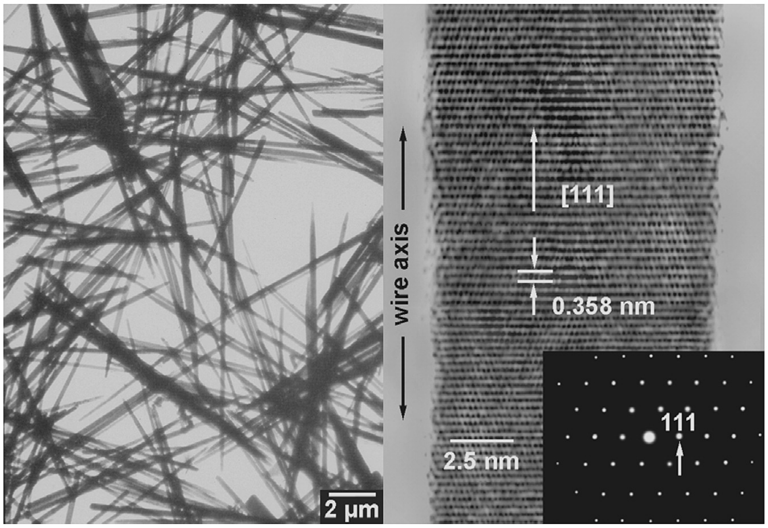
Communication

The First Fluoride One-Dimensional Nanostructures: Microemulsion-Mediated Hydrothermal Synthesis of BaF Whiskers

Minhua Cao, Changwen Hu, and Enbo Wang

J. Am. Chem. Soc., **2003**, 125 (37), 11196-11197• DOI: 10.1021/ja036939c • Publication Date (Web): 20 August 2003



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

JACS COMMUNICATIONS

The First Fluoride One-Dimensional Nanostructures: Microemulsion-Mediated Hydrothermal Synthesis of BaF_2 Whiskers

Minhua Cao,[†] Changwen Hu,*[,†,‡] and Enbo Wang[†]

Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun 130024, P. R. China, and Department of Chemistry, Beijing Institute of Technology, Beijing 100081, P. R. China

Received June 27, 2003; E-mail: huchw@nenu.edu.cn

Barium fluoride is one of the dielectric fluorides (CaF_2, SrF_2, and BaF_2) that have a wide range of potential applications in microelectronic and optoelectronic devices, such as wide-gap insulating overlayers, gate dielectrics, insulators and buffer layers in semiconductor-on-insulator structures, and more advanced three-dimensional structure devices.[1] BaF_2 activated with rare-earth ions has also been reported to display unique luminescence properties and can be used as scintillators.[2] With the rapid shrinking in size in electronic devices, nanometer-scale fluorides may play an essential role for their applications in future electronic nanodevices. Recently, Bender et al. have reported the synthesis of Nd:BaF_2 nanoparticles by the reverse microemulsion technique,[3] Stouwdam et al. have fabricated lanthanide-doped LaF_3 nanoparticles by the use of capping agents,[4] and Li et al. have reported CaF_2 nanocubes by a hydrothermal method with the absence of surfactants.[5] These indicate that the synthesis of fluoride nanocrystals is just beginning to emerge. However, to the best of our knowledge, there have been no reports on fluoride one-dimensional (1D) nanostructures to date. Therefore, the development of methods for the synthesis of fluoride 1D nanostructures is a major challenge.

1D nanostructures have attracted considerable attention because of their potential use in a wide range of advanced applications in the past decade. As a consequence, many synthetic methods have been developed to prepare various 1D nanostructures. Recently, we have reported a surfactant-assisted method for the synthesis of PbO_2, Pb_3O_4, Cu, Cu_2O, and CuO 1D nanostructures.[6] Studies have shown that the key to fabricating a 1D nanostructure can be focused on the way in which atoms or other building blocks are rationally assembled into structures with nanometer-sized diameters but much higher lengths.[7] Reverse micelles or microemulsion systems have been widely used as ideal media to prepare nanoparticles.[8−10] A water-in-oil (w/o) microemulsion is a transparent and isotropic liquid medium with nanosized water pools dispersed in a continuous phase and stabilized by surfactant and cosurfactant molecules at the water/oil interface. These water pools offer ideal microreactors for the formation of nanoparticles. However, some studies, for example, the fabrication of ZnO, $BaCO_3$ nanowires, $BaSO_4$ nanofilaments, and CdS, $BaWO_4$, and $K_3[PMo_{12}O_{40}]\cdot nH_2O$ nanorods,[11−16] have shown that the microemulsion method can also be used to prepare some 1D nanostructures under certain conditions. In this Communication, we first report the synthesis of high aspect ratio (>1000), uniform BaF_2 whiskers through a simple microemulsion-mediated hydrothermal procedure.

A quaternary microemulsion, cetyltrimethylammonium bromide (CTAB)/water/cyclohexane/*n*-pentanol, was selected for this study. As a typical synthesis, two identical solutions were prepared by dissolving CTAB (2 g) in 50 mL of cyclohexane and 2 mL of *n*-pentanol. The mixing solution was stirred for 30 min until it became transparent. Next, 2 mL of 0.5 M $BaCl_2$ aqueous solution and 2 mL of 5% HF aqueous solution were added to the solutions, respectively. After substantial stirring, the two optically transparent microemulsion solutions were mixed and stirred for another 10 min. The resulting microemulsion solution was then transferred into a 125 mL stainless Teflon-lined autoclave and heated at 120 °C for 12 h. The resulting suspension was immediately cooled to room temperature right after the heating and was then stored at a constant temperature of 25 °C. After 12 h of aging, samples were collected and washed several times with absolute ethanol and distilled water. Finally, the BaF_2 whiskers were obtained after the samples were centrifuged and dried in a vacuum at room temperature. Results with samples prepared with different aging times as well as at different CTAB concentrations were also compared.

The overall crystallinity and purity of the as-synthesized sample were examined by X-ray diffraction (XRD) measurements performed on a Rigaku X-ray diffractometer with Cu Kα radiation. All of the diffraction peaks in Figure 1 can be readily indexed to a pure cubic phase [space group: $Fm3m$ (225)] with a lattice constant $a = 6.198$ Å, which is in good agreement with the standard values for the bulk cubic BaF_2 (JCPDS 85-1341). No other impurities have been found in the synthesized products. In addition, it was found that peak (111) is the only peak that gains a substantial increase in relative intensity, indicating that the whisker growth may occur along the (111) direction.

After an aging time of 12 h, BaF_2 whiskers were formed. Examination by scanning electron micrograph (SEM) found that the products are primarily composed of whiskers with lengths of up to several tens of micrometers (Figure 2a). Most of the whiskers are straight and uniform along their axis direction, which is further confirmed from the image (Figure 2b) obtained with transmission electron microscopy (TEM). According to the SEM and TEM images, the whiskers are 30−50 μm in length, and 40−80 nm in diameter, which accounts for their aspect ratios as high as 1000. More details about the structure of whiskers were investigated by the selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM). The SAED image (inset in Figure 2d) taken from the whisker indicated in Figure 2c can be indexed as a cubic BaF_2 single crystal, in good agreement with the XRD results presented above. Moreover, the SEAD images taken from different positions along the whisker (without tilting the sample with respect to the electron beam) are found to be almost identical. This indicates that the entire whisker is a single crystal. Figure 2d shows a typical HRTEM image of the same whisker indicated in Figure 2c. This image reveals that the whisker is structurally uniform with a clearly resolved interplanar spacing of about 0.358 nm, which corresponds to [111] planes. In addition, the [111] direction is parallel to the axis of the whisker, indicating that the whiskers grow along the [111] direction, which is consistent with the observations from the XRD image.

[†] Northeast Normal University.
[‡] Beijing Institute of Technology.

10.1021/ja036939c CCC: $25.00

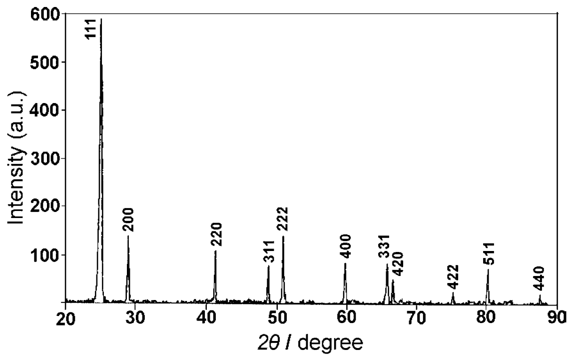


Figure 1. XRD pattern of the BaF_2 whiskers.

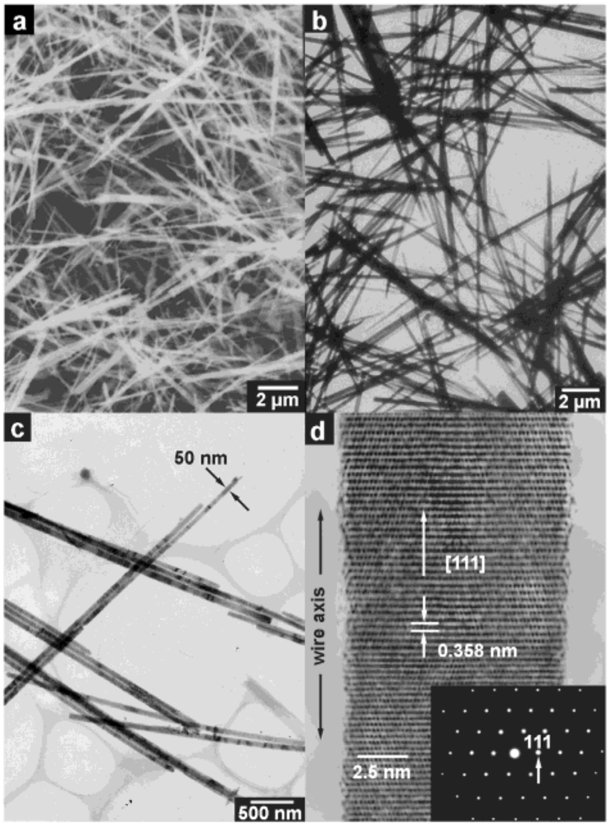


Figure 2. (a) SEM image of BaF_2 whiskers. (b) TEM image of BaF_2 whiskers. (c) High-magnification TEM image of BaF_2 whiskers. (d) HRTEM image of a single BaF_2 whisker indicated in (c) with a diameter of 50 nm; the inset is an SAED image of the same whisker.

Clearly, with the above-mentioned synthetic method, BaF_2 whiskers with much higher aspect ratios are obtained instead of nanoparticles, most of which are achieved via the reverse micelles or microemulsions method. The results also indicate that it is not likely to lead to the formation of water nanochannels in oil in such a low water content environment, although reaction conditions (especially the reaction temperature) may have significant effects on the micellar size and shape.[17] To investigate the formation process of whiskers, nonaged samples and samples with different aging times (0.5, 2, and 5 h) were compared. The TEM micrographs (see Supporting Information) at early stages of the whisker formation indicate that the nonaged samples exhibit uniform nanoparticles, while the samples prepared with different aging times show rodlike 1D nanostructures with different lengths. Consequently, it is during the aging process rather than in reverse micelles that BaF_2 whiskers are formed. Because of preferential adsorption of cationic surfactant CTAB headgroups, only uniform and well-crystallized BaF_2 nanoparticles with a preferential growth direction may be formed within the water pools of reverse micelles under hydrothermal conditions. In this case, the hydrothermal treatment is used to improve the crystallinity of materials in microemulsions.[18] The nanoparticles can be seen as building blocks for the formation of whiskers. During aging, the nanoparticle building blocks are gradually assembled into whiskers by a directed aggregation growth process in a directional manner.[12] Certainly, this mechanism proposed needs to be confirmed by more studies. In addition, our results show that CTAB concentration has significant effects on the formation of whiskers. A lower CTAB concentration ([CTAB] = 0.06 M) gave aggregated particles, and a higher surfactant concentration of 1.5 M also resulted in aggregated particles larger than those observed at 0.06 M (see Supporting Information).

In summary, we have developed a microemulsion-mediated hydrothermal method to prepare BaF_2 whiskers. A directed aggregation growth process mediated by the microemulsion droplet building blocks is proposed for the formation of BaF_2 whiskers. Further work is in progress to evaluate the possibility of synthesizing other fluoride 1D nanostructures using a similar method. Meanwhile, studies of the properties of this novel whiskerlike morphology are underway.

Acknowledgment. This work was supported by the NSFC (No. 20071007 and 20271007).

Supporting Information Available: Detailed characterization results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Singh, R.; Sinha, S.; Chou, P.; Hsu, N. J.; Radpour, F. *J. Appl. Phys.* **1989**, *66*, 6179.
(2) Wojtowicz, A. J. *Nucl. Instrum. Methods A* **2002**, *486*, 201.
(3) Bender, C. M.; Burlitch, J. M. *Chem. Mater.* **2000**, *12*, 1969.
(4) Stouwdam, J. W.; van Veggel, F. C. J. M. *Nano Lett.* **2002**, *2*, 733.
(5) Sun, X. M.; Li, Y. D. *Chem. Commun.* **2003**, 1768.
(6) (a) Cao, M. H.; Hu, C. W.; Peng, G.; Qi, Y. J.; Wang, E. B. *J. Am. Chem. Soc.* **2003**, *125*, 4982. (b) Cao, M. H.; Hu, C. W.; Wang, Y. H.; Guo, Y. H.; Guo, C. X.; Wang, E. B. *Chem. Commun.* **2003**, 1884.
(7) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435.
(8) Schwuger, M.; Stickdom, K.; Schomacker, R. *Chem. Rev.* **1995**, *95*, 849.
(9) Gan, L. M.; Liu, B.; Chew, C. H.; Xu, S. J.; Chua, S. J.; Loy, G. L.; Xu, G. Q. *Langmuir* **1997**, *13*, 6427.
(10) Feng, P.; Bu, X.; Stucky, G. D.; Pine, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 994.
(11) Zhang, J.; Sun, L. D.; Pan, H. Y.; Liao, C. S.; Yan, C. H. *New J. Chem.* **2002**, *26*, 33.
(12) Qi, L. M.; Ma, J. M.; Cheng, H. M.; Zhao, Z. G. *J. Phys. Chem. B* **1997**, *101*, 3460.
(13) Hopwood, J. D.; Mann, S. *Chem. Mater.* **1997**, *9*, 1819.
(14) Zhang, P.; Gao, L. *Langmuir* **2003**, *19*, 208.
(15) Kwan, S.; Kim, F.; Akana, J.; Yang, P. D. *Chem. Commun.* **2001**, 447.
(16) Zhang, X. H.; Xie, S. Y.; Jiang, Z. Y.; Zhou, L. C.; Xie, Z. X.; Huang, R. B.; Zheng, L. S. *Chem. Commun.* **2002**, 2032.
(17) Seto, H.; Okuhara, D.; Kawabata, Y.; Takeda, T.; Nagao, M.; Suzuki, J.; Kamikubo, H.; Amemiya, Y. *J. Chem. Phys.* **2000**, *112*, 10608.
(18) Xu, S. J.; Chua, S. J.; Liu, B.; Gan, L. M.; Chew, C. H.; Xu, G. Q. *Appl. Phys. Lett.* **1998**, *73*, 478.

JA036939C