

A Room-Temperature Route to Bismuth Nanotube Arrays

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

Keywords: Bismuth / Nanostructures / Nanotubes / Synthesis design

A room-temperature aqueous-chemical route has been developed to synthesize a high proportion (above 80%) of bamboo-raft-like bismuth nanotube arrays using bismuth chloride and metallic zinc powder as reagents. The prepared Bi nanotubes have uniform diameters of approximately 3–5 nm and lengths from several hundred nanometers to several mi-

crometers. HRTEM observations show that the axial direction of the prepared nanotubes is along the normal direction of the (012) lattice planes of the rhombohedral bismuth. The possible formation mechanism is discussed.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

The discovery of carbon nanotubes^[1] has initiated enormous interest in one-dimensional (1D) nanostructured materials, such as nanorods, nanowires, nanobelts and nanotubes, due to both their interesting physical properties and the wide range of their potential applications.^[2] Over the past several years, various nanotubular materials, including oxides,^[3] sulfides,^[4] BN,^[5] NiCl₂,^[6] Te,^[7] Au,^[8] Ni,^[9] Pt,^[10] and Bi^[11] have been successfully synthesized.

Bismuth (Bi) is a semimetal with a quasi-layered structure formally like that of rhombohedral graphite and black phosphorus.^[12] The distances between one Bi atom and its three close neighbors in the same layer and the neighboring layers are 3.072 and 3.529 Å, respectively. Bismuth has unusual electronic properties that result from its highly anisotropic Fermi surface, low carrier concentration, small effective mass and long mean free path of the carriers.^[13] These properties make Bi a good candidate to study quantum-confinement effects in 1D systems and very promising materials for thermoelectric applications. However, due to the relatively low melting point of Bi (273.1 °C), most of the existing high-temperature approaches, such as laser ablation, plasma-arc, or CVD (chemical vapor deposition) are inappropriate to synthesize 1D Bi nanomaterials. Hence, a low-temperature chemical approach may provide a more

rational technique to prepare 1D Bi nanomaterials. Recently, Bi nanowires^[14] (with a proportion of about 20%) have been solvothermally synthesized at 160 °C, using bismuth nitrate [Bi(NO₃)₃·5H₂O] and ethylenediamine as starting materials. Bi nanotubes^[11a] (with a proportion of about 30%) have been hydrothermally synthesized at 120 °C, using bismuth nitrate and aqueous hydrazine [N₂H₄·H₂O] as starting materials. Bi nanotube arrays^[11b] have been solvothermally synthesized at 200 °C, using bismuth oxide (Bi₂O₃) and ethylene glycol as starting materials.

Herein, we report a novel room-temperature aqueous-chemical route that has been developed in our synthesis of a high proportion (above 80%) of bamboo-raft-like bismuth nanotube arrays through the reduction of bismuth chloride by metallic zinc powder. The prepared bismuth nanotubes are arrayed side by side along the axial direction with uniform diameters of approximately 3–5 nm and lengths from several hundred nanometers to several micrometers. This method requires no complex apparatus or technique, and requires no catalyst or template.

Results and Discussion

Figure 1 shows a typical XRD pattern of a prepared sample. All of the sharp peaks can be indexed to a pure rhombohedral phase [space group: $R\bar{3}m$ (166)] of crystalline Bi. The calculated cell constants are $a = 4.544$ Å and $c = 11.85$ Å, which are in good agreement with the literature values of $a = 4.547$ Å and $c = 11.86$ Å (JC,PDS 44-1246). This XRD pattern indicates that the reduction of Bi³⁺ to elemental Bi is complete and pure phase crystalline Bi products can be obtained under current synthetic conditions.

The morphologies and the size of the prepared Bi samples were characterized by TEM. As shown in Figure 2A and 2B, a high proportion (above 80%) of the

^[a] Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.
Fax: (internat.) + 86-551/360-7402
E-mail: ytqian@ustc.edu.cn

^[b] The School of Chemical Engineering, Hefei University of Technology, Hefei, Anhui 230009, P. R. China.
Fax: (internat.) + 86-551/290-2956
E-mail: lhmybigy@mail.ustc.edu.cn

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

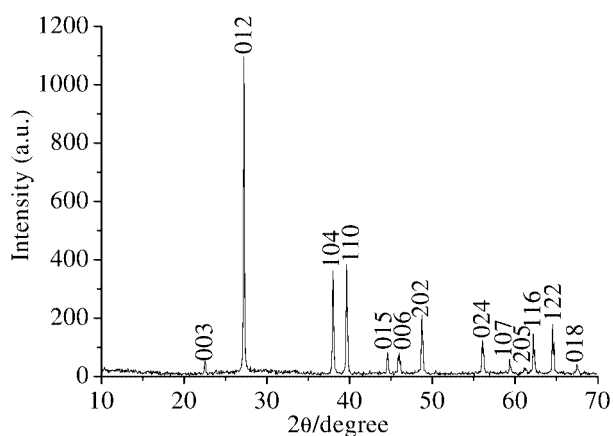


Figure 1. Typical XRD pattern of the prepared bismuth samples

sample dispersed on the TEM copper grids exhibits a nanotubular morphology. Small amounts of flake-like Bi were also observed. Interestingly, except for a small amount of individual Bi nanotubes (marked by the arrow in Figure 2A), almost all these bismuth nanotubes are arrayed like bamboo rafts. Each “bamboo raft” is comprised of several parallel straight bismuth nanotubes lying side by side along the axial direction. It can be seen that these Bi nanotubes have uniform diameters of approximately 3–5 nm and lengths from several hundred nanometers to several micrometers. Energy-dispersive X-ray spectrum (EDS) analysis (Figure 2D) shows that the prepared sample is pure bismuth. This result is consistent with the XRD pattern presented above, in which no impurity phase is observed.

The prepared samples are highly sensitive to electron beam irradiation during the TEM examination due to the relatively low melting point of Bi (273.1 °C), which makes it much more difficult to get clear HRTEM images. The TEM image of a prepared sample after several seconds of

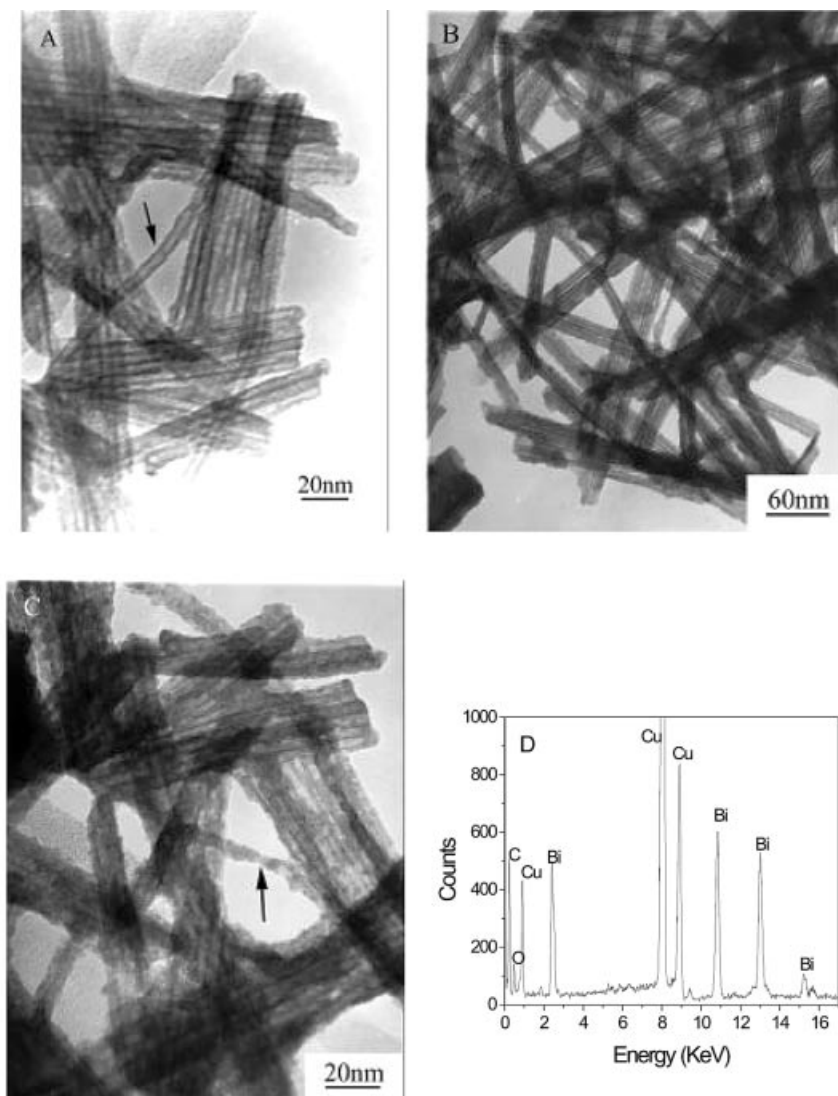


Figure 2. Typical TEM images (A-C) and EDS spectrum (D) of the prepared bismuth nanotubes

intensive electron beam irradiation is shown in Figure 2C. It can be seen that the morphologies of the bismuth nanotubes have become blurry, some individual Bi nanotubes have melted (marked by the arrow in Figure 2C) and transformed into polycrystalline nanowires. A similar phenomenon was also reported previously.^[11a,15] However, some distinguishable HRTEM images have been obtained in our experiments. A representative HRTEM image of one section of a “bamboo raft” is shown in Figure 3. It can be seen that there are four Bi nanotubes which are lying side by side in the image. The discriminable lattice fringes, which are perpendicular to the axial direction of the nanotubes, illustrate that the prepared Bi nanotubes are single crystals in the area shown. The fringe spacing is about 3.2 Å, which is close to the interplanar spacing of the (012) lattice planes of the rhombohedral bismuth. This means that the axial direction of the prepared nanotubes is along the normal direction of the (012) lattice planes of the rhombohedral bismuth.

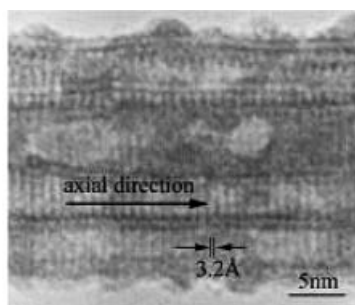
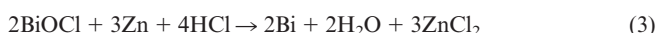


Figure 3. HRTEM image of a “bamboo raft” comprised of four parallel nanotubes

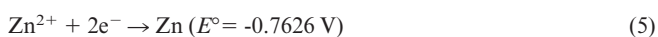
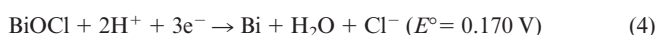
The overall reaction in our system can be simply formulated as shown in Equation (1):



The reaction above includes two following steps formulated as Equations (2) and (3):



First, BiCl_3 hydrolyzes in water to form BiOCl , a white precipitate [Equation (2)], which is then reduced by metallic zinc powder to form metallic Bi. The reduction reaction [Equation (3)] is comprised of two half reactions [Equations (4) and (5)]:



According to the standard of the formal potential of half reactions (4) and (5), it can be seen that there is a strong tendency for reduction reaction (3) to the formation of metallic Bi. According to the added quantity of BiCl_3 , the yield of metallic Bi is above 90% by weight.

The specific formation mechanism of the Bi nanotubes is not yet clear and warrants further investigation. Concerning the formation mechanisms for nanotubes, several models have been suggested. For instance, curving followed by seaming of molecular layers (CSML) has been proposed to be responsible for the tube-formation process of materials with layered structure.^[16] Direct growth through concentration depletion at the surfaces of cylindrical seeds has been suggested to explain the formation process of Te nanotubes containing chain-like building blocks,^[7a] and helical nanobelt-twist-join-growth has been suggested for the formation of Te nanotubes.^[7b] Li and co-workers^[11a] have described that the formation of metallic Bi nanotubes may be associated with the quasi-layered structure of metallic Bi. Similarly, the observation of tubular and flake-like structures of Bi strongly induce us to speculate that the formation of Bi nanotubes under our experimental conditions is closer to the CSML model, though further investigation about a reliable model for the structure and growth of nanotubes is necessary. As regards the formation of the “bamboo raft”, we hypothesize that it might be due to the well-known surface effects of nanostructured materials. The small diameters and the high aspect ratios cause the surface of the newly formed bismuth nanotubes to have large numbers of surface atoms, a lack of atomic coordination and high surface energy. These may lead to a strong tendency of the newly formed bismuth nanotubes to get close to each other and then arrange side by side along the 1D direction (the axial direction), thus forming the bamboo-raft-like nanostructure. The observations that almost all of these nanotubes exhibit a bamboo-raft-like nanostructure, and only a small amount of tubes exist as individual nanotubes, may indirectly confirm the hypothesis described above. However, the intermediate process of the formation of the bamboo-raft-like Bi nanostructure is not yet clear.

The proper reducing agent is crucial for the formation of bismuth nanotubes. Further investigation shows that similar bamboo-raft-like bismuth nanotubes can also be obtained in alkaline solution at room temperature, using tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) as reducing agent (see Supporting Information). But we failed to get Bi nanotubes at room temperature by using sodium borohydride or aqueous hydrazine as reducing agent. The specific reasons for these observations are unknown.

Conclusion

In summary, we have described a room-temperature aqueous-chemical route to obtain a high proportion (above 80%) of bamboo-raft-like bismuth nanotubes, which are comprised of several parallel straight bismuth nanotubes lying side by side along the axial direction. HRTEM observations show that the axial direction of the prepared nanotubes is along the normal direction of the (012) lattice planes of the rhombohedral bismuth. The present study

may be advantageous over most of the previously reported approaches in terms of no requirement of complex apparatus or techniques, and the possibility of production on a large scale. In addition, as a tubular sacrificing template, the prepared Bi nanotubes might also be potentially converted into 1D nanostructures of many technologically important materials, such as Bi_2S_3 , Bi_2Se_3 , Bi_2Te_3 , and so forth.

Experimental Section

All reagents used in our experiments were analytical pure grade, purchased from Shanghai Chemicals Co. (China), and were used without further purification. In a typical procedure, 2 mmol of BiCl_3 was added to 50 mL of distilled water whilst stirring with a magnetic stirrer to yield a white precipitate. Then, 4 mmol of metallic zinc powder (about 200 mesh) was added to the above system, and the mixture was continuously stirred at room temperature for 2–4 h. The obtained mixture was added to dilute hydrochloric acid (1 M) and left to react for several minutes to remove the excess metal zinc and by-products. The mixture was then filtered, washed with distilled water several times, and the resulting black powder was finally dried in a vacuum at 60 °C for 4 h.

The samples were characterized by X-ray powder diffraction data (XRD), which were recorded on a Japan Rigaku Dmax- γA X-ray powder diffractometer with graphite monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images, accompanied by Energy-dispersive X-ray spectrum (EDS), were obtained with a JEOL-2010 transmission electron microscope, employing an accelerating voltage of 200 kV.

Acknowledgments

Financial support from the National Natural Science Funds and the 973 Projects of China is gratefully acknowledged. The author would like to thank Prof. Shuyuan Zhang for HRTEM observations and Dr. Maosong Mo for helpful discussions.

- [1] S. Iijima, *Nature* **1991**, 354, 56–58.
- [2] J. T. Hu, T. W. Odom, C. M. Lieber, *Acc. Chem. Res.* **1999**, 32, 435–445.
- [3] [3a] A. Doble, K. Ngala, S. F. Yang, P. Y. Zavalij, M. S. Whittingham, *Chem. Mater.* **2001**, 13, 4382–4386. [3b] B. D. Yao, Y. F. Chan, X. Y. Zhang, W. F. Zhang, Z. Y. Yang, Z. Wang, *Appl. Phys. Lett.* **2003**, 82, 281–283.
- [4] [4a] R. Tenne, L. Margulis, M. Genut, G. Hodes, *Nature* **1992**, 360, 444–446. [4b] M. Hershfinkel, L. A. Gheber, V. Volterra, J. L. Hutchison, L. Margulis, R. Tenne, *J. Am. Chem. Soc.* **1994**, 116, 1914–1917. [4c] Y. Q. Zhu, T. Sekine, K. S. Brigatti, S. Firth, R. Tenne, R. Rosentsveig, H. W. Kroto, D. M. R. Walton, *J. Am. Chem. Soc.* **2003**, 125, 1329–1333. [4d] M. Nath, C. N. R. Rao, *J. Am. Chem. Soc.* **2001**, 123, 4841–4842.
- [5] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zettl, *Science* **1995**, 269, 966–967.
- [6] Y. R. Hachohen, E. Grunbaum, R. Tenne, J. Sloan, J. L. Hutchison, *Nature* **1998**, 395, 336–337.
- [7] [7a] B. Mayers, Y. N. Xia, *Adv. Mater.* **2002**, 14, 279–282. [7b] M. S. Mo, J. H. Zeng, X. M. Liu, W. C. Yu, S. Y. Zhang, Y. T. Qian, *Adv. Mater.* **2002**, 14, 1658–1662.
- [8] C. R. Martin, M. Nishizawa, K. Jirage, M. Kang, *J. Phys. Chem. B* **2001**, 105, 1925–1934.
- [9] [9a] J. C. Bao, C. Y. Tie, Z. Xu, Q. F. Zhou, D. Shen, Q. Ma, *Adv. Mater.* **2001**, 13, 1631–1633. [9b] J. C. Bao, K. Y. Wang, Z. Xu, H. Zhang, Z. H. Lu, *Chem. Commun.* **2003**, 208–209.
- [10] Y. Oshima, H. Koizumi, K. Mouri, H. Hirayama, K. Takayanagi, Y. Kondo, *Phys. Rev. B* **2002**, 65, 121401–14.
- [11] [11a] Y. D. Li, J. W. Wang, Z. X. Deng, Y. Y. Wu, X. M. Sun, D. P. Yu, P. D. Yang, *J. Am. Chem. Soc.* **2001**, 123, 9904–9905. [11b] X. Y. Liu, J. H. Zeng, S. Y. Zhang, R. B. Zheng, X. M. Liu, Y. T. Qian, *Chem. Phys. Lett.* **2003**, 374, 348–352.
- [12] R. W. G. Wyckoff, *Crystal Structures*; 2nd. Ed.; Interscience: New York, **1973**; Vol. 1, p 32.
- [13] [13a] F. Y. Yang, K. Liu, K. M. Hong, D. H. Reich, P. C. Searson, C. L. Chien, *Science* **1999**, 284, 1335–1337. [13b] X. Sun, Z. Zhang, M. S. Dresselhaus, *Appl. Phys. Lett.* **1999**, 74, 4005–4007.
- [14] Y. H. Gao, H. L. Niu, C. Zeng, Q. W. Chen, *Chem. Phys. Lett.* **2003**, 367, 141–144.
- [15] Z. B. Zhang, D. Gekhtman, M. S. Dresselhaus, J. Y. Ying, *Chem. Mater.* **1999**, 11, 1659–1665.
- [16] C. H. Ye, G. W. Meng, Z. Jiang, Y. H. Wang, G. Z. Wang, L. D. Zhang, *J. Am. Chem. Soc.* **2002**, 124, 15180–15181.

Received June 6, 2003