Evolution of Lead Titanate Nanostructures from Nanoparticle Self-Assembly

Maybelyn Leong, Dylan J. Bayerl, Jian Shi, and Xudong Wang*

Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

ABSTRACT

Ferroelectric nanostructures are promising building blocks for advanced electromechanical devices. In this paper, we report a hydrothermal synthesis of PbTiO$_3$ nanoring and nanoring-nanowire hybrid structures. Evolution of the nanoring structure was suggested to be caused by the self-directed assembly of PbTiO$_3$ nanoparticles, where polarization of the ferroelectric nanoparticles might direct the epitaxial arrangement. Vertically aligned NWs were grown epitaxially on the surfaces of the nanorings following the same morphological patterns. All the morphologies were found to simultaneously coexist due to the continuous nucleation and crystal growth during the entire growth period. This research presented a new growth behavior of ferroelectric nanocrystals from a wet-chemistry method. Understanding of the growth mechanism would enhance our capability of controlled synthesizing ferroelectric perovskite nanostructures at large scales and with low cost.


1. INTRODUCTION

Ferroelectric nanomaterials are a focus of much research interest on exploiting the nanometer-scale polarization, piezoelectric and dielectric properties. The one-dimensional (1D) morphological form, such as that of the nanowire (NW), is of particular interest due to the unique ferroelectric domain structure, superior mechanical properties, and possible electromechanical coupling enhancement. Ferroelectric NWs are also promising building blocks for the recently developed nanogenerator concept that converts nanoscale mechanical energy into electricity. Although perovskite thin films can be easily prepared via various means, the synthesis of single-crystalline NWs is rather more challenging due to their multi-component composition and cubic or tetragonal lattice structures. Wet-chemical methods were usually used to grow perovskite NWs via a strategy of surface passivation/modification to enhance the anisotropic crystal growth. The easy scaling-up and cost effectiveness also makes wet-chemical methods promising for potential industrial-level manufacturing. To fully realize the potential of perovskite nanostructure synthesis, it is essential to obtain good understanding of the nanoscale growth mechanisms, size and crystallography relationships, and controlling factors of size and morphology of the targeted nanomaterials. Lead titanate (PbTiO$_3$) is a perovskite ferroelectric material with the Curie temperature of 490 °C. It is also one of the end members of several very important ferroelectric ceramics, such as Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ (PZT) and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_5$-PbTiO$_3$ (PMN-PT). Therefore, synthesis of PbTiO$_3$ nanostructures could fundamentally improve our capability of fabricating ferroelectric nanomaterials with complex compositions as well as developing advanced piezoelectric nanodevices. A number of previous researches investigated the growth of PbTiO$_3$ nanostructures by template-assisted deposition or hydrothermal processes. Aligned NW structures were also realized via epitaxial substrate directed growth. In this paper, we report a synthesis of PbTiO$_3$ nanorings, nanoplates and NW hybrid structures by a hydrothermal method. These morphologies imply a multi-step self-directed arrangement mechanism of PbTiO$_3$ nanostructure growth. A series of experiments were conducted varying the time and conditions of the reaction in order to elucidate the growth mechanism. This result provided a new insight into the unique growth behavior of ferroelectric nanocrystals.

2. EXPERIMENTAL DETAILS

To prepare PbTiO$_3$ nanostructures, 2 mL of 1.5 M citric acid (99.5+%, Sigma-Aldrich) was pipetted into a glass beaker and sealed with paraffin film. The solution was heated to a temperature of 60 °C, at which point 0.28426 g (1 mmol) of liquid titanium isopropoxide (97%, Sigma-Aldrich) was added during vigorous stirring. A white precipitate formed immediately. Then, 2 mL concentrated
ammonium hydroxide (28–30% NH₃, Sigma-Aldrich) was added to the mixture. Next, 0.37977 g (1 mmol) lead acetate trihydrate (99.99+%, Sigma-Aldrich) was added followed by 0.4202 g (6.77 mmol) ethylene glycol (99.9%, Fisher Scientific) and stirred until the mixture was homogenized. 1 g potassium hydroxide (99%, Sigma-Aldrich) was then added, which briefly raised the temperature of the mixture. The mixture was allowed to cool back to 60 °C. Finally, 0.34848 g (1 mmol) dodecylbenzenesulfonic acid (Aldrich-Chemistry) was added and mixed thoroughly. The temperature of the precursor mixture was reduced to 50 °C and stirred for another 30 minutes. The prepared precursor mixture of approximately 5 mL was then transferred into a 20 mL PTFE cup with the addition of 1 mL concentrated ammonium hydroxide (28–30% NH₃, Sigma-Aldrich). The PTFE cup was sealed in an autoclave bomb and put into a convection oven at 32 °C. The oven temperature was then increased to 180 °C at a ramp rate of 5 °C/min. After reacting for 24 hours at 180 °C, bomb was slowly cooled in the oven back to 32 °C. Autoclave bomb was taken out of the oven and rested in a fume hood for half a day. The reaction products were then collected and the solid precipitate was washed with DI water and ethanol. Dilute suspensions of purified precipitate in water were dried on Si substrate in a convection oven at 90 °C for 2 hours for further characterization.

The as-received PbTiO₃ nanostructures were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

3. RESULTS AND DISCUSSION

SEM observation shows that the morphology of the as-received PbTiO₃ nanostructures is dominated by a ring-like structure (Fig. 1(a)). All nanorings exhibited a square-like shape with side lengths of ∼4–5 μm. The wall thickness of the nanorings ranged from ∼300 nm to ∼1 μm. There were typically two nanoring morphology variants, as shown in Figures 1(b) and (c). Some nanorings had a uniform wall thickness on each side and were considered as perfect nanorings (Fig. 1(b)). Some nanorings had their centers partially filled by the accumulation of nanocrystals (Fig. 1(c)). The ratio and portion of the filled center area was random. Occasionally, nanorings with 100% filled center were observed. Both morphologies appeared to be constructed by the assembly of small rectangular nanocrystals, which were epitaxially stacked together. Thus, serrated edges of the nanorings (both inside and outside) were created. Contrast differences also revealed the arrangement of small crystals on top of the walls of the nanorings (Fig. 1(b)). The center-filling crystals also showed the same orientation as the nanoring itself, indicating they were assembled via the same process (Fig. 1(c)). The small crystal arrangement is an important phenomenon for understanding the growth mechanism of the nanoring structure.

The phase of the PbTiO₃ nanostructures was first characterized by XRD. The pure tetragonal perovskite PbTiO₃ structure was confirmed by the spectrum shown in Figure 2. No other PbTiO₃ phases or reactant residues were observed. This information suggested that the
The detailed crystal structure of a single nanoring was studied by TEM. Figure 3(a) shows low-magnification TEM image of a perfect PbTiO$_3$ nanoring, where the small crystal ($\sim$10–20 nm in size) arrangement can be clearly observed. This image also proved that the nanoring was not a single crystal. The bright contrast inside the nanoring wall indicates that there were open or hollow spaces left inside the nanoring, which was a reasonable outcome of the stacking of small crystals. Selected area electron diffraction (SAED) was taken at different locations on the nanoring and exactly the same patterns were obtained, as shown in the inset of Figure 3(a). This observation suggests that all small crystals were epitaxially assembled together, exhibiting the same crystal orientation. The SAED pattern further confirmed the tetragonal perovskite structure of the PbTiO$_3$ nanoring. The overall nanoring had its basal plane aligned with the (001) facet of PbTiO$_3$ and serrations of the side walls were composed of many equivalent (100) and (010) surfaces from the small PbTiO$_3$ crystals. A closer observation of the serrated edge is shown in Figure 3(b). The 90$^\circ$ crystal corners exhibited a degree of overlap, indicating a multilayer arrangement of the small crystals. High resolution TEM image at the boundary region is shown in Figure 3(c). It can be clearly seen that at this interface, all the crystals exhibited the same continuous lattice orientation. The identical SAED patterns on the nanoring and continuous crystal lattice at the interfaces confirmed that the nanorings were composed by many small rectangular single-crystalline nanocrystals that were stacked and merged together epitaxially.

Further experiments demonstrated that the nanorings (filled or unfilled) could serve as templates for orientated NW growth. By extending the growth time (from 24 hours to 48 hours) or increasing the amount of ammonia (from 2 mL to 3 mL), NW morphology was developed on the basis of the nanoring structures. Typical morphologies are shown in Figure 4. All the NWs were perfectly aligned perpendicular to the basal plan of the nanorings, suggesting all the NWs were grown along the [001] direction. These NWs showed a very high density and were frequently merged together.

Similar to the two observed nanoring morphologies (perfect ring and filled ring), the aligned NWs also showed such two types of arrangements. As shown in Figure 4(a), aligned NWs could form a seamless wall with almost identical height on both sides of an obvious mirror plane at the center. Longer NWs could be observed with the same distribution but their length variance became significant (Fig. 4(b)). Another configuration of aligned NWs was similar to the filled rings. On both sides of a center mirror plane, vertically aligned NWs formed a highly packed plate (Fig. 4(c)). Occasionally, aligned NWs with less density could also be found, where the NWs exhibited larger length variance (Fig. 4(d)). From such a configuration, the
center plane can be clearly seen and it showed a very similar structure as the filled nanorings. It should be noticed that under elongated reaction time or more active reaction conditions (higher pH), the nanoring-NW hybrid structure could always been coexisting with the nanoring structures. Independent NWs with different lengths were also a common occurrence of the PbTiO₃ nanostructure samples.

Based on these observations, the evolution of the PbTiO₃ nanostructures was proposed as schematically shown in Figure 5. When desired growth conditions were reached in the initial precursor solution, small PbTiO₃ nanoparticles were formed first (step (i) in Fig. 5). The polarization of these ferroelectric nanoparticles possibly aligned and connected them together, forming larger pieces. Further growth and additional nanoparticle attachment led to the growth of the epitaxial polycrystalline plates. As the growth progressed, the crystals in the plate centers could gradually deplete, migrating to the side, possibly driven by a reduction of overall surface energy for the entire structure (step (ii) in Fig. 5). Observation of a large percentage (>30%) of partially filled nanoring structures suggested such a relationship between the perfect nanorings and fully filled nanorings (or nanoplate). The nanoring structures could then serve as substrates for homoepitaxial growth. Thus, most nanoring-NW hybrid structures had a symmetric structure about the nanoring which was considered as the center mirror plane. As such, a perfect nanoring would lead to the formation of a cylindrical wall of packed vertical NWs. For a filled nanoring, NWs could grow epitaxially anywhere on either face of the nanoring, allowing the density of these NWs to vary significantly. It should be noted that the NW nucleation and growth could occur anytime during the growth, simultaneously with the formation of nanoring structures. Therefore, mixture of all the morphologies were always found in the same sample and the NWs exhibited a large variation in their length.

4. CONCLUSION

In summary, PbTiO₃ nanoring and nanoring-NW hybrid structures were synthesized by a hydrothermal method. Evolution of the nanoring structure was suggested to be caused by the self-directed assembly of PbTiO₃ nanoparticles, where polarization of the ferroelectric nanoparticles would direct the epitaxial arrangement. Vertically aligned NWs could be further grown epitaxially on the surfaces of the nanorings following the same morphological patterns. All the morphologies were found existing together due to the continuous nucleation and crystal growth during the entire growth period. More precise growth condition control may enable selectively obtaining one particular morphology. This research presented a new growth behavior of ferroelectric nanocrystals from a wet-chemistry method. Understanding of the growth mechanism would enhance our capability of controllably synthesizing ferroelectric perovskite nanostructures at large scales and with low cost.

Acknowledgment: We thank the support of National Science Foundation under grant No DMR-0905914 and UW-Madison graduate school.

References and Notes