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Synthesis and Characterization of Barium Sulfate Nanotubes

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Tubular barium sulfate, having diameters in the range of 200–350 nm and length up to 30 microns, was fabricated by a nanochannel reactor and characterized by scanning electron microscope, transmission electron microscope, and X-ray diffractometer. The process is very simple, efficient and easy to control, which can be used to prepare a wide range of tubular inorganic nanomaterials.

Since the discovery of carbon nanotubes,[1] one-dimensional (1-D) hollow nanostructures are currently the focus of considerable interest because of their unique architectures and unusual chemical, electrical, optical, and mechanical properties.[2–7] Therefore various methods to prepare a number of tubular inorganic materials such as BN, dichalcogenides, $NiCl_2$, metal oxides, and some metals have been reported.[4–7] There is increasing interest in template-synthesized nanotubes because of its ability to control the dimensions of the nanotubes obtained. The outside diameter of the nanotubes is determined by the diameter of the pores in the template, and the length of the nanotubes is determined by the thickness of the template. In recent years, porous alumina membranes have been widely used to confine the growth of the nanosized materials owing to their remarkable hardness, uniform pore size, and high pore density.[8–16]

$BaSO_4$ is a structural analogue of the ubiquitous biomineral aragonite ($CaCO_3$) which is deposited in a number of biological systems, stabilized in conjunction with structure-directing biomolecular recognition of specific crystal faces.[17,18] $BaSO_4$ differs from $CaCO_3$ in that it possesses tetrahedral sulfate moieties in place of the planar carbonate anions. Consequently, crystal growth of $BaSO_4$ has been studied as a model to probe the relative structure and growth-directing efficacies of carboxylates, phosphonates, sulfonates, and other organic template molecules.[19] $BaSO_4$ has also been used as a model system to test different theories of crystal growth.[20] $BaSO_4$ particles with unusual sizes, shapes, texture, and morphology have been synthesizd by designing suitable organic templates.[21–25] Barium sulfate nanoparticles have been synthesized by the reversed micelles and microemulsions method,[26–28] and by polymer-controlled mineralization reactions.[29] However, the reports for the tubular $BaSO_4$ are limited. In this communication, we report a high-yield synthesis of $BaSO_4$ nanotubes using porous alumina membrane channel as a reaction vessel, a very simple, low-cost method.

Porous alumina membranes (Anodise®) made by Whatman Inc. (SEM images revealed a pore diameter range of 200–360 nm) were cleaned for 15 min in an ultrasonic bath using solvents of water, ethanol, acetone, chloroform and hexane, respectively. After dried in vacuum, the alumina membrane was put in the middle of two silica half-cells which separates the two cells.[30] 0.02 M $BaCl_2$ and 0.02 M Na_2SO_4 of the same volume were dropped into each cell, respectively. The reaction remained for 48 h at ambient temperature. Ba^{2+} and $SO_4{}^{2-}$ would enter the pores of the alumina membranes and form nanotubes. After completion of the reaction, the resulting $BaSO_4/Al_2O_3$ composite was washed several times with deionized water, then it was dipped into 2 M NaOH aqueous solution for 70 min in order to partly remove alumina membrane and for 3 h to remove the membrane substrate completely. Finally the product was rinsed with deionized water ten times.

Field emission scanning electron microscopic (FE-SEM; LEO-1350 VP) image of the products is shown in Figure 1. As can be seen, the products consist of a tubular 1-D nanostructure with outer diameters of 200–350 nm, inner diameters of 100–250 nm, and length up to 30 μm which corresponds to the thickness of the template membrane used. Some open ends of the tubes can be seen as indicated by arrows, inset in Figure 1 shows a typical open end. The nanotubes were individually separated from one another. The individual $BaSO_4$ nanotubes were dense with a uniform diameter throughout their entire length although some defects are presented.

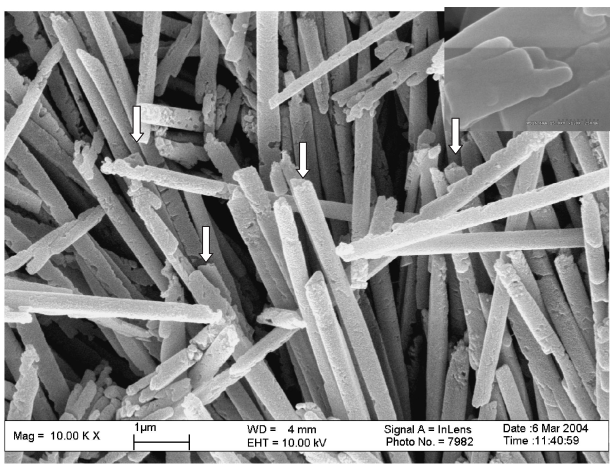


Figure 1. Typical scanning electron micrograph of $BaSO_4$ nanotubes (inset shows an open end) from the reaction of 0.02 M $BaCl_2$ with 0.02 M Na_2SO_4 for 48 h.

X-ray powder diffraction (XRD; Shimadzu XRD-600 diffractometer with Cu Kα radiation, $\lambda = 1.54060$ Å) pattern of $BaSO_4$ nanotubes is shown in Figure 2. The positions of the XRD peaks show good agreement with those of the JCPDS (No.72-1390) data of the barium sulfate with orthorhombic phase ($a = 8.909$ Å, $b = 5.467$ Å, $c = 7.188$ Å). The peaks at 2θ values of 20.21°, 24.61°, 25.59°, 32.56°, 32.82°, 42.30°, 42.38°, 50.52°, and 68.56° correspond to the crystal planes of (011), (002), (210), (301), (020), (113), (401), (004), and (040), respectively, of the crystalline barium sulfate.

TEM (H-800) image is shown in Figure 3a. The outer diameters of nanotubes vary from 200 to 350 nm, which correspond to

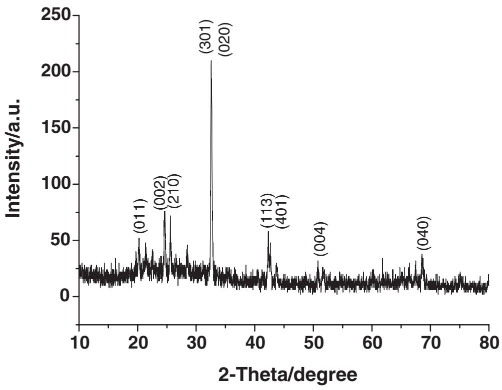
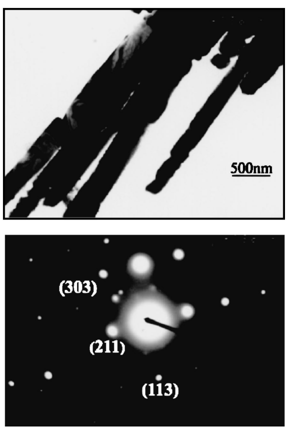


Figure 2. XRD pattern of $BaSO_4$ samples obtained.

the pore diameter of the alumina membrane. It is difficult to see the hollow cavity of the tube in the TEM image because the tube wall is very thick (40–50 nm). It is also shown that the nanotubes have been shorten in some extent after the ultrasonication.

The selected-area electron diffraction pattern of the $BaSO_4$ nanotubes shows the presence of diffraction spots due to the (211), (113) and (303) planes, as shown in Figure 3b, signifying the single crystalline nature of orthorhombic $BaSO_4$.



(a)

(b)

Figure 3. (a) TEM image and (b) Selected-area electron diffraction pattern of $BaSO_4$ samples obtained.

In summary, we firstly report the preparation of long and dense $BaSO_4$ nanotubes using porous alumina membrane as reactor vessel. The process is very simple, efficient and easy to control, which can be used to prepare a wide range of tubular inorganic nanomaterials. Further investigation on the properties and applications of as-prepared $BaSO_4$ nanotubes is in progress.

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References

1 S. Iijima, *Nature*, **354**, 56 (1991).
2 J. Hu, T. W. Odom, and C. M. Lieber, *Acc. Chem. Res.*, **32**, 435 (1999).
3 R. H. Baughman, A. A. Zakhidov, and W. A. De Heer, *Science*, **297**, 787 (2002).
4 C. N. R. Rao and M. Nath, *Dalton Trans.*, **2003**, 1, and references therein.
5 W. Tremel, *Angew. Chem., Int. Ed.*, **38**, 2175 (1999).
6 R. Tenne, *Chem.—Eur. J.*, **8**, 5297 (2002).
7 G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.*, **41**, 2446 (2002).
8 C. R. Martin, *Science*, **266**, 1961 (1994).
9 K. B. Jirage, J. C. Hulteen, and C. R. Martin, *Science*, **278**, 655 (1997).
10 S. B. Lee, D. T. Mitchell, L. Trofin, T. K. Nevanen, H. Soderlund, and C. R. Martin, *Science*, **296**, 2198 (2002).
11 M. Steinhart, J. H. Wendorff, A. Greiner, R. B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, and U. Gosele, *Science*, **196**, 1997 (2002).
12 I. Mikulskas, S. Juodkazis, R. Tomasiunas, and J. G. Dumas, *Adv. Mater.*, **13**, 1574 (2001).
13 J. Y. Liang, H. Chik, A. J. Yin, and J. Xu, *J. Appl. Phys.*, **91**, 2544 (2002).
14 B. D. Reiss, R. G. Freeman, I. D. Walton, S. M. Norton, P. C. Smith, W. G. Stonas, C. D. Keating, and M. J. Natan, *J. Electroanal. Chem.*, **522**, 95 (2002).
15 S. H. Zhang, Z. X. Xie, Z. Y. Jiang, X. Xu, J. Xiang, R. B. Huang, and L. S. Zheng, *Chem. Commun.*, **2004**, 1106.
16 G. S. Wu, L. D. Zhang, B. C. Cheng, T. Xie, and X. Y. Yuan, *J. Am. Chem. Soc.*, **126**, 5976 (2004).
17 S. Mann, B. R. Heywood, S. Rajam, and J. D. Birchall, *Nature*, **334**, 692 (1988).
18 S. Mann, J. M. Didymus, N. P. Sanderson, B. R. Heywood, and E. J. Aso Samper, *J. Chem. Soc., Faraday Trans.*, **86**, 1873 (1990).
19 R. J. Davey, S. N. Black, L. A. Bromley, D. Cottier, B. Dobbs, and J. E. Rout, *Nature*, **353**, 549 (1991).
20 C. M. Pina, U. Becker, P. Risthaus, D. Bosbach, and A. Putnis, *Nature*, **395**, 483 (1998).
21 B. R. Heywood and S. Mann, *J. Am. Chem. Soc.*, **114**, 4681 (1992).
22 L. Qi, H. Cölfen and M. Antonietti, *Angew. Chem., Int. Ed. Engl.*, **39**, 604 (2000).
23 M. Dinamani, P. V. Kamath, and R. Seshadri, *Chem. Mater.*, **13**, 3981 (2001).
24 L. Qi, H. Cölfen, M. Antonietti, M. Li, J. D. Hopwood, A. J. Ashley, and S. Mann, *Chem.—Eur. J.*, **7**, 3526 (2001).
25 D. Rautaray, A. Kumar, S. Reddy, S. R. Sainkar, and M. Sastry, *Cryst. Growth Des.*, **2**, 197 (2002).
26 J. D. Hopwood and S. Mann, *Chem. Mater.*, **9**, 1819 (1997).
27 M. Li and S. Mann, *Langmuir*, **16**, 7088 (2000).
28 M. Summers, J. Eastoe, and S. Davis, *Langmuir*, **18**, 5023 (2002).
29 S. H. Yu, M. Antonietti, H. Cölfen, and J. Hartmann, *Nano Lett.*, **3**, 379 (2003).
30 Y. Z. Piao and H. Kim, *Chem. Commun.*, **2003**, 2898.

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