A Rational Self-Sacrificing Template Route to β-Bi_2O_3 Nanotube Arrays

Baojun Yang,[a,b] Maosong Mo,[a] Hanmei Hu,[a] Cun Li,[a] Xiaogang Yang,[a] Qiaowei Li,[a] and Yitai Qian*[a]

Keywords: Bismuth oxide / Nanostructures / Nanotubes / Synthesis design

Arrayed β-Bi_2O_3 nanotubes (NTs) were synthesized for the first time through a rational "self-sacrificing template" route, simply by oxidizing the precursor metallic bismuth NT arrays in air at 200–220 °C for 14–18 h. XRD, TEM, and HRTEM characterizations show that the prepared β-Bi_2O_3 samples are all phase pure and the β-Bi_2O_3 NTs have uniform diameters of approximately 3–6 nm and lengths up to several micrometers. The optical absorption and photoluminescence (PL) characteristics of the prepared samples were investigated.

Introduction

The discovery of carbon nanotubes (NTs) in 1991 has lead to a fruitful and growing interest in NTs for both basic and application-oriented industrial research.[1] Over the past years, various template-directing synthetic methods have been used to generate tubular forms of different oxides. For example, template-assisted soft chemistry routes have lead to the synthesis of VO_x,[2] TiO_2,[3] and SiO_2[4] NTs; pre-structured materials (including carbon NTs and polymer fibers) have been employed as structure-directing templates for tubular forms of SiO_2, Al_2O_3, V_2O_5,[5] TiO_2,[6] MoO_3, RuO_2,[7] ZrO_2,[8] and SnO_2;[9] porous aluminum oxide and polymer membrane templates for NTs or ordering arrays of oxide NTs[10] have also been used.

Bismuth trioxide (Bi_2O_3) and various bismuth-containing materials are very important in modern solid-state technology, owing to their peculiar physical properties (electrical, optical, and excellent ionic conductivity, etc.). They are widely used in gas sensors,[11] optoelectronic devices, optical coatings, transparent ceramic glass manufacturing,[12] cathode ray tubes,[13] as catalysts for the soft oxidation of hydrocarbons,[14] and so on. This special interest explains the great effort devoted to the investigation of Bi_2O_3 polymorphs over the last years.

Bi_2O_3 shows four main structures that are denoted by α-, β-, γ-, and δ-Bi_2O_3.[15] Among them, the tetragonal β-Bi_2O_3, which has a distorted defect-fluorite structure, is a metastable phase at ambient conditions, and usually transforms into the stable monoclinic α-Bi_2O_3 at about 870 K. The formation of the tetragonal β-Bi_2O_3 is observed at about 920 K on cooling the high-temperature cubic-phase δ-Bi_2O_3, although several synthetic procedures for obtaining these materials at relatively low temperatures have been reported.[14−16]

Recently, we have developed an aqueous chemical route to synthesize bamboo raft-like bismuth NT arrays at room temperature.[17] Herein, we also report on a novel "self-sacrificing template" approach for the synthesis of crystalline tetragonal β-Bi_2O_3 NT arrays, by oxidizing the precursor bismuth NT arrays directly in air at 200−220 °C. To the best of our knowledge, this is the first time that a method for the synthesis of β-Bi_2O_3 NTs has been reported.

Results and Discussion

Figure 1 shows a typical XRD pattern of a prepared sample. All the intensive and sharp reflection peaks can be indexed to a pure tetragonal phase (space group: $C\bar{4}b2$)

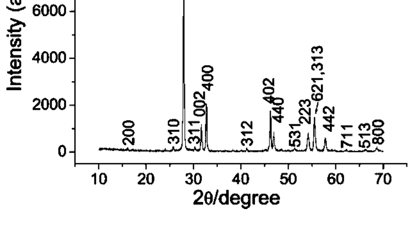

Figure 1. Typical XRD pattern of the prepared β-Bi_2O_3 samples

---

[a] Structure Research Laboratory and Department of Chemistry,
University of Science and Technology of China,
Hefei, Anhui 230026, P. R. China
Fax: (internat.) +86-551-3607402
E-mail: ytqian@ustc.edu.cn
[b] The School of Chemical Engineering, Hefei University of Technology,
Hefei, Anhui 230009, P. R. China
Fax: (internat.) +86-551-2902956
E-mail: lhmybigy@mail.ustc.edu.cn

DOI: 10.1002/ejic.200300966

of crystalline β-Bi_2O_3. The calculated cell constants are a = 10.94 Å and c = 5.64 Å [the root mean square value (RMS) is 1.5×10^{-4}] and are in good agreement with the literature values of a = 10.93 Å and c = 5.62 Å (JC,PDS 74−1374). This XRD pattern indicates that the oxidization of metallic bismuth is complete and phase-pure crystalline β-Bi_2O_3 products can be obtained under the present synthetic conditions.

The morphologies and the size of the prepared samples were characterized by TEM. As shown in Figure 2 (see a, b, and c), a significant amount of the sample dispersed on the TEM copper grids exhibited nanotubular morphology, although other block-like morphologies also appeared. All of the β-Bi_2O_3 NTs are straight with uniform diameters of approximately 3−6 nm and lengths up to several micrometers. Most of them are also surprisingly aligned together, side by side, along the axial direction, in a similar way to that of the precursor metallic Bi NT arrays, to form bamboo raft-like NT arrays. This phenomenon suggests that the precursor bismuth NT arrays may serve as self-sacrificing templates and maintain their original tubular morphology in the oxidizing process. The SAED pattern, of a "bamboo raft", indicates the crystalline nature of the NT array (see a, the inset of Figure 2). The concentric diffraction rings could be indexed outwards as [110], [311], and [400] diffractions of tetragonal β-Bi_2O_3. Figure 2 (d) shows a representative HRTEM image of a section of a "bamboo raft". The lattice fringes are perpendicular to the axial direction of the NTs; the fringe spacing is about 7.8 Å, close to the interplanar spacing of the [110] lattice planes of the tetragonal β-Bi_2O_3. This means that the axial direction of the NTs is along the normal direction of the [110] lattice planes of the tetragonal β-Bi_2O_3.

Figure 2 (see e) shows the typical optical absorption spectrum of a prepared β-Bi_2O_3 sample, along with the PL of the same sample (λ_{exe} = 291 nm). The band edge is found to be around 3.90 eV (318 nm) and it shifts to much higher energy than that of the bulk bandgap at 2.58 eV.[15] The material also exhibits photoluminescence. A Stokes shift is observed; such effects have been attributed to either band-edge emission or shallow-trap emission in recent publications.[18]

Here, the use of precursor metallic bismuth NT arrays is crucial to the formation of β-Bi_2O_3 NT arrays. The reaction between the precursor metallic bismuth and oxygen in air can be simply formulated as:Bi (NT arrays) + O_2 (in air) → β-Bi_2O_3 (NT arrays)

In this reaction, the precursor metallic Bi NT arrays may serve as "self-sacrificing templates" which maintain their original tubular morphology in the oxidizing process, thus resulting in the formation of the β-Bi_2O_3 NT arrays.

The materials and experimental conditions have significant effects on the formation of the β-Bi_2O_3 NT arrays. Under similar experimental conditions, almost no Bi_2O_3 is formed after oxidization (24 h) by using commercial Bi powder (about 200 mesh) instead of the precursor metallic Bi NT arrays. On the other hand, the relatively low melting point of metallic Bi (273.1 °C) greatly limited the selection of reaction temperature for our experiments. When the reaction temperature is below 160 °C, a mixture of β-Bi_2O_3 and unreacted metallic Bi was detected by XRD . When the reaction temperature was above 240 °C, a great deal of block-like and a small amount of tube-like β-Bi_2O_3 was observed by TEM. This phenomenon can be simply explained as follows: the precursor metallic Bi NTs may have a lower melting point than the bulk Bi due to the well-known small-size effects. When the experimental temperature (above 240 °C) is close to the melting point of the Bi precursor, local melting and aggregation of the precursor may occur before oxidization, which may further result in the formation of block-like β-Bi_2O_3. Based on the results mentioned above, we believe that the ratio of the NTs in the final β-Bi_2O_3 products can be greatly affected by varying the temperature of thermal oxidization of the Bi precursor. Thus, the optimal experimental temperature we selected is 200−220 °C. Under these conditions, the precursor metallic Bi NT arrays

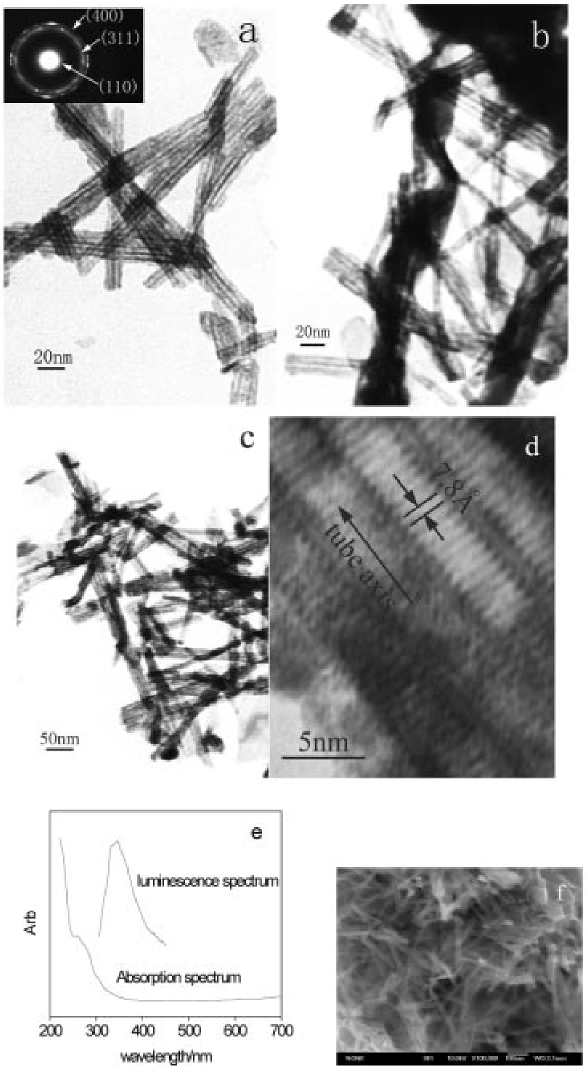

Figure 2. Typical TEM images (a, b, c), HRTEM image (d), UV/Vis absorption, PL spectra (e) of theprepared β-Bi_2O_3 samples and FESEM image (f) of the Bi precursor

may keep their origin tubular morphology during oxidization, and once the β-Bi_2O_3 NTs are formed, the tubular morphology of β-Bi_2O_3 could be kept due to its thermal stability, which is higher than that of the Bi NTs.

Conclusion

In summary, we have presented a simple self-sacrificing template route for the synthesis of β-Bi_2O_3 NT arrays, by oxidizing the precursor Bi NT arrays. The prepared β-Bi_2O_3 samples are all phase-pure and stable at room temperature. This method requires no complex apparatus or technique and the conditions are much more mild, which makes it possible to produce β-Bi_2O_3 NTs on a large scale. The present study supplies a novel route to synthesize phase-pure β-Bi_2O_3, enlarges the family of oxide NTs, and may provide a facile method for the synthesis of other one-dimensional oxide nanomaterials.

Experimental Section

Reactions and Conditions: All reagents used in our experiments were analytically pure, purchased from Shanghai Chemicals Co. (China), and used without further purification. The precursor metallic bismuth NT arrays were prepared following a prodecure found in the literature,[17] as shown in Figure 2 (see f). A high proportion of the precursor sample exhibits 1D morphology with lengths from several hundred nanometers to several micrometers. TEM observations show that the 1D morphology is in fact present as nanotubular arrays (special TEM images and descriptions have been shown in our previously published paper).[17] Then, an appropriate amount of the prepared precursor bismuth powder was transferred into a ceramic boat. The boat was placed into the center of a temperature-controlled electrothermal oven (DHG-9076A) in which the temperature was previously kept at 200−220 °C (dry air), and maintained for 14−18 h. After the reaction was complete, the boat was taken out and the yellow powder obtained was immediately sealed in a small glass bottle filled with anhydrous alcohol to prevent direct contact with carbon dioxide in air (see Figure 3). The samples were characterized by X-ray powder diffraction (XRD), which was recorded on a Japan Rigaku Dmax-γA X-ray powder diffractometer with graphite-monochromatized Cu-K_α radiation (λ = 1.54178 Å). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL-2010 transmission electron microscope, employing an accelerating voltage of 200 kV. Field-emission scanning electron microscope (FESEM) images were taken on a field-emission microscope (JEOL JSM-6700F, 15 kV). UV/Vis absorption spectra were recorded on a Shimadzu UV-2401PC UV/Vis spectrophotometer. Photoluminescence spectroscopy was carried out on a Shimadzu RF-5301PC spectrofluorophotometer with an Xe lamp at room temperature.

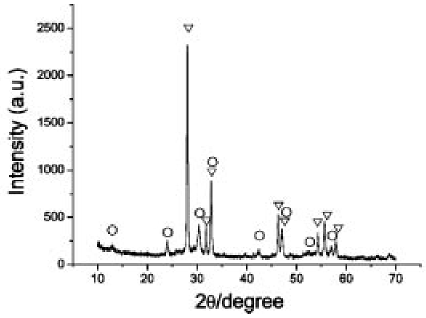

Figure 3. Typical XRD pattern of a prepared β-Bi_2O_3 sample exposed directly to air for about two hours (the triangle represent β-Bi_2O_3, the circle represent $Bi_2O_2CO_3$)

Acknowledgments

This work was financially supported from the National Natural Science Funds and the 973 Projects of China.

---

[1] [1a] S. Iijima, *Nature* **1991**, *354*, 56−58. [1b] G. R. Patzke, F. Krumeich, R. Nesper, *Angew. Chem. Int. Ed.* **2002**, *41*, 2446−2461.

[2] [2a] M. E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, H.-U. Nissen, *Angew. Chem.* **1998**, *37*, 1263−1265. [2b] F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, R. Nesper, *J. Am. Chem. Soc.* **1999**, *121*, 8324−8331.

[3] S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai, *Chem. Mater.* **2000**, *12*, 1523−1525.

[4] [4a] H. P. Lin, C. Y. Mou, S. B. Liu, *Adv. Mater.* **2000**, *12*, 103−106. [4b] J. H. Jung, Y. Ono, S. Shinkai, *Langmuir* **2000**, *16*, 1643−1649.

[5] B. C. Satishkumar, A. Govindaraj, E. M. Vogl, L. Baumallick, C. N. R. Rao, *J. Mater. Res.* **1997**, *12*, 604−606.

[6] R. A. Caruso, J. H. Schattka, A. Greiner, *Adv. Mater.* **2001**, *13*, 1577.

[7] B. C. Satishkumar, A. Govindaraj, M. Nath, C. N. R. Rao, *J. Mater. Chem.* **2000**, *10*, 2115−2119.

[8] C. N. R. Rao, B. C. Satishkumar, A. Govindaraj, *Chem. Commun.* **1997**, 1581−1582.

[9] W. Q. Han, A. Zettl, *J. Am. Chem. Soc.* **2003**, *125*, 2062−2063.

[10] [10a] C. R. Martin, *Science* **1994**, *266*, 1961−1966. [10b] J. C. Hulteen, C. R. Martin, *J. Mater. Chem.* **1997**, *7*, 1075−1087. [10c] B. Cheng, E. T. Samulki, *J. Mater. Chem.* **2001**, *11*, 2901−2902.

[11] [11a] Z. N. Adamian, H. V. Abovian, V. M. Aroutiounian, *Sens. and Actuators B* **1996**, 35−36, 241−243. [11b] E. Kanazawa, G. Sakai, K. Shimanoe, Y. Kanmura, Y. Teraoka, N. Miura, N. Yamazoe, *Sens. and Actuators B* **2001**, *77*, 72−77.

[12] L. Leontie, M. Caraman, M. Delibas, G. I. Rusu, *Mater. Res. Bull.* **2001**, *36*, 1629−1637.

[13] M. Yamamoto, M. Koitabashi, H. Kimura, *Jpn. J. Appl. Phys.* **2001**, *40*, 4691−4695.

[14] A. N. Romanov, D. P. Shashkin, E. V. Khaula, *Russ. J. Inorg. Chem.* **2000**, *45*, 500−503.

[15] [15a] P. Shuk, H.-D. Wiemhöfer, U. Guth, W. Göpel, M. Greenblatt, *Solid State Ionics* **1996**, *89*, 179−196. [15b] S. K. Blower, C. Greaves, *Acta Crystallogr., Sect. C* **1988**, *44*, 587−589.

[16] [16a] X. L. Chen, W. Eysel, *J. Solid State Chem.* **1996**, *127*, 128−130. [16b] O. Monnereau, L. Tortet, P. Llewellyn, F. Rouquerol, G. Vacquier, *Solid State Ionics* **2003**, *157*, 163−169.

[17] B. J. Yang, C. Li, H. M. Hu, X. G. Yang, Q. W. Li, Y. T. Qian, *Eur. J. Inorg. Chem.* **2003**, 3699−3702.

[18] W. T. Dong, C. S. Zhu, *J. Phys. Chem. Solids* **2003**, *64*, 265−271.

Received December 24, 2003