

Synthesis of Well-isolated Barium Titanium Trioxide Nanocubes

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(Received May 26, 2005; CL-050691)

Almost perfectly cubic shaped BaTiO₃ nanocrystallites are generated by seed-mediated growth of BaTiO₃ nanospheres, which are produced by a low-temperature aqueous synthetic method. The formation mechanism of the nanocubes is also proposed on the basis of dissolution–recrystallization mechanism.

Controlling the shape of nanoparticles has been a subject of intensive research to understand the behavior of materials at the nanoscale because the particles with different shapes can have electric, optic, and magnetic properties distinct from those observed in their spherical counterparts.^{1,2} Ternary transition metal oxides with nonspherical shapes, for example, single-crystalline BaTiO₃ nanowires with a principal axis preferentially aligned along the wire axis, induce a spontaneous electric polarization that is potentially useful in the fabrication of nonvolatile memory devices.³ Hence, it is desirable to develop strategies for shape-controlled synthesis and properties exploitation of BaTiO₃ nanoparticles.

Regarding previous related works, the solution-phase chemical routes can provide a means of producing high purity, crystalline nanoscale materials with a specific shape and variable size.⁴ Strategies for the preparation of specific shapes of nanostructures in these previous works include the formation by the use of capping reagents, template-inspired reagents, and surfactant. In contrast to the general methods for size and morphology control, the seeding technique is known as an effective alternative one that can avoid the size distribution broadening by adding seeds in a system at a low supersaturation. Also, monocrystalline particles can be prepared by additional growth of cubic or polyhedral particles in the presence of different kinds of organic adsorptives or anions controllers.⁵ To this end, we propose a low-temperature aqueous synthesis (LTAS)⁶ combined with the seed-mediated growth method,⁷ using an aqueous medium under alkaline conditions.

The general strategy is to utilize BaCl₂ and Ti(OH)₄ aqueous solution as precursors in a LTAS process to synthesize BaTiO₃ spherical nanoparticles with a mean diameter of 30 nm. Such 30-nm nanospheres then serve as seeds to grow larger cubic nanoparticles in the seed-mediated growth process. In a typical synthesis, an excess of BaCl₂ was added at 80 °C to an aqueous Ti(OH)₄ solution to form a mixture solution A, with Ba/Ti mole ratio of 1.5 and total concentration of Ba²⁺ and hydrated titanium ions kept at 1.25 mol·L⁻¹. The solution A and the 6.0 mol·L⁻¹ Aqueous NaOH solution B at 95 °C were mixed by simultaneously and continuously pumping from their storage tanks into their individual slotted pipe distributors in the rotating packed bed reactor (RPB, see details reactor structure in the literature⁸), resulting in a white precipitate and spherical BaTiO₃ nanoparticles with a diameter of 30 nm. Then, 40 mL of suspen-

sions were introduced into a Teflon-lined autoclave and subsequently heated at 240 °C for 3 h. The reaction was carried out at the precursors' autogenic pressure (3.4 MPa). Upon reaction completion, the hydrothermal cell was cooled to room temperature, and the supernatant liquid was discarded. The remaining product was washed with formic acid and distilled water and dried under ambient conditions at 80 °C for 24 h. This resulted in a white powder, consisting of well-isolated BaTiO₃ nanocubes.

The low magnification scanning electron microscopy (SEM) image (Figure 1a) shows that the products formed by the seed-mediated growth consist of uniform nanocubes. The higher magnification image (Figure 1b) indicates that the products are made of nanocubes and have a mean edge length of 80 ± 8 nm. Energy dispersive X-ray spectroscopy (EDS) results showed that the nanocubes are composed of Ba, Ti, and O with the atomic ratio close to 1:1:3.

Figure 2a shows the high-resolution transmission electron microscopy (HRTEM) image of a BaTiO₃ cube. The inset shows the corresponding selected area diffraction (SAED) pattern, obtained by directing the incident electron beam perpendicular to one of the square facets of the cube. The square spot array was indexed to [200] and [100] of the cube. The 2D lattice fringes of the HRTEM image were examined to be 0.282 nm, close to the (110) lattice spacing of the cube. Figure 2b also indicates that all corners and edges of cube are slightly truncated. Because the HRTEM image was recorded from the area along one upright facet as marked by a white pane in Figure 2b, the drawing in

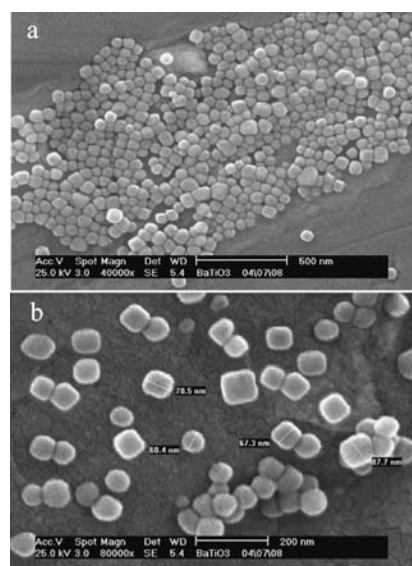


Figure 1. SEM images of the products: (a) low-magnification image of the sample on the substrate, (b) high-magnification image.

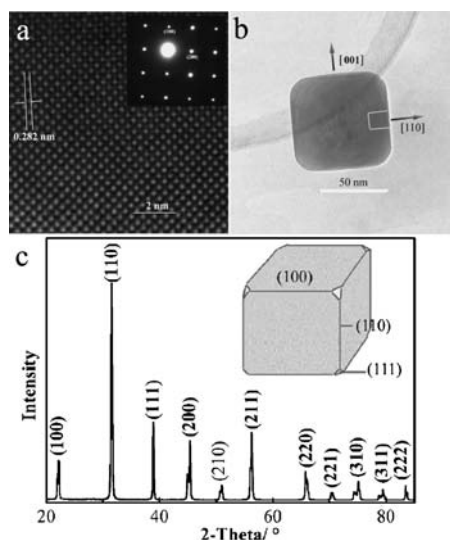


Figure 2. (a) A typical HRTEM image of a selected area of an individual BaTiO_3 nanocube with the SAED pattern shown in the inset. (b) The nanocube used for the HRTEM and SAED studies. (c) XRD pattern obtained from BaTiO_3 nanocubes.

Figure 2c clearly delineates these truncations and their corresponding crystallographic planes.

To verify which parameters controlled the growth of the nanocubes, some comparative experiments were carried out. LTAS BaTiO_3 suspensions were washed with distilled water to remove impurities such as OH^- , Cl^- , and Ba^{2+} . The 30-nm BaTiO_3 nanocrystals are used as seeds in the seed-mediated growth. In the solution of NaOH or NaCl precursors, the particle size and shape did not change after the reaction completed. Moreover, when the experiment was conducted in the $\text{Ba}(\text{OH})_2$ precursors, spherical particles with increased particle size were obtained. To further understand the effect of OH^- during the growth process, we intentionally add BaCl_2 into seeds suspensions and find that no BaTiO_3 nanocubes were formed. These results indicate that Ba^{2+} , OH^- , and Cl^- in the precursors are critical factors for the growth of BaTiO_3 nanocubes. Finally, the seed-mediated growth conducted at a lower temperature, i.e., 200°C , results in a noncubic morphology, which suggests that temperature is an important kinetic factor in the seed-mediated growth process.

On the basis of the above experimental results, we propose a dissolution–recrystallization mechanism for the formation of BaTiO_3 nanocubes. Samples prepared by LTAS consist of both crystalline and amorphous particles as revealed by HRTEM graph shown in Figure 3a. Under the hydrothermal environment, a possibility is that the increased temperature promotes the dissolution of BaTiO_3 seeds and the preferential regrowth of larger crystals, which is similar to Ostwald ripening.⁹ As the growth rate in the $[111]$ direction is greater than that in the $[100]$ direction, the $\{100\}$ sides of the cube will become enlarged at the expense of the $\{111\}$ corners,¹⁰ which is demonstrated by the HRTEM observations shown in Figures 3b–3d. These conditions result in the fast nucleation and growth of the BaTiO_3 nanocubes. After the cubic shape is formed, each face of the BaTiO_3 nanocubes will have the same growth rate, and further growth will mainly increase the size with no significant morphological variation.

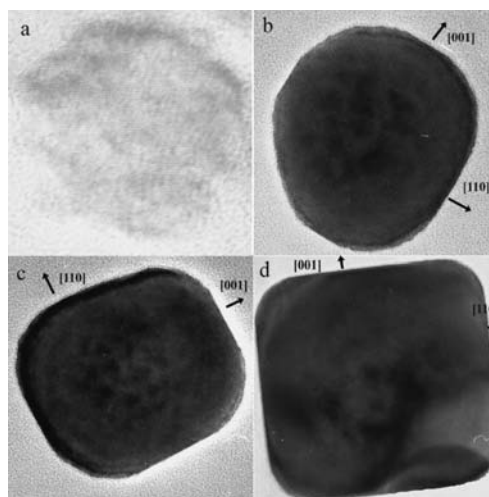


Figure 3. (a) A typical HRTEM image of a selected individual BaTiO_3 nanospheres produced by LTAS. The next three typical HRTEM images of BaTiO_3 powders generated by seed-mediated growth for different times: (b) 1 h, (c) 2 h, and (d) 3 h.

In summary, we succeed in the preparation of single-crystalline BaTiO_3 nanocubes by a simple method. The nanocubes have uniform edge length and highly aligned with smooth surface. A dissolution–recrystallization mechanism is proposed on the basis of some comparative experiments. Future work involves the detailed investigation of ferroelectricity, piezoelectricity, and paraelectricity as well as mechanistic studies of nanocube formation for the purpose of synthetic optimization.

We acknowledge support of this work through startup funds provided by the National Natural Science Foundation of China (Nos. 20236020 and 20325621), the National High Technique Program (“863” program) of China (Nos. 2001AA325014 and 2003AA302760), the Talent Training Program of the Beijing City (No. 9558103500), and the Fok Ying Tung Foundation (No. 81063).

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