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Synthesis and Characterization of Bowl-Like Single-Crystalline $BaTiO_3$ Nanoparticles

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Abstract Novel bowl-like single-crystalline $BaTiO_3$ nanoparticles were synthesized by a simple hydrothermal method using $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 as precursors. The as-prepared products were characterized by XRD, Raman spectroscopy, SEM and TEM. The results show that the bowl-like $BaTiO_3$ nanoparticles are single-crystalline and have a size about 100–200 nm in diameter. Local piezoresponse force measurements indicate that the $BaTiO_3$ nanoparticles have switchable polarization at room temperature. The local effective piezoelectric coefficient d_{33}^* is approximately 28 pm/V.

Keywords $BaTiO_3$ · Bowl-like · Single-crystalline · Piezoelectric properties

Introduction

In recent years, increasing attention has been devoted to the synthesis of various nanostructured $BaTiO_3$, such as nanoparticles, nanocubes, nanorods, nanowires, and nanotubes, because of the dependence of their ferroelectric and piezoelectric properties on the dimension and size, which is essential for realizing nanoscale devices for a wide range of applications, including memory, transducers, sensors, energy-harvesting devices,[1–6]. For instance, $BaTiO_3$ nanoparticles transformed from tetragonal to cubic phase at room temperature with the critical crystallite size of approximately 40 nm due to the size effect [7]. One-dimensional, stable ferroelectric monodomain was found in an 80 nm diameter single-crystalline $BaTiO_3$ nanowire [8]. And periodic voltage was generated from the $BaTiO_3$ nanowire by applying periodically varying tensile mechanical strain [9]. Furthermore, Fu and Bellaiche reported that the local dipoles in small $BaTiO_3$ dots prefer to form a vortex-like pattern rather than the traditional viewed structures as arrayed in straight lines in neat rectangular rows and columns based on a first-principles approach [10, 11]. Following their research, Wang et al. [12] and Prosandeev et al. [13] also reported that, in sufficient small nanoscale ferroelectric objects (nanoparticles or nanodots), conventional domain structures should be replaced by vortex domain states based on atomistic simulation modeling. On the other side, Scott et al. [14–16] tried to experimentally verifying the existence of vortex domains, they pointed out that magnetic vortex domains can be stabilized through the physical removal of the vortex 'core', ferroelectrics with hollow structure should offer the greatest opportunity for experimentally creating polarization vortices in ferroelectrics. Periodic arrays of PZT nanorings were fabricated using a self-assembly technique namely the nanosphere lithography (NSL) method [15]. PZT nanorings were synthesized through solution deposition inside of an anodized aluminum oxide nanopores thin film [16]. However, these kinds of polarization vortices have not yet been experimentally observed in these PZT nanorings. Based on these points, the synthesis of hollow single-crystalline $BaTiO_3$ will also offer the opportunity for experimental observation of such vortices domain. But comparatively little work has been

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performed on the fabrication of $BaTiO_3$ with hollow structure. Only, Nakano et al. [17] and Buscaglia et al. [18] reported the synthesis of hollow poly-crystalline $BaTiO_3$ structures by a layer-by-layer colloidal templating method and a two-step process combining colloidal chemistry and solid-state reaction, respectively. But the ferroelectric properties of the above hollow $BaTiO_3$ structures were not yet investigated. All these features make the synthesis of hollow single-crystalline $BaTiO_3$ of great significance.

Hydrothermal method has been considered as one of the most promising routes to synthesize oxide powders with controlled morphology, high crystallinity in a one-step process [19, 20]. This method has been widely used for the synthesis of $BaTiO_3$ powders, nanotabulars and nanowires [21–23]. But there is no literature available about the synthesis of bowl-like $BaTiO_3$ particles based on hydrothermal method. In this study, we report the novel single-crystalline $BaTiO_3$ nanoparticles with bowl-like structure via hydrothermal method. Piezoresponse force microscope measurement has been employed to characterize the properties of the $BaTiO_3$ nanoparticles.

Experimental

Typical synthesis procedure: 0.0102 mol of $Ba(OH)_2{\cdot}8H_2O$ and 0.006 mol of TiO_2 were mixed in 80 ml distilled water. The mixture was transferred into a Teflon-lined stainless steel autoclave (inner volume of 100 ml) and heated at 180°C for 72 h under autogenous pressure. The resulting $BaTiO_3$ powders were filtered, washed with 0.1 M formic acid and deionized water several times, and finally dried at 80°C for 12 h in an oven. In our synthesis, after Titania was added with $Ba(OH)_2$ in solution, TiO_2 would interact with the OH^- and H_2O to form titanium hydroxyl species (probably $HTiO_3^-$). Then, $HTiO_3^-$ reacted with Ba^{2+} ions to form $BaTiO_3$ particles [24].

X-ray powder diffraction patterns (XRD) of the products were obtained on an X-ray diffractometer (Philips PW3050/60, MPSS) using Cu Kα radiation. Raman spectroscopy was performed at room temperature in a Raman spectrometer (Renishaw RM-1000), employing an Ar+ laser for excitation ($\lambda = 514$ nm). Scanning electron microscope (SEM) images were obtained by a scanning electron microscope (JEOL, JSM-5610LV). Transmission electron microscope (TEM) images and high-resolution electron microscope (HREM) images were recorded on a transmission electron microscope (JEOL, JEM-2100F). For TEM observations, the nanoparticles were ultrasonically dispersed in ethanol and then dropped onto carbon-coated copper grids.

The local polarization switching behaviors of the nanoparticles were characterized using high sensitivity piezoresponse force microscopy (PFM) [25, 26]. The characterization was conducted on scanning probe microscope (SEIKO, SPI4000N). A silicon tip coated with Ru (Micro cantilever, SI-DF3-R) was used. The spring constant of the cantilever was 1.6 N/m, and the free resonance frequency was 27 kHz. For sample preparation, $BaTiO_3$ nanoparticles dispersed in water were drop-coated directly onto a highly oriented pyrolytic graphite (HOPG) substrate.

Results and Discussion

The purity and crystallinity of the synthesized samples were examined by the powder XRD technique. The XRD pattern of the prepared $BaTiO_3$ samples is shown in Fig. 1, which could be readily indexed to tetragonal $BaTiO_3$ (JCPDS No. 01-075-0583) with a lattice parameters $a = b = 3.9950$ Å, $c = 4.0340$ Å. The peak splitting around $2\theta = 45°$ is observable in the inset of Fig. 1. Dash lines are positions of each profile of 200 and 002 peaks obtained by the best fit to a mixed Gaussian–Lorentzian distribution. Solid line is the calculated data. Dot line is the observed data. This result suggests that $BaTiO_3$ samples prepared by the hydrothermal method can be assigned to tetragonal symmetry (space group $P4$ mm).

Raman spectroscopy analysis as supplementary method was chosen to identify the $BaTiO_3$ products. Figure 2 shows the Raman spectrum of the $BaTiO_3$ sample. The Raman shift peaks located at around 261, 304, 517 and 715 cm^{-1} match well with the typical Raman peaks of $BaTiO_3$ [27]. The bands around 261 and 517 cm^{-1} are assigned to the transverse optical (TO) modes of A_1 symmetry. The peak at 304 cm^{-1} is assigned to the B1 mode indicating asymmetry within the TiO_6 octahedra of $BaTiO_3$ on a local scale. The peak at 715 cm^{-1} is related to the highest frequency longitudinal optical mode (LO) with A1

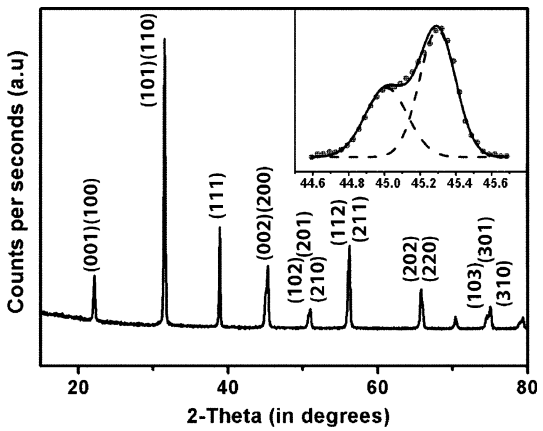

Fig. 1 XRD pattern of the synthesized $BaTiO_3$ product. The inset shows the reflection around 45° 2θ (200)/(002) peak (*filled circle* measured, *thine line* fitted, *thick line* calculated.)

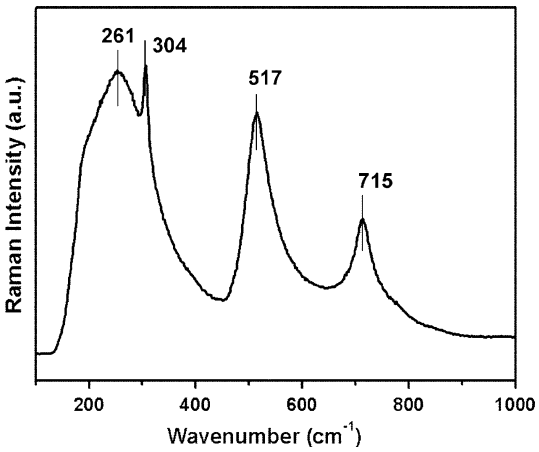

Fig. 2 Raman spectrum of the synthesized $BaTiO_3$ product

symmetry. The intense band at 304 cm^{-1} indicates the presence of tetragonal phase.

Figure 3 shows the representative SEM micrographs of the as-prepared bowl-like $BaTiO_3$ nanoparticles. The low magnification SEM image (Fig. 3a) illustrates that the $BaTiO_3$ product mainly consisted of well-defined bowl-like nanoparticles with a uniform size about 100–200 nm in diameter. A closer examination of these $BaTiO_3$ nanoparticles in Fig. 3b indicates that the nanoparticles all have a concave structure.

TEM and HRTEM provide further insight into the microstructural details of the bowl-like nanoparticles. Figure 4 (a) (b) is the TEM images of typical bowl-like $BaTiO_3$ nanoparticle with a concave in the center. Figure 4(c) shows the corresponding portions of the nanoparticle in Fig. 4(b). The distances of 4.03 and 3.99 Å of lattice fringes can be indexed to the (001) plane and (010) plane of tetragonal $BaTiO_3$, respectively. And the corresponding selected-area electron diffraction pattern (SAED) pattern shown in Fig. 4(d) can be indexed to the reflection of a tetragonal $BaTiO_3$ crystal recorded from the [100] zone axis. The same lattice fringes are observed in the four HRTEM images of Figure c. It well proves that the whole bowl-like nanoparticle is a single-crystalline $BaTiO_3$. Different with the hollow poly-crystalline $BaTiO_3$ spheres reported by Nakano [17] and Buscaglia [18], this novel single-crystalline bowl-like nanoparticle is good candidate for experimental observation of polarization vortices in ferroelectrics.

The local polarization switching behavior and effective piezoelectric coefficients d_{33}^* of the bowl-like $BaTiO_3$ nanoparticles were characterized using PFM. Figure 5(a) gives the scheme of the test and the topography of a typical nanoparticle with a diameter about 150 nm. Figure 5(b) shows the local piezoelectric displacement-voltage loops and piezoelectric hysteresis loops at particle edge (I) and the center concave (II) area marked by arrows in Fig. 5(a). The measurement was achieved by keeping the PFM tip fixed above the nanoparticle and applying a DC voltage from −9 to 9 V while recording the piezoresponse signal [25, 26]. As shown in Fig. 5(b), typical well-shaped "butterfly" loops are observed in both area I and II. The maximum displacements of the two areas are 0.19 and 0.21 nm, which appear at −8.1 and −8.3 V, respectively. The effective piezoelectric coefficient d_{33}^* is calculated from the displacement-voltage loop. The maximum effective d_{33}^* values are estimated to be about 23 and 28 pm/V for area I and area II, respectively, comparable to the reported value (∼22 pm/V) on 20 nm $BaTiO_3$ ceramics based on the same measure method [25]. The measurement clearly shows that polarizations are switchable.

Ferroelectrics with hollow structure should offer the greatest opportunity for experimentally creating polarization vortices domain. But till now, similar with the forerunners' research about the PZT nanorings [15, 16], detailed resolution of polarization behavior in hollow $BaTiO_3$ particles has not been found to be achievable due to the lack of characterization technique, the vortices domains also cannot be measured. But the research of ferroelectric domain state in the unusual way should be a fertile area for further theory and experiment. The unique bowl-like single-crystalline $BaTiO_3$ nanoparticles shown in

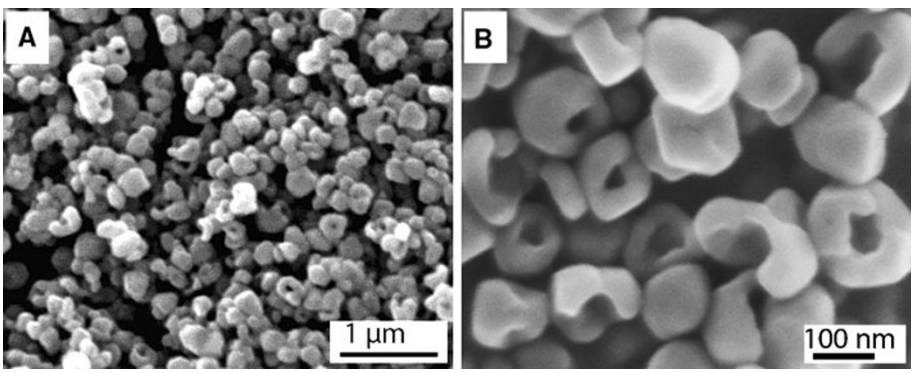

Fig. 3 SEM micrographs of the synthesized $BaTiO_3$ nanoparticles

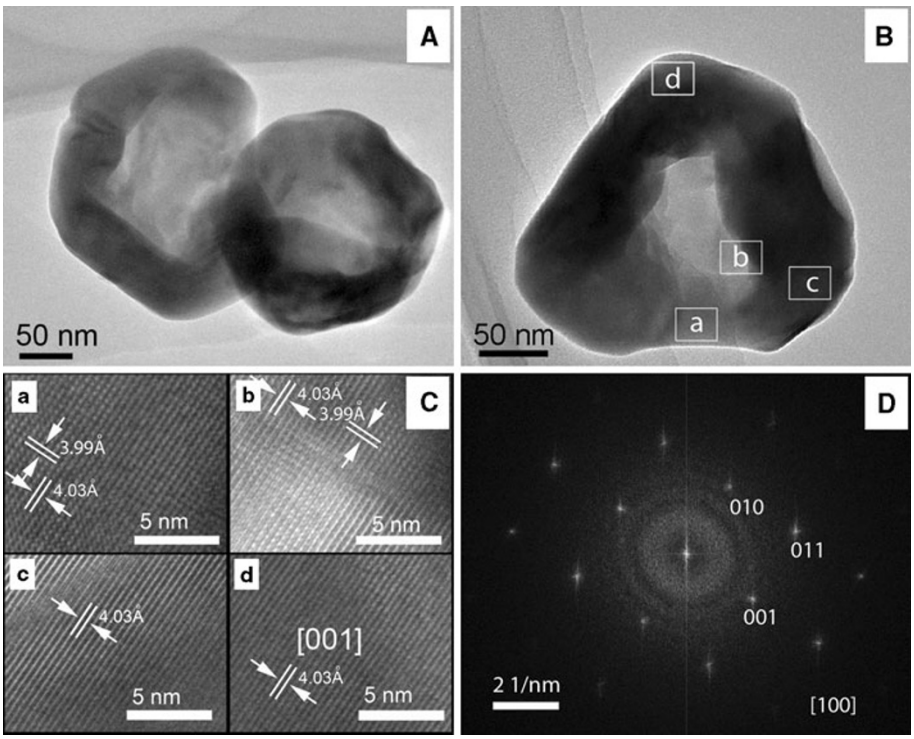

Fig. 4 **a**, **b** TEM images of typical bowl-like $BaTiO_3$ nanoparticles with a concave in the center. **c** HRTEM images of the corresponding portions (*a*), (*b*), (*c*), (*d*) in (**b**). **d** The corresponding fast Fourier transformation (FFT) pattern of portion (*a*)

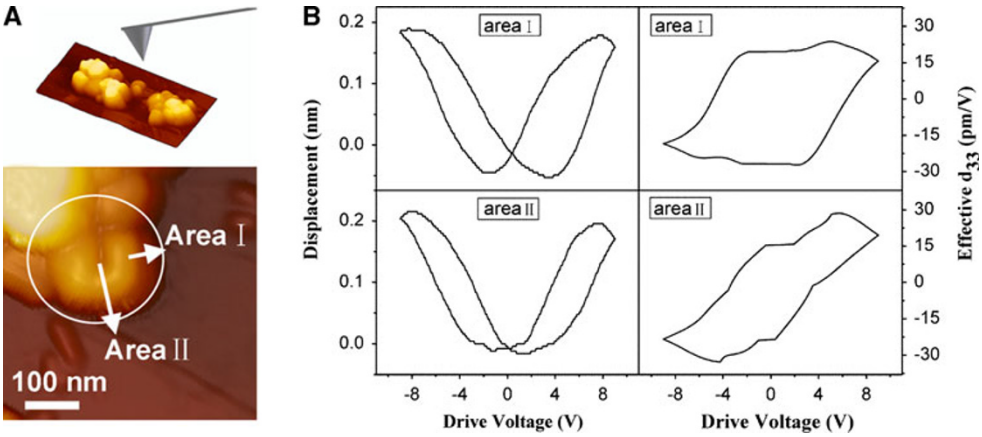

Fig. 5 **a** Topography of the bowl-like $BaTiO_3$ nanoparticle. **b** Local piezoelectric displacement-voltage loops and effective piezoelectric coefficient d_{33}^* of the bowl-like particle at edge (I) and the center concave (II) area

the present study will provide an ideal candidate to investigate the polarization vortices in ferroelectric nanostructures. And this is clearly an objective for our future research.

Conclusions

In summary, bowl-like single-crystalline $BaTiO_3$ nanoparticles have been synthesized through a hydrothermal method using $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 as starting materials. The bowl-like nanoparticles are about 100–200 nm in diameter. HRTEM characterization reveals that the whole nanoparticle is single-crystalline. Piezoresponse force microscope measurements indicate that the local polarization of the $BaTiO_3$ nanoparticle is switchable at room temperature. The local effective piezoelectric coefficient d_{33}^* is approximately 28 pm/V, which is comparable to the reported value ($\sim$22 pm/V) of the $BaTiO_3$ ceramics. These unique $BaTiO_3$ nanoparticles will provide an ideal candidate for fundamental studies of the ferroelectricity and piezoelectricity, which may prove useful in fabricating a variety of nanoscale functional devices.

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