam exposure. It is observed that after several seconds of intensive electron beam irradiation, the Bi nanotube transforms into a polycrystalline nanowire. It is also observed that the Bi nanowires transform into small liquid droplets with further intense beam irradiation. The beam sensitivity of the Bi materials was previously reported for Bi nanocrystallites and nanowires.[12b,14] This beam sensitivity makes the analysis of electron diffraction difficult. Nonetheless, our XRD, TEM, and composition analysis have unambiguously demonstrated that the tubular structures in our sample are metal Bi nanotubes.

The observation of the tubular and sheetlike structures of metal Bi shows that the tendency of metallic Bi to form tubular structures may be associated with its layered structure. The formation mechanism of the Bi nanotubes warrants further investigation. We believe that the rational low-temperature synthetic route is universal and can be adapted for the preparation novel nanotubes of numerous materials with layered structures in solution. For example, it might be possible to prepare As, Sb, SnS, SnSe, and GaSe nanotubes via methods similar to those described in this work.

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