Experimental and simulation-based understanding of morphology controlled barium titanate nanoparticles under co-adsorption of surfactants

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Well dispersed single-crystalline BaTiO₃ nanoparticles with controlled morphologies were synthesized using a thermohydrolysis route. The nanoparticles were tuned from spherical to cubic upon changing the NaOH concentration under a critical molar ratio of oleic acid to hydrazine. Density functional theory (DFT) and molecular dynamics (MD) calculations indicated that hydrazine molecules adsorbed preferably on the Ti position of the Ti–O terminated surface; meanwhile, oleic acid molecules tended to adsorb on the Ba position of the Ba–O terminated surface. The added hydrazine changed the formation mechanism of BaTiO₃ nanoparticles from an in situ growth to a dissolution–precipitation growth. Excellent dispersibility in aqueous solution was achieved for the BaTiO₃ nanoparticles under the assistance of hydrazine. Meanwhile, a high-quality self-assembled film with a stable dielectric constant of 30 in the frequency range from 0 Hz to 1 MHz was prepared using the well dispersed BaTiO₃ nanoparticles, providing a novel low-temperature route for the fabrication of perovskite films.

1. Introduction

Barium titanate (BaTiO₃) is widely used as a dielectric material for preparing multilayer ceramic capacitors (MLCCs), embedded capacitors in printed circuit boards, positive temperature coefficient of resistance (PTCR) thermistors, high-performance nanocomposites, and electro-optic devices.1–7 With the desired miniaturization of developed MLCCs possessing high performance, controlled morphology and good dispersibility on the nanoscale are necessary for using BaTiO₃ particles because the crystal face, morphology and size distribution of source nanoparticles significantly influence the electrical properties of BaTiO₃ ceramics. Due to successful industrialization of the hydrothermal synthesis of BaTiO₃ nanoparticles in aqueous solution, wet methods, such as co-precipitation, hydrothermal and sol–gel have been intensely reported for the preparation of BaTiO₃ nanoparticles.8–11 Surfactants, NaOH concentration, microwave, and sonochemistry are the most commonly used approaches to improve the crystallinity, size distribution and morphology of BaTiO₃ nanoparticles.12–14 Monodispersed BaTiO₃ nanoparticles were fabricated by using wet methods.15–18 For example, an in situ growth process was designed to control the morphology of BaTiO₃ nanoparticles in aqueous solution.15 Nucleation and growth of BaTiO₃ nanoparticles occurred in the Ti-based hydrogel that was formed from the hydrolysis of bis(ammonium lactate) titanium dihydroxide (TALH). The BaTiO₃ nanocubes with a size of ca. 15 nm and their superlattices were obtained through changing the molar ratio of oleic acid (OLA) to tert-butylamine. During the process, high concentrations of surfactant and long time (72 h) were necessary, and the morphology control of BaTiO₃ nanoparticles was not easy to achieve. Due to the strong coordination effect of OLA molecules with metal ions, a high concentration of OLA limited the dissolution of Ba ions from the Ti–O hydrogel through the hydrolysis of a Ti precursor, and thus tert-butylamine had to be added as a co-surfactant to control the adsorption of OLA at the initial formation stage of the BaTiO₃ phase.15 Thus, a novel additive is urgently needed for the morphology control and low cost synthesis of BaTiO₃ nanoparticles in this process. Based on this thought, we found that hydrazine was an ideal additive for low cost, high speed and morphology controlled synthesis of BaTiO₃ nanoparticles in...
this work. The synthesis design developed in this work shows notable breakthroughs compared with previously reported discoveries. First, the minimum concentration of oleic acid needed for morphology control was only one quarter compared to tert-butylamine as the surfactant. Second, morphology control of BaTiO3 particles such as cubic, polyhedral and spherical shapes was realized through tuning the NaOH concentration. Furthermore, the growth mechanism of BaTiO3 nanoparticles became a dissolution–precipitation growth process instead of an in situ growth process as reported earlier. Although alkylamines and OLA are usually used as the surfactants for the morphology control of nanocrystals, their effects on crystal control have been reported. However, their detailed roles in the morphology control and interaction with certain crystalline planes have not been well revealed yet.

In this work, we applied density functional theory (DFT) and molecular dynamics (MD) methods to investigate the effect of hydrazine and OLA on the formation mechanism and morphology control of BaTiO3 nanoparticles. DFT calculation is an accurate method in physical analysis on the atomic scale. Meanwhile in some large atomic systems, MD calculations were carried out due to the limitation of computer capacity. For example, Padilla et al. calculated the surface energies of BaTiO3 crystal faces by DFT calculation. Yasui et al. theoretically studied the formation of BaTiO3 mesocrystals. We found that the favorite adsorption positions of hydrazine and OLA are different. Hydrazine molecules were identified to be the Ti top position on the Ti–O terminated faces. Meanwhile, the favorite adsorption position for oleic acid molecules was identified to be the Ba–O terminated face. Different adsorption characters of hydrazine and oleic acid favored the selective adsorption of OLA on BaTiO3 faces and good dispersion of the BaTiO3 nanoparticles in aqueous solution. Only nanocubes showed the tendency to form superlattices through oriented aggregation in the synthesis process. Owing to high stability and good dispersion in aqueous solution, high quality self-assembled films of BaTiO3 nanocubes were prepared and their dielectric related properties were evaluated.

2. Experimental

2.1 Particle synthesis

In a typical synthesis process, 0.72 mL TALH (TALH, 0.05 mol L\(^{-1}\), Ba:Ti = 1:1) was added into 24 mL Ba(OH)\(_2\) aqueous solution (Ba(OH)\(_2\), 0.05 mol L\(^{-1}\)), and then 6 mL NaOH aqueous solution (5 M) was added under mechanical stirring. The initial concentration of NaOH was 1 mol L\(^{-1}\). The aqueous solution was transferred into a 50 mL autoclave, and then hydrazine and oleic acid (OLA) (Ba:OLA:hydrazine = 1:2:4 in molar ratio) were added into the solution. The sealed autoclave was heated at 220 °C for 48 h, and then cooled down to room temperature. After the synthesis, the precipitate was centrifugally separated and washed twice with ethanol, and then dispersed into deionized water.

2.2 Adsorption energy calculation

Density functional theory (DFT) calculations were performed to investigate the adsorption of hydrazine on BaTiO3 crystal faces, using the CASTEP code aided by the Material Studio graphical front-end interface. The generalized gradient approximation (GGA) in the Perdew, Burke, and Ernzerhof (PBE) form was used in energy calculations in different adsorption models. Ultrasoft pseudo potentials were used in the treatment of core electrons. The kinetic cutoff energy was set to be 300 eV and the Monkhorst-Pack special \(k\)-point mesh was 2 \(\times\) 2 \(\times\) 1.

The BaTiO3 surfaces were studied systematically by theoretical calculations. The (100) face was selected for the DFT calculation because of its highest density of metal ions in the BaTiO3 crystal structure. The (100) face has two typical flat terminations, the Ba–O and Ti–O terminations. In our calculations, a periodic slab with the Ba–O terminated surface containing four Ba–O layers and three Ti–O layers, and a periodic slab with the Ti–O terminated surface containing four Ti–O layers and three Ba–O layers were created, as shown in Fig. 1a and b. The vacuum thickness was set to be 15 Å, in order to avoid the influences of periodic boundary conditions.
The BaTiO$_3$ nanoparticles were characterized by X-ray diffraction (XRD, D5005HR 3 kw), scanning electron microscopy (SEM, FESEM SU-70), transmission electron microscopy (TEM, JEOL JEM-4010), dynamic light scattering (DLS, ELSZ-1000S), and Fourier transform infrared spectrometry (FT-IR, IRPrestige-21) methods and using a Precision LCR meter (Quadtech 7600 Plus).

3. Results and discussion

Fig. 2 shows the XRD patterns of the BaTiO$_3$ particles synthesized at different NaOH concentrations with Ba : OLA : hydrazine = 1 : 2 : 4 for 48 h. The XRD patterns of all the samples revealed good crystallinity and corresponded to diffraction peaks of the cubic BaTiO$_3$ phase. The weak peaks of the BaCO$_3$ phase at about 24$^\circ$ were identified from the XRD pattern of the particles synthesized at 1.5 mol L$^{-1}$ NaOH. The morphology of BaTiO$_3$ particles can be controlled through the synthesis conditions and this is summarized in Table 1. Fig. 3 shows the TEM images of the particles synthesized at different NaOH concentrations with Ba : OLA : hydrazine = 1 : 2 : 4 for 48 h. The morphology of the BaTiO$_3$ nanoparticles changed with increasing the NaOH concentration. Few BaTiO$_3$ nanocubes with a size of ca. 20 nm and unreacted Ti-based gel were observed for the particles synthesized at 1.0 mol L$^{-1}$ NaOH, as shown in Fig. 3a. When the NaOH concentration was increased to 1.2 mol L$^{-1}$, polyhedral particles with a size of ca. 20 nm (Fig. 3b) were mainly observed. For the particles synthesized at 1.5 mol L$^{-1}$ NaOH, nanocubes with round edges were obtained and the particle size ranged from 13 to 18 nm (Fig. 3c). When the NaOH concentration was increased to 2.0 mol L$^{-1}$, spherical particles with a size of ca. 20 nm were obtained (Fig. 3d). These results indicated that the morphology of BaTiO$_3$ particles could be adjusted through changing the NaOH concentration.

Fig. 4 shows the TEM images of the particles synthesized at different NaOH concentrations with Ba : OLA : hydrazine = 1 : 2 : 4 for 72 h. After a long reaction time, only BaTiO$_3$ nanoparticles were identified for the samples synthesized at 1.0 mol L$^{-1}$ NaOH (Fig. 4a). Meanwhile, nanocrystals with an

For each model, three typical initial adsorption positions were selected (Fig. 1c and d) to calculate the adsorption energy.

Molecular dynamics (MD) calculations, which are more suitable for the simulations of large molecules, were also performed to identify the adsorption energy of a single oleic acid molecule, using the forcite module aided by the Material Studio graphical front-end interface. The canonical ensemble (NVT) and universal force field$^{35}$ were used for the calculations. The temperature was set to be 298 K and the equations of motion were integrated with a 1 fs time step.$^{36}$ For each model, the total number of dynamics steps was 200 000.$^{37}$

The models used in MD calculations were constructed as follows. Firstly, a BaTiO$_3$ unit cell was constructed and then optimized by MD calculation. The lattice parameter of the optimized unit cell (4.01 Å) is close to the experimental data (4.00 Å)$^{37}$ which suggests that the universal force field can describe our models well. The (100) surface model was created from the unit cell with 7 layers in the z direction (similar to the models used in DFT calculations). The size of the surface was enlarged to 4 × 4 (in fractional units where 1 represents the lattice parameter) along the x and y directions and the vacuum thickness was adjusted to 40 Å to adapt to the large size of an oleic acid molecule. The surface model was then optimized by MD calculations to simulate the reconstruction of the surface atoms. During the MD simulations of oleic acid molecules adsorbed onto the BaTiO$_3$ surface, the optimized surface model was fixed.$^{37,39}$

In both the DFT calculations and the MD calculations, the models of the hydrazine molecules and the oleic acid molecules were constructed according to molecular formula and then optimized by the DFT calculations or MD calculations.$^{40,41}$ The number of hydrazine molecules or oleic acid molecules used in the adsorption model is one.

The adsorption energy was calculated using eqn (1):$^{42,43}$

$$E_{\text{ads}} = E_{\text{tot(slab + adsorbate)}} - E_{\text{tot(slab)}} - E_{\text{adsorbate}}$$

where $E_{\text{tot(slab + N$_2$H$_4$)}}$ is the total energy of the optimized slab with a hydrazine molecule adsorbed, $E_{\text{tot(slab)}}$ is the total energy of the optimized bare slab and $E_{\text{N$_2$H$_4$}}$ is the energy of a single N$_2$H$_4$ molecule.

2.3 Thin film preparation

0.03 mL dispersed BaTiO$_3$ nanocubes (4 mg mL$^{-1}$) were dropped onto a Pt-coated SiO$_2$/Si substrate (0.5 × 0.5 cm$^2$) at room temperature, and then the dispersion was evaporated under UV irradiation (Photo Surface Processor PL21-200, Sen Lights Corp.) in air for 30 min to prepare a particulate film. The top electrodes of Pt, which are 0.4 mm in diameter, were ion-sputtered onto the surface of the self-assembled film for the measurements of the dielectric properties.

2.4 Characterization

The BaTiO$_3$ nanoparticles were characterized by X-ray diffractometry (XRD, D5005HR 3 kw), scanning electron microscopy (SEM, FESEM SU-70), transmission electron microscopy (TEM, JEOL JEM-4010), dynamic light scattering (DLS, ELSZ-1000S), and Fourier transform infrared spectrometry (FT-IR, IRPrestige-21) methods and using a Precision LCR meter (Quadtech 7600 Plus).
irregular morphology and a size of ca. 10 nm were also observed. The small particles were thought to be obtained from the unreacted Ti-based gel (Fig. 4a). This result indicated that the formation process of BaTiO₃ nanoparticles synthesized at low concentrations of NaOH was inhomogeneous and resulted in a broad size distribution. The morphologies of the particles synthesized at high NaOH concentrations did not change largely after a long reaction time (Fig. 4b–d). It is worth noting that large cubes over 150 nm were observed for the particles synthesized at 1.5 mol L⁻¹ NaOH for 72 h (Fig. 4e). The ED pattern of the large cubes showed a single crystal structure. Small oriented nanotubes were attached on the surface of the large cubes. Meanwhile, some aggregates of nanocubes were also observed (Fig. 4f). It can be seen that the oriented nanocubes are attached and fused with each other through the (100) face. This result provides strong evidence that large cubic particles were formed through the oriented aggregation of nanocubes. Furthermore, the aggregation of nanoparticles was only identified from the particles with a cubic morphology; no aggregates or large particles were observed for the spherical and polyhedral particles. This result indicates that a cubic morphology has the tendency to form oriented aggregations.

Table 1  Relationship of synthesis conditions and morphology types of BaTiO₃ nanoparticles

<table>
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<tr>
<th>NaOH concentration (mol L⁻¹)</th>
<th>Ba : OLA : hydrazine</th>
<th>1 : 2 : 0</th>
<th>1 : 2 : 2</th>
<th>1 : 2 : 4</th>
<th>1 : 2 : 8</th>
<th>1 : 0 : 4</th>
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<td>1.0</td>
<td>Irregular/amorphous</td>
<td>Irregular</td>
<td>Irregular</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
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<td>Irregular/amorphous</td>
<td>Irregular</td>
<td>Polyhedral</td>
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<td>—</td>
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<tr>
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<td>Cube/amorphous</td>
<td>Cube/irregular</td>
<td>Cube</td>
<td>Cube (large)</td>
<td>Irregular (large)</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>Irregular/amorphous</td>
<td>Irregular</td>
<td>Spherical</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
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</table>

Fig. 3  TEM images of the BaTiO₃ synthesized with Ba : OLA : hydrazine = 1 : 2 : 4 for 48 h at NaOH concentrations of: (a) 1.0, (b) 1.2, (c) 1.5, and (d) 2.0 mol L⁻¹.
particles evolved into a spherical morphology. The HRTEM image of a spherical particle showed good crystallinity. Two sets of (110) and (100) planes were identified from the FFT (Fig. 5b).
In this study, BaTiO\(_3\) nanoparticles with uniform morphology and narrow size distribution were synthesized using a critical molar ratio of OLA to hydrazine. To investigate the effect of OLA and hydrazine on the formation and morphology, BaTiO\(_3\) particles were synthesized using different molar ratios of OLA to hydrazine at 200 °C and 1.5 mol L\(^{-1}\) NaOH for 72 h, as shown in Fig. 6. Few BaTiO\(_3\) nanocubes and an amorphous phase were obtained for the particles synthesized without the addition of hydrazine (Fig. 6a) (Ba : OLA = 1 : 2). When synthesized at a low concentration of hydrazine (Ba : OLA : hydrazine = 1 : 2 : 2), BaTiO\(_3\) nanoparticles with an irregular morphology were obtained (Fig. 6b). When synthesized at a high concentration of hydrazine with Ba : OLA : hydrazine = 1 : 2 : 8, ordered arrangements of BaTiO\(_3\) nanocubes with a well-defined cubic morphology and sizes ranging from 20 to 30 nm were obtained (Fig. 6c). Large particles over 100 nm with an irregular morphology were obtained for the particles synthesized without the addition of oleic acid (Fig. 6d). These results indicate that the formation of BaTiO\(_3\) nanocubes and spheres must be obtained at an appropriate ratio of OLA to hydrazine. Furthermore, hydrazine was important for the formation of the BaTiO\(_3\) phase.

To investigate the formation mechanism of BaTiO\(_3\) nanoparticles, the formation kinetics of nanocubes synthesized at 1.5 mol L\(^{-1}\) NaOH and 220 °C with a molar ratio of Ba : OLA : hydrazine = 1 : 2 : 4 was monitored. Fig. 7 shows the TEM images of the particles synthesized at different reaction times. It can be seen that the formation of nanocubes started from Ti-based hydrous gel, as shown in Fig. 7a. No nuclei or nanocrystals were observed in the Ti-based hydrous gel. After 12 h, BaTiO\(_3\) nanoparticles with a size of ca. 20 nm and an irregular morphology were obtained (Fig. 7b). No Ti-based hydrous gel was observed at this stage. They have transformed into the BaTiO\(_3\) nanocrystals completely. After 24 h, cube-like particles with a size of ca. 20 nm were obtained (Fig. 7c). Based on the observation of the particles synthesized for 48 h as shown in Fig. 3c, the BaTiO\(_3\) nanoparticles synthesized for 12 h took a long time to transform into a cubic morphology. Based on the observation of the formation kinetics of nanocubes, it can be concluded that the formation of BaTiO\(_3\) nanocubes is a dissolution–precipitation process under hydrothermal conditions.\(^8,\)^\(^10\) Hydrazine not only contributed to the morphology control of BaTiO\(_3\) nanoparticles but also triggered and accelerated the formation of the BaTiO\(_3\) phase.

Furthermore, the application of hydrazine in the synthesis of BaTiO\(_3\) nanoparticles can decrease the needed concentration of OLA. Our previous work has synthesized BaTiO\(_3\) nanocubes using OLA and \(t\)-butylamine as the surfactants.\(^15\) It needed a very high concentration of surfactants (Ba : OLA : butylamine = 1 : 8 : 8) to control the morphology of BaTiO\(_3\) particles. The formation of BaTiO\(_3\) nanocubes was an \textit{in situ} growth mechanism. The BaTiO\(_3\) nuclei were formed and grew
from the Ti-based hydrous gel. It took a long time (72 h) for BaTiO3 nuclei to transform into nanocubes through the loss of the Ti-based hydrous gel. In this process, a superlattice of nanocubes could be obtained as an intermediate. It is identified that the formation of BaTiO3 nanocubes was mainly attributed to the selective adsorption of OLA on the (100) face of BaTiO3 with a high atomic density of metal ions.\textsuperscript{15,19,24–26} Meanwhile, in the present work, BaTiO3 nanocubes and nanospheres were synthesized at a low concentration of OLA (Ba: OLA: butylamine = 1 : 2 : 4) through the application of hydrazine. Furthermore, the growth mechanism of BaTiO3 nanoparticles changed from an \textit{in situ} growth process into a dissolution–precipitation process through the application of hydrazine with OLA as surfactant during the synthesis process. These results indicate that hydrazine accelerated the formation of the BaTiO3 phase significantly and had an effect on the morphology control of BaTiO3 nanoparticles.

In this work, the influences of hydrazine on the fabrication of BaTiO3 nanoparticles were concluded. The first is the accelerated formation of the BaTiO3 phase. The second is the morphology control of BaTiO3 nanoparticles. For example, Nair \textit{et al.}\textsuperscript{44} studied the effect of hydrazine on the self-assembly of CdTe nanocrystals. They found that the zeta potential of OLA stabilized nanoparticles decreased significantly after the addition of hydrazine. Hydrazine could replace the organic ligand adsorbed on the nanoparticle surface. In the dissolution–precipitation process for the formation of BaTiO3 nanoparticles, the Ti monomers dissolved from the hydrous gel form a Ti–O–Ti cross-linked network via dehydration at a high concentration of NaOH. The Ba species must break the Ti–O bond and incorporate into the Ti–O cluster, and rearrange to form the BaTiO3 structure.\textsuperscript{8,10} The adsorption of OLA will limit the formation of the BaTiO3 phase based on the observation of the results synthesized at different ratios of OLA to hydrazine.\textsuperscript{19,24–26} The replacement effect of hydrazine on the adsorbed surfactant molecule can accelerate the dissolution of Ti and Ba species and trigger the formation of the BaTiO3 phase.

Based on the aforementioned results and discussion, the morphology control of BaTiO3 nanocubes could be realized at a proper molar ratio of OLA to hydrazine. In this work, DFT calculations were performed to investigate the adsorption of hydrazine on BaTiO3 faces. The optimized molecular structure of hydrazine and the calculated adsorption energy are shown in Fig. 8. On the Ba–O terminated surface, the largest adsorption energy of –1.92 eV (Fig. 8a) was obtained for the hcp position, which was thought to be the favorite adsorption position. On the Ti–O terminated surface, the favorite adsorption positions were the Ti and O top positions, of which the adsorption energies were –2.94 and –2.96 eV, respectively (Fig. 8e and f), which are significantly larger than that on the Ba–O terminated surface. Meanwhile, it is identified that the hydrazine molecule placed on the O top position moved to the Ti top position for the optimized structure. These results indicate that when a hydrazine molecule gets adsorbed onto the BaTiO3 (100) surface, it prefers to adsorb on the Ti top position on the Ti–O terminated surface.\textsuperscript{40,42,43}

The real space view of the electron density difference for a hydrazine molecule adsorbed on the BaTiO3 TiO-terminated surface is shown in Fig. 9a. The purple and yellow parts represent the depletion and accumulation of electron density. It can be seen that there is a slight increase of electron density around the N atom of the hydrazine molecule and a slight decrease of electron density around the Ti atom on the surface, suggesting that there is an interaction between N and Ti atoms. However, the increase and decrease of the electron density are mainly centralized in areas around the N atom and the Ti atom, illustrating the electron transfer is quite weak between the hydrazine molecule and the surface atoms.\textsuperscript{45,46} We also calculated the partial density of states (PDOS) of the N atom of the hydrazine molecule and the interacting Ti atom on the surface. The PDOS of N 2s, 2p states of the hydrazine molecule and Ti 3p, 3d, 4s states of the surface are displayed in Fig. 9b. There are only two main resonance peaks at the energy of 3.5 eV and –1.9 eV between the N 2p state and Ti 3p state. The small overlap between the N 2p state and Ti 3p state and the weak strength of resonance peaks also imply that the interaction between N and Ti atoms is quite weak.\textsuperscript{45,46} These results indicate that the adsorption of the hydrazine molecule on the BaTiO3 surface is physical adsorption.\textsuperscript{47}
The adsorption energy of an OLA molecule on the BaTiO₃ surface was also calculated through the molecular dynamics (MD) method. The adsorption energies on Ba–O and Ti–O terminated surfaces are −6.72 eV and −5.92 eV, respectively. This result indicates that the OLA molecule prefers to adsorb on the Ba–O terminated surface. The adsorption of OLA and hydrazine molecules on the BaTiO₃ surface are completely different. Our previous work has demonstrated that OLA molecules are chemically adsorbed on the BaTiO₃ surface through coordination with metal ions. The present work clarified that the OLA molecules prefer to adsorb on the BaTiO₃ surface through coordination with the Ba ions. For the formation of BaTiO₃ nanocubes, the (100) face needs to be stabilized through the selective adsorption of OLA. On the other hand, the surface energies of the (100), (110) and (111) faces of BaTiO₃ are similar and the (110) face has a higher atom density than the (100) face. Because hydrazine molecules physically adsorb preferably on the Ti–O terminated surface, OLA molecules will mainly adsorb on the BaTiO₃ surface through intercalation with Ba ions. Because the Ba ion density on the (100) face is higher than that of other crystal faces, OLA molecules will selectively adsorb on the (100) face.
of BaTiO$_3$ under the assistance of hydrazine. It is concluded that the preferred adsorption on the Ti–O terminated surface of hydrazine molecules favors the selective adsorption of OLA molecules on the specific crystal faces of BaTiO$_3$. Because hydrazine mainly physically adsorbs on the BaTiO$_3$ surface, the added hydrazine can accelerate the formation of the BaTiO$_3$ phase in the synthesis process.$^{10}$

The BaTiO$_3$ nanoparticles exhibit excellent dispersibility in aqueous solution (Fig. 10a). The zeta potential of BaTiO$_3$ nanocubes in aqueous solution was $-52$ mV (pH 10), which was higher than that ($-25$ mV) of the nanocubes synthesized using tert-butyramine as the surfactant. It should be attributed to the physically adsorbed hydrazine. The DLS result of the aqueous dispersion of the nanocubes showed a narrow size distribution. The size of the nanocubes was concentrated from 15 to 20 nm. Due to high dispersibility and stability in aqueous solution, BaTiO$_3$ nanocubes can offer many advantages in the low-temperature processing of ultra thin films on many kinds of substrates, such as Si wafer, metal sheets, plastic, or glass by a variety of solution-based processes including spraying, cast-coating, ink-jet printing, and photolithographic patterning.$^{19,24,48}$ Fig. 10b and c show the SEM images of the self-assembled film of BaTiO$_3$ nanocubes using a UV-assisted self-assembly process for the in situ decomposition of organic phase on a Pt/SiO$_2$/Si substrate. The self-assembled film obtained a uniform, continuous, and crack-free surface structure with a thickness of ca. 200 nm.

The self-assembled film showed a stable dielectric constant and a dissipation loss in the frequency range from 0 Hz to 1 MHz, only with a slight decrease in capacitance towards high frequency Fig. 10d. The dielectric constant (27–30) is comparable to that reported by Huang et al.$^{48}$ This further confirms the good homogeneity and quality of the self-assembled film.

4. Conclusions

Sub-20 nm BaTiO$_3$ nanoparticles with controlled morphologies (including nanocubes, spheres and polyhedra) were successfully synthesized with narrow size distribution, good crystallinity and high dispersibility in aqueous solution. Theoretical calculation and kinetics observation indicate that the presence of hydrazine during the synthesis changed the growth mechanism of BaTiO$_3$ nanoparticles and promoted the selective adsorption of OLA on the critical crystal faces. Only BaTiO$_3$ nanocubes showed the tendency towards oriented aggregation. A high quality self-assembled film was prepared at room temperature under UV irradiation using the aqueous solution of BaTiO$_3$ nanocubes. This method has many advantages including mild reaction conditions without high pressure, rapid formation (4 h) and well controlled size and morphology of the product. This work provides a good understanding of the formation mechanism and morphology control of BaTiO$_3$ nanoparticles and demonstrates a methodology for large-scale industrial production of high quality perovskite oxide powders for different applications including thermoelectric power generation.$^{49}$ solar

![Fig. 10](image-url)
energy harvesting and electromagnetic interference shielding.

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