Synthesis and characterization of perovskite PbTiO$_3$ nanoparticles with solution processability$^\dagger$

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Ferroelectrics with perovskite structure (ABO$_3$), for example, lead titanate (PbTiO$_3$), are the most studied ferroelectric oxides because of their versatile properties for use in thin film capacitors, electronic transducers, actuators, high-k dielectrics, pyroelectric sensors, and nonlinear optics. The studies on nanostructured PbTiO$_3$ are limited, mainly due to the lack of facile synthetic techniques to prepare nano-sized PbTiO$_3$, i.e., colloidal PbTiO$_3$ nanoparticles. Herein, we presented a novel nonaqueous, relatively low temperature, and highly scalable route to PbTiO$_3$ nanoparticles. The use of oleic acid as surface capping ligand provides nanoparticles with good solubility in organic solvents, thereby enabling the low-cost solution based processing. Rather than the use of expensive bimetallic alkoxide precursors, common chemicals were utilized in this non-hydrolytic thermal decomposition approach; moreover, there is no need for extremely high temperature and long reaction time, making it possible for the large scale synthesis.

Introduction

Ferroelectric materials are a class of materials that possess high dielectric constants, relatively low dielectric loss, high electrical resistivity, moderate dielectric breakdown strength, and strong electromechanical and electrooptical behaviors.$^{1,2}$ They exhibit spontaneous polarization and the ability to switch polarization direction. Ferroelectrics with perovskite structure (ABO$_3$), such as barium titanate (BaTiO$_3$) and lead titanate (PbTiO$_3$), are the most studied ferroelectric oxides because of their versatile properties for use in thin film capacitors, electronic transducers, actuators, high-k dielectrics, pyroelectric sensors, and nonlinear optics. The particles with nanoscopic dimensions have received considerable research attention due to the unconventional chemical and physical properties (e.g., electronic, optical) at the nanoscale, for example, the size dependent optoelectronic properties of semiconducting quantum dots$^{3-6}$ and the size dependent magnetic properties of multiferroic nanocrystals.$^7$ Moreover, nanoparticles can serve as ideal building blocks for bottom-up nanofabrication for developing low-cost, miniaturized electronic devices whose functionalities are enabled by the properties of the individual nanoparticles and their arrangement.

PbTiO$_3$ is widely used in various electronic devices as a result of a large pyroelectric coefficient and relatively low permittivity.$^8-10$ In stark contrast to numerous reports on the synthesis of BaTiO$_3$ particles, there exists few for the PbTiO$_3$ particles, including sol–gel process$^{10,11}$ (e.g., the hydrolysis of metal alkoxides), hydrothermal synthesis,$^{9,12}$ and dip-pen nanolithography,$^{13}$ liquid-solid-solution strategy,$^{14}$ and solid-state metathesis reaction.$^{15}$ The size of PbTiO$_3$ particles is often not well controlled.$^{11}$ and certain stringent experimental condition may be required.$^{11}$ Furthermore, the lack of solvent solubility, for example, particles that are produced by hydrothermal approach, limits the use of low-cost, solution processing techniques, such as spin coating, spraying and evaporative self assembly.$^{16}$

Herein we presented a novel nonaqueous, relatively low-temperature, and highly scalable route to PbTiO$_3$ nanoparticles. The use of oleic acid as surface capping ligand provides nanoparticles with good solubility in organic solvents, thereby enabling the low-cost solution based processing. Rather than the use of expensive bimetallic alkoxide precursors, common chemicals were utilized in this non-hydrolytic thermal decomposition approach; moreover, there is no need for extremely high temperature$^{10,15}$ and long reaction time,$^{10,11}$ making it possible for the large scale synthesis. The formation of ferroelectric PbTiO$_3$ nanoparticles depends on the reaction time, surface capping ligand and temperature, and was systematically studied. X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the crystalline structures and chemical compositions of PbTiO$_3$ nanoparticles.

Experimental

Synthesis of PbTiO$_3$ nanoparticles

In an argon protected glove box, 1 mmol of lead acetate (99.99%, Sigma Aldrich) was first dissolved in 10 ml of anhydrous benzyl alcohol (Sigma Aldrich) to form a transparent solution, to which 1 mmol of titanium isopropoxide (97%, Sigma Aldrich) was added. The mixture was magnetically stirred for 30 min to form a uniform solution, followed by adding 0.3 ml oleic acid (technical grade, Sigma Aldrich) to the solution and stirred for another 10 min. The reaction mixture was then transferred to a Teflon lined autoclave (45 ml, Parr Instrument). The autoclave...
was then taken out from the glove box and heated in an oven at 200 °C for 2 h. After cooling down to room temperature, the white jelly-like product was collected (Fig. 1a) and purified by a precipitation-redissolution process with ethanol and toluene. The purification process was repeated for three times and the final product was dried at the elevated temperature in air, yielding yellow powder (Fig. 1b), a typical color of lead titanate (PbTiO$_3$).

All chemicals were used as received without further purification.

Characterization

Transmission electron microscopy (JEOL 2100, operating at 200 kV, MNIF at Iowa State University), X-ray powder diffraction (XRD), and Thermalgravimetric analysis (TGA) were used to characterize the obtained PbTiO$_3$ nanocrystals. To prepare TEM samples, a drop of dilute PbTiO$_3$ nanocrystal toluene solution was casted on a carbon coated copper TEM grid (400 mesh) and allowed to dry in air. For XRD samples, concentrated PbTiO$_3$ nanocrystal toluene suspension was drop-casted on Si wafer and dried to form a yellowish thin film. Dry powders of as-synthesized PbTiO$_3$ nanoparticles were used for TGA analysis, in both air and N$_2$ atmospheres.

Results and discussion

Lead acetate and titanium isopropoxide were used as Pb and Ti sources, and the reaction was conducted in benzyl alcohol in a Teflon lined autoclave placed in an oven (see Experimental). It has been shown that benzyl alcohol is a versatile solvent for controlling crystallization and stabilization of oxide nanocrystals.\textsuperscript{20,21} Fig. 1 shows the digital images of jelly-like PbTiO$_3$ nanoparticles in toluene; and (b) PbTiO$_3$ nanoparticles after purification and dried. PbTiO$_3$ nanoparticles were obtained after heating at 200 °C for 2 h in an oven.

The TEM images of as-synthesized, oleic acid-capped PbTiO$_3$ nanoparticles are shown in Fig. 2. The nanoparticles have an average diameter of 4 nm (Fig. 2a), which is two orders of magnitude smaller than those prepared by hydrothermal approach.\textsuperscript{13} The high resolution TEM (HRTEM) image of individual nanoparticle revealed its crystalline nature, with the lattice spacing of 2.76 Å and 2.29 Å (Fig. 2b) that can be indexed to $<110>$ and $<111>$ crystalline planes of tetragonal phase of PbTiO$_3$.

Fig. 3 shows the XRD patterns of as-synthesized, oleic acid-functionalized PbTiO$_3$ nanoparticles and that after subsequent thermal annealing at 600 °C for 10 min. For the as-synthesized nanoparticles, no specific diffraction peaks were observed except a broad peak around $2\theta = 30^\circ$, which may be due primarily to the fact that the particle size is quite small (~4 nm) and the nanoparticles were not fully crystallized, as revealed by HRTEM (Fig. 4a). To this end, high temperature annealing was performed to promote the crystallization of nanoparticles. The emergence of XRD peaks, indexed to tetragonal PbTiO$_3$, was resulted from the aggregation of nanoparticles and improved crystalization of nanoparticles (Fig. 3). The aggregation was confirmed by TEM measurement on the annealed PbTiO$_3$ solid powders (Fig. 5a), in which particles with the average size of 60 nm were obtained after annealed at 500 °C for 10 min. It is clearly evident that the characteristic peaks of tetragonal PbTiO$_3$ start to emerge at the annealing temperature of 400 °C (Fig. 6).

Notably, longer time heating (i.e., 6 h) at 200 °C did not yield fresh nanoparticles with increased crystallinity, as evidenced by HRTEM (Fig. 4b) and XRD (Fig. 7) measurements. Subsequent annealing at 600 °C yielded tetragonal PbTiO$_3$ (Fig. 7), similar to
the 2 h heating samples (Fig. 3). Fig. 8a shows the TEM image of dispersed PbTiO₃ nanoparticles obtained after heating at 200 °C for 6 h, having an average diameter of 4 nm. It is noteworthy that no change in the nanoparticle size after a lengthy reaction (i.e., 48 h; Fig. S1), suggesting that a short reaction of 2 h is sufficient to achieve nanoparticles in the study.

Intriguingly, partially crystalline PbTiO₃ nanoparticles can also be produced without the use of oleic acid as surface ligand (Fig. 4c and 8b); the particles have a diameter of 4 nm, same as those passivated with oleic acid (Fig. 2 and 8a). However, these particles tend to aggregate in both polar and non-polar solvents.

Fig. 4 HRTEM images of PbTiO₃ nanoparticles that are partially crystalline (only crystalline nanoparticles are marked; the others are amorphous). (a) particles obtained after heating at 200 °C for 2 h with the oleic acid used as surface capping ligand; (b) particles obtained after heating at 200 °C for 6 h with the oleic acid used as surface capping ligand; and (c) particles obtained after heating at 200 °C for 2 h without the addition of oleic acid. Scale bars = 5 nm.

Fig. 5 TEM images of PbTiO₃ nanoparticles annealed at 500 °C for 10 min. (a) particles obtained after heating at 200 °C for 2 h with the oleic acid utilized as surface capping ligand; (b) particles obtained after heating at 200 °C for 2 h without the addition of oleic acid. Scale bars = 200 nm. To prepare samples for TEM characterization, annealed PbTiO₃ nanoparticles were dispersed in ethanol by ultrasonication, followed by drop casting the suspension on carbon coated copper TEM grid and allowed to dry in air.

Fig. 6 XRD pattern of PbTiO₃ nanoparticles annealed at different temperatures, ranging from 200 °C to 500 °C. The fresh PbTiO₃ nanoparticles were obtained after heating at 200 °C for 2 h with the oleic acid utilized as surface capping ligand.

Fig. 7 XRD patterns of fresh PbTiO₃ nanoparticles (black curve) and the sample after annealed at 600 °C (red curve). The characteristic peaks can be assigned to tetragonal phase of PbTiO₃ crystal (PDF # 06-0452). The fresh PbTiO₃ nanoparticles were obtained after heating at 200 °C for 6 h with the oleic acid utilized as surface capping ligand.

Fig. 8 TEM images of PbTiO₃ nanoparticles obtained at different reaction conditions. (a) heating at 200 °C for 6 h, with oleic acid used as the surface ligand; and (b) heating at 200 °C for 2 h, without the addition of oleic acid. Scale bar = 20 nm.
Fig. 8b). XRD patterns of this sample after annealed at 500 °C are shown in Fig. 9. Unlike the PbTiO3 nanoparticles passivated with oleic acid, an annealing temperature of 500 °C was found to be necessary for the emergence of characteristic peaks; TEM imaging shows that the size of nanoparticle aggregates obtained after annealed at 500 °C is larger than 100 nm (Fig. 5b), demonstrating the formation of larger aggregates, compared to the 60-nm aggregates obtained from the annealing of oleic acid functionalized nanoparticles at the same temperature (Fig. 5a). High resolution TEM results indicate that these nanoparticle aggregates are near single crystalline (Fig. S3).

The capping of oleic acid on the particle surface was further verified by TGA (Fig. 10 and Fig. S4). Under both air and N2 atmosphere, a difference in mass loss observed for nanoparticles with and without the oleic acid passivation was due to the monolayer of oleic acid attached to the particles surface. According to the TGA measurements (Fig. 10 and Fig. S4), negligible difference in mass loss was seen from the analysis performed under the air and N2 flows, confirming that the fresh nanoparticles possess the same chemical composition as the annealed samples (i.e., PbTiO3), although the obvious difference in XRD patterns was observed (e.g., Fig. 3).

Conclusions

In summary, PbTiO3 nanoparticles with good solvent solubility were synthesized via a non-aqueous route. This method may also be scaled up, thereby providing practical potential. The crystallinity of as-synthesized nanoparticles was low. Subsequent high temperature annealing promoted crystallization and aggregation of nanoparticles, leading to tetragonal phase of PbTiO3. The PbTiO3 nanoparticles can be utilized as building blocks for assembly of intriguing nanodevices, as well as for exploring the fundamental nanoscale properties of PbTiO3, which has not yet been well studied. They can also be used to prepare intriguing ferroelectric/superparamagnetic core/shell nanoparticles (e.g., PbTiO3/Y3Fe5O12), which are potentially useful for tunable multifunctional (i.e., coexistence of ferroelectricity, piezoelectricity, and superparamagnetism) devices. These PbTiO3 nanoparticles with fine particle size also offers a good sinterability to yield advanced ceramic materials.

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Notes and references


Fig. 9 XRD patterns of fresh PbTiO3 nanoparticles (black curve) and the samples annealed at different temperatures, ranging from 200 °C to 600 °C. The characteristic peaks can be assigned to tetragonal phase of PbTiO3 crystal (PDF # 06-0452). The fresh PbTiO3 nanoparticles were obtained after heating at 200 °C for 2 h without the addition of oleic acid (e.g., ethanol and toluene, as shown in Fig. S2) due to the lack of coating with surfactant, which has been considered essential for providing the solvent solubility to nanoparticles. The aggregation is witnessed when casting the nanoparticle suspension on the carbon coated TEM grids (Fig. 8b). XRD patterns of this sample are shown in Fig. 9. Unlike the PbTiO3 nanoparticles passivated with oleic acid, an annealing temperature of 500 °C was found to be necessary for the emergence of characteristic peaks; TEM imaging shows that the size of nanoparticle aggregates obtained after annealed at 500 °C is larger than 100 nm (Fig. 5b), demonstrating the formation of larger aggregates, compared to the 60-nm aggregates obtained from the annealing of oleic acid functionalized nanoparticles at the same temperature (Fig. 5a).

Fig. 10 TGA curves of PbTiO3 nanoparticles obtained after heating at 200 °C for 2 h with the oleic acid used as surface capping ligand (Black curve was obtained under air flow, and red curve was obtained under N2 flow).