J|A|C|S
COMMUNICATIONS

Published on Web 01/29/2002

Synthesis of Single-Crystalline Perovskite Nanorods Composed of Barium Titanate and Strontium Titanate

Jeffrey J. Urban, Wan Soo Yun, Qian Gu, and Hongkun Park*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

Received December 6, 2001

Over the past decade one-dimensional chemical nanostructures,[1] including carbon nanotubes[2−4] and inorganic nanorods and nanowires,[5−14] have received considerable attention from the scientific community. Much effort has been directed toward understanding the electronic,[2−4] magnetic,[12] and optical[15] properties of these nanostructures because they exhibit physical and chemical properties different from their bulk counterparts.[1] These one-dimensional nanostructures are also promising candidates for realizing nanoscale electronic,[16] optical,[15] and mechanical[1] devices because they retain wire-like connectivity despite their nanoscale radial dimension. To date, most synthetic efforts have been directed toward carbon nanotubes[2−4] and semiconductor,[5−9] metallic,[10−12] and binary oxide nanowires.[13,14] In this communication, we report the first solution-based synthesis of nanorods composed of ternary perovskite oxides.

Transition metal oxides with a cubic-perovskite structure represent a particularly interesting class of materials that exhibit a variety of unique electronic, magnetic, and optical properties, such as ferroelectricity,[17] piezoelectricity,[17] colossal magnetoresistivity,[18] and large nonlinear optical coefficients.[19] Previous investigations of thin-film and nanocrystalline samples have shown that their physical properties are critically dependent on their dimension.[17,20−22] Despite intensive experimental efforts, however, a general method to synthesize well-isolated crystalline nanostructures of perovskite oxides has been lacking, which has hindered detailed experimental investigations on the size-dependent properties of these oxides.[17,20] The synthesis of well-isolated perovskite nanocrystals is just beginning to emerge.[23,24]

The synthesis of $BaTiO_3$ and $SrTiO_3$ nanorods is accomplished by solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands, similar to the methods used to prepare inorganic nanocrystals and nanorods.[5,7,11,24−27] This reaction yields well-isolated nanorods with diameters ranging from 5 to 60 nm and lengths reaching up to >10 μm. These nanorods are composed of single-crystalline cubic perovskite $BaTiO_3$ and $SrTiO_3$ with a principal axis of the unit cell preferentially aligned along the wire length. Nanorods of $BaTiO_3$ and $SrTiO_3$ provide promising materials for fundamental investigations on nanoscale ferroelectricity, piezoelectricity, and paraelectricity. The present synthetic method based on the solution-phase decomposition of bimetallic alkoxides may also provide a general route to synthesize other cubic perovskite materials into a nanorod form.[24]

In a typical reaction, a 10-fold molar excess of 30% H_2O_2 (Aldrich) was added at 100 °C to 10 mL of a heptadecane (Alfa Aesar, 99%) solution containing 10 mmol of bimetallic alkoxide precursors and 1 mmol of oleic acid (Aldrich, 99+%). The precursors, barium titanium isopropoxide ($BaTi[OCH(CH_3)_2]_6$) and strontium titanium isopropoxide ($SrTi[OCH(CH_3)_2]_6$), were prepared following the procedures reported in the literature.[28,29] The reaction mixture was subsequently heated to 280 °C for 6 h, resulting in a white precipitate composed of nanorod aggregates. Anisotropic nanorod growth is most likely due to precursor decomposition and crystallization in a structured inverse micelle medium formed by precursors and oleic acid under these reaction conditions.[7,11,24] Well-isolated nanorods were obtained by sonication of the reaction product followed by fractionation between water and hexane. Nanorods were collected from the hexane layer for further analysis.

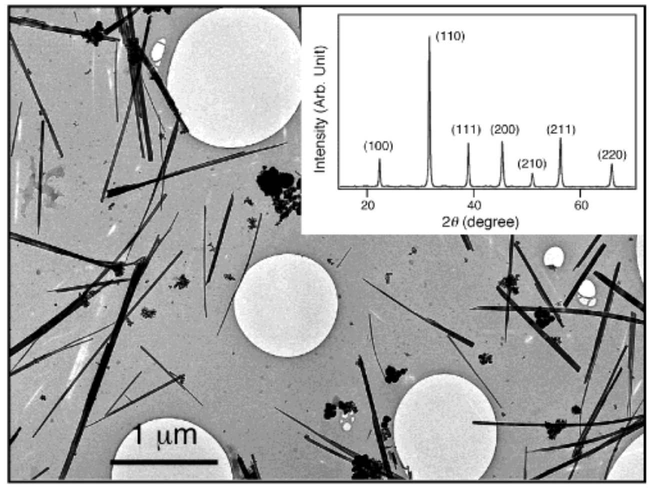

Figure 1. Transmission electron microscopy (TEM) image of $BaTiO_3$ nanorods, showing that the reaction produces mostly nanorods and minor quantities (∼10%) of nanoparticle aggregates. The TEM image of $SrTiO_3$ nanorods is essentially indistinguishable. Inset: Powder X-ray diffractogram of the reaction product composed of randomly oriented $BaTiO_3$ nanorod ensembles.

Representative transmission electron microscope (TEM) images of $BaTiO_3$ and $SrTiO_3$ nanorods obtained from the syntheses are presented in Figures 1 and 2. Analysis of these images reveals that the diameters of the $BaTiO_3$ and $SrTiO_3$ nanorods range from 5 to 60 nm. Nanorod lengths vary from a few hundred nanometers to tens of microns, and they increase with reaction time. Elemental analysis indicates that these nanorods have stoichiometric proportions of Ba (or Sr) and Ti. Analysis of the powder X-ray (Figure 1 inset) and electron diffraction patterns (Figure 2) demonstrates that these nanorods are composed of crystalline $BaTiO_3$ and $SrTiO_3$ with a cubic perovskite structure. The unit cell parameters for $BaTiO_3$ and $SrTiO_3$ are determined to be 4.03 and 3.90 Å, respectively, which are identical with those of the bulk cubic materials.[30]

Convergent beam electron diffraction (CBED) patterns obtained from representative $BaTiO_3$ and $SrTiO_3$ nanorods are presented in Figure 2, panels a and b, respectively. These CBED patterns exhibit

10.1021/ja017694b CCC: $22.00

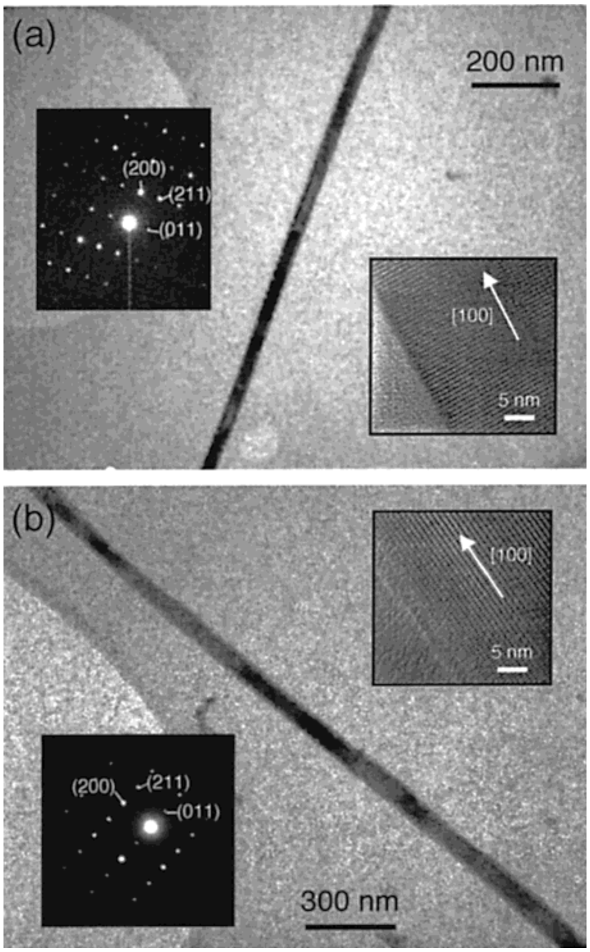

Figure 2. (a) TEM image of a 30-nm diameter $BaTiO_3$ nanorod. Left inset: Convergent beam electron diffraction (CBED) pattern obtained from the same nanorod. Right inset: A high-resolution TEM image of the nanorod that shows lattice fringes perpendicular to the [100] direction. (b) TEM image of a 55-nm diameter $SrTiO_3$ nanorod. Left inset: Convergent beam electron diffraction (CBED) pattern obtained from the same nanorod. Right inset: A high-resolution TEM image of the nanorod that shows lattice fringes perpendicular to the [100] direction.

sharp diffraction spots characteristic of crystalline $BaTiO_3$ and $SrTiO_3$, in agreement with X-ray diffraction results obtained from randomly oriented nanowire ensembles in Figure 1. Moreover, the CBED patterns taken from different positions along the nanorod are found to be identical within experimental accuracy, indicating that the entire nanorod is a single crystal. Representative high-resolution TEM (HRTEM) images of respective nanorods in Figure 2 (panels a and b) also confirm the single-crystalline nature of these nanorods. Both the electron-diffraction patterns and the HRTEM image in Figure 2 show that the principal axes of the $BaTiO_3$ and $SrTiO_3$ unit cells are aligned along the wire axis. Essentially all $BaTiO_3$ and $SrTiO_3$ nanorods prepared from over 30 independent synthesis runs exhibited identical crystalline behavior.

The present study shows that single-crystalline nanorods composed of $BaTiO_3$ and $SrTiO_3$ with a cubic perovskite structure can be synthesized by a solution-based decomposition of bimetallic alkoxide precursors. These nanorods should provide an ideal candidate for fundamental studies of nanoscale ferroelectricity, piezoelectricity, and paraelectricity. The synthetic strategy presented here may be extended to other cubic perovskite nanorods with different chemical compositions by choosing the appropriate bimetallic alkoxide precursors.

Acknowledgment. This work is supported by NSF (DMR-0076593), DARPA, the Dreyfus Foundation, the Research Corporation, and Harvard University. We thank C. M. Lieber for helpful discussions and W. J. Croft, Y. Lu, and W. J. MoberlyChan for technical assistance.

References

(1) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435.
(2) Odom, T. W.; Huang, J.-L.; Kim, P.; Lieber, C. M. *J. Phys. Chem. B* **2000**, *104*, 2794.
(3) Bockrath, M.; Liang, W.; Bozovic, D.; Hafner, J. H.; Lieber, C. M.; Tinkham, M.; Park, H. *Science* **2001**, *291*, 283.
(4) Liang, W.; Bockrath, M.; Bozovic, D.; Hafner, J. H.; Tinkham, M.; Park, H. *Nature* **2001**, *411*, 665.
(5) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Sher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
(6) Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.
(7) Manna, L.; Sher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2000**, *122*, 12700.
(8) Holmes, J. D.; Johnston, K. P.; Doty, R. C.; Korgel, B. A. *Science* **2000**, *287*, 1471.
(9) Gudiksen, M. S.; Lieber, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 8801.
(10) Park, S.-J.; Kim, S.; Lee, S.; Khim, Z. G.; Char, K.; Hyeon, T. *J. Am. Chem. Soc.* **2000**, *122*, 8581.
(11) Puntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.
(12) Thurn-Albrecht, T.; Schotter, J.; Kästle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.
(13) Huang, M. H.; Wu, Y.; Feick, H.; Tran, N.; Weber, E.; Yang, P. *Adv. Mater.* **2001**, *13*, 113.
(14) Lei, Y.; Zhang, L. D.; Fan, J. C. *Chem. Phys. Lett.* **2001**, *338*, 231.
(15) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.
(16) Cui, Y.; Lieber, C. M. *Science* **2001**, *291*, 851.
(17) Scott, J. F. *Ferroelec. Rev.* **1998**, *1*, 1.
(18) Millis, A. J. *Nature* **1998**, *392*, 147.
(19) Wessels, B. W. *Annu. Rev. Mater. Sci.* **1995**, *25*, 525.
(20) Tsunekawa, S.; Ito, S.; Mori, T.; Ishikawa, K.; Li, Z.-Q.; Kawazoe, Y. *Phys. Rev. B* **2000**, *62*, 3065.
(21) Wang, R.; Zhu, Y.; Shapiro, S. M. *Phys. Rev. Lett.* **1998**, *80*, 2370.
(22) Zhang, J.; Yin, Z.; Zhang, M.-S.; Scott, J. F. *Solid State Commun.* **2001**, *118*, 241.
(23) Liu, C.; Zou, B.; Rondinone, A. J.; Zhang, Z. J. *J. Am. Chem. Soc.* **2001**, *123*, 4344.
(24) O'Brien, S.; Brus, L.; Murray, C. B. *J. Am. Chem. Soc.* **2001**, *123*, 12085−12086.
(25) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
(26) Trentler, T. J.; Denler, T. E.; Bertone, J. F.; Agrawal, A.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 1613.
(27) Rockenberger, J.; Scher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1999**, *121*, 11595.
(28) Suyama, Y.; Nagasawa, M. *J. Am. Ceram. Soc.* **1994**, *77*, 603.
(29) The precursors were synthesized by the following procedure in an inert atmosphere: 65.0 mmol of barium (strontium) metal (Aldrich, 99%) was added to a flask containing 112 mL of anhydrous benzene (Aldrich, 99.8%), 21 mL of 2-propanol (Aldrich, 99.5%), and 19.5 mL of titanium-(IV) isopropoxide (Alfa Aesar, 99.999%) and stirred vigorously until the added metal was completely dissolved. The solution exhibited a deep purple color within minutes and gradually became white. Once the metal was dissolved, the solution was placed at 4 °C as the precursor precipitated out of the solution. The precipitated precursors were dried overnight, resulting in a fine white powder.
(30) At room temperature, the bulk $BaTiO_3$ unit cell exhibits tetragonal symmetry with a slight elongation along the *c* axis ($c/a = 4.038$ Å/3.994 Å $= 1.011$). This small distortion cannot be unambiguously established based on the powder diffraction pattern of $BaTiO_3$ nanowires alone due to the broadening of diffraction peaks.

JA017694B