Tuning Shape of Barium Titanate Nanocubes by Combination of Oleic Acid/tert-Butylamine Through Hydrothermal Process

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The shape and surface morphology of mono-dispersed barium titanate (BaTiO_3) nanocrystals were controlled by tuning the composition of hydrothermal reaction system. High quality BaTiO_3 nanocubes with the smooth surface and 90 degree standard corner angle were synthesized by the hydrothermal method using a relatively low concentration of oleic acid and tert-butylamine, which were used as surfactant and additive, respectively. The average size of BaTiO_3 nanocubes was ~ 25 nm and the size distribution was relatively narrow. As a large amount of surfactant and additive was employed, BaTiO_3 nanocrystals with convex structure were synthesized. The terrace structure were developed at the $\{100\}$ surface of the nanocrystals. Here, we analyzed systematically the role of oleic acid and tert-butylamine on the surface morphology of BaTiO_3 nanocrystals. Our study demonstrates the possibility of synthesizing high quality BaTiO_3 nanocubes for commercial application. These findings can be applied on other perovoskite nanomaterials.

Keyword: Barium titanate, Nanocubes, Hydrothermal crystal growth, Shape controlling, Oleic acid, t-Butylamine.

1. Introduction:

As one of important perovskite ferroelectric oxides, barium titanate (BaTiO_3) is widely used in microwave devices and modern microelectronics such as multilayer ceramic capacitors (MLCC), random access memories, radar, communication systems, pressure transducers, etc [1-8]. BaTiO_3 nanomaterials have been fabricated by many routines, such as solid-state calcination, sol–gel technique, hydrothermal treatment, and polymeric precursor method [9-12]. Among these methods, hydrothermal treatment is an environmentally friendly method, easily synthesizing mono-dispersed nanopowders [13, 15]. Moreover, the control of the particle size and the morphology can be realized by modifying the parameters of hydrothermal synthesis, such as the raw material ratios, reaction time, temperature, and surfactants, etc [16, 18]. Compared with other kinds of morphology, the cubic shape of BaTiO_3 nanomaterials is of interest because of its peculiar symmetries and the specific superstructures. BaTiO_3 nanocubes can produce a close-packed structure and impulse the development of “bottom-up” process, which is important for the next generation devices. BaTiO_3 nanocubes possess unique physical and chemical properties that are strongly related with their size, shape, and surface chemistry [19]. It has been reported BaTiO_3 nanocubes with several tens nm edge length maintained dielectric property. Therefore, the synthesis of BaTiO_3 nanocubes with well-controlled shape and surface morphology is fundamentally and technologically

interest to pave the way to the miniaturization of the dielectric device.

Our group has successfully synthesized BaTiO_3 nanocubes with 15 nm in size by hydrothermal method using Ti-based hydrous gel with surfactant and additives and has also found after sintering highly ordered BaTiO_3 nanocube-assembled films possess a high dielectric constant of approximately 3000 with relatively low loss tangent [18, 20-21]. Recently, the size of BaTiO_3 nanocubes were controlled by tuning barium and titanium precursor concentration. The average size of nanocubes varied from ~15 nm to ~30 nm [22]. However, when the size of nanocubes increased, the surface of BaTiO_3 nanocubes became rough and their corner angles deviated from 90° . The kind of irregular morphology of nanocubes not only influences the study of “size effect”, but also hinders their applications on the “bottom-up” assembling process. Self-assembly of nanocubes into tailored structures is a promising strategy for production and design of materials with new functions. So, to synthesize size-controlled BaTiO_3 nanocubes with neat surface morphology and standard corner angle is important for both their theoretical investigation and technological applications.

In this work, the main research target is to study an effective way to synthesize high-quality larger-sized BaTiO_3 nanocubes with standard cubic structure. We explored the effects of reaction conditions such as molar ratio of surfactant and additive, reaction

time, and the concentration of hydroxide ions on the structure and surface morphology of BaTiO₃ nanocubes. We found that the molar ratio of precursor solution played a critical role in determining the shape of BaTiO₃ nanocubes. Size-controlled nanocubes with standard cubic structure and smooth surface morphology were synthesized by tuning the molar ratios of oleic acid and tert-butylamine. In addition, BaTiO₃ nanocrystals with convex structure could be produced, and the step structure were developed at the {100} surface of the nanocrystals.

2. Experimental

In our case, the bis(ammonium lactate) titanium dihydroxide (TALH) was used as the Ti source, which could resolve into water. In a typical synthesis process, Ba(OH)₂ and TALH was added into 45mL of distilled water in a 100mL autoclave. The Ba/Ti ratios were 1: 1. NaOH aqueous solution (5M) was added into the aqueous solution under mechanical stirring to tune the pH value. Then, the tert-butylamine and oleic acid were added into the solution. The sealed autoclave was heated at 220°C for 72h under mechanical stirring, and then cooled at room temperature. After the synthesis, the precipitate was centrifugally separated and washed twice by absolute ethanol. After drying, the precipitate was dispersed into toluene. The BaTiO₃ nanocubes were characterized by X-ray diffractometry (XRD, Rigaku RINT-2100V). The morphology

of the prepared BaTiO₃ nanocubes was investigated by using a field emission scanning electron microscope (FESEM, JEOL JSM-6335FM) and a transmission electron microscopy (TEM; Model JEM-2010F, with an accelerating voltage of 200 kV).

3. Results and Discussion:

Figure 1 shows FE-SEM image, TEM image, high-resolution TEM (HR-TEM) image and XRD result of BaTiO₃ nanocubes with an average size of ~30 nm, which were synthesized by the hydrothermal process. Several diffraction peaks were showed in the XRD pattern of BaTiO₃ nanocubes (Figure 1 (d)) [17, 23-24]. No peaks of any other phases or impurities were detected. The XRD result and HRTEM image provided evidence that the BaTiO₃ nanocubes belonged to the perovskite structure. As shown in the HR-TEM images of Figure 1 (c), the surface of nanocubes was rough. As well known, the amount of surfactant and additives can modify the shape of nanocrystals [16, 18-19]. To investigate the synthesis of nanocubes with standard cubic structure and neat surface morphology, the molar ratios of oleic acid and tert-butylamine were tuned step by step in our case. The synthesis recipe of 15 nm BaTiO₃ nanocubes was used as reference to estimate the preliminary values of these parameters [18, 21].

During the crystal growth process, oleic acid adsorbed on the surface of nanocrystals through coordination with barium metal ion. Thus, as for oleic acid, the total surface

area of BaTiO₃ nanocubes with an average size of ~ 30 nm was utilized to estimate the molar ratio of oleic acid in this work. Ideally, the ratio of total surface area of 30 nm nanocubes to 15 nm nanocubes was calculated by the follow equation:

$$\frac{S_{30\text{ nm}}}{S_{15\text{ nm}}} = \frac{N_{30\text{ nm}} * 30^2 * 6}{N_{15\text{ nm}} * 15^2 * 6}$$

where $S_{30\text{ nm}}$ and $S_{15\text{ nm}}$ were the surface area of 30 nm nanocubes and 15 nm nanocubes, respectively. $N_{30\text{ nm}}$ and $N_{15\text{ nm}}$ were the total number of 30 nm nanocubes and 15 nm nanocubes, respectively. If all of starting materials reacted into BaTiO₃ nanocubes, $N_{30\text{ nm}}$ and $N_{15\text{ nm}}$ could be calculated by the follow equation:

$$\frac{N_{30\text{ nm}}}{N_{15\text{ nm}}} = \frac{\frac{C_{30\text{ nm}}}{n_{30\text{ nm}}}}{\frac{C_{15\text{ nm}}}{n_{15\text{ nm}}}}$$

where $C_{30\text{ nm}}$ and $C_{15\text{ nm}}$ were the concentration of starting materials for synthesizing 30 nm nanocubes and 15 nm nanocubes, respectively. The $n_{30\text{ nm}}$ and $n_{15\text{ nm}}$ were the number of barium ion in single nanocube. Under ideal condition, $n_{30\text{ nm}}$ and $n_{15\text{ nm}}$ were proportional with the volume of single BaTiO₃ nanocube, which were denoted as $V_{30\text{ nm}}$ and $V_{15\text{ nm}}$.

$$\frac{n_{30\text{ nm}}}{n_{15\text{ nm}}} = \frac{V_{30\text{ nm}}}{V_{15\text{ nm}}}$$

In this case, the concentrations of Ba(OH)₂ and TALH were half of those of 15 nm nanocubes recipe. Combining with the concentration of starting materials, it was

calculated that the total surface area of 30 nm BaTiO₃ nanocubes was about the fourth part of that of 15 nm nanocubes. Based on the recipe of 15 nm BaTiO₃ nanocubes (The molar ratio of barium to oleic acid is 1: 12.), the ideal molar ratios of Ba/ oleic acid for 30 nm BaTiO₃ nanocubes is calculated as 1: 3.

The previous articles reported that one of the roles of tert-butylamine was to connect with the hydroxyl group of Ti octahedral and stabilize them [18, 21]. So, as for tert-butylamine, the concentration of TALH was utilized to estimate its molar ratio for synthesizing larger-sized BaTiO₃ nanocubes. The preliminary values of the molar ratio of tert-butylamine in this work were set to half of that of 15 nm nanocubes recipe (The molar ratio of barium to oleic acid is 1: 12.). According on above calculation, the preliminary value of the molar ratios of Ba: tert-butylamine: oleic acid was 1:6:3.

Figure 2 showed the morphology of BaTiO₃ nanocubes, which were synthesized by using the hydrothermal method at 220°C under different molar ratios of reaction environment. Basing on the TEM images, it can be inferred that the shape and surface morphology of the synthesized BaTiO₃ nanocubes has been affected by the molar ratios of aqueous system (Ba(OH)₂ : tert-butylamine: oleic acid). As the molar ratio varied from 1: 6: 3 to 1: 6: 8, the surface morphology of BaTiO₃ nanocubes became smooth and their shapes showed standard cubic structure. When the molar ratios reached 1: 6:

10 times, wavy surface and damaged corners appeared in most of BaTiO₃ cubic structures. When the molar ratio was 1: 6: 12, the similar results were obtained and almost all of BaTiO₃ nanocrystals showed quasi-cubic structure. Once the molar ratio of oleic acid was increased into 18 times of that of Ba(OH)₂, BaTiO₃ nanocrystals with convex structure were produced. The results indicated the amount of oleic acid played an important role on the shape and surface morphology of BaTiO₃ nanocubes.

In the present synthesis procedure, oleic acid ensured the stability of the colloidal solutions through electrostatic (via the COO⁻ groups) and steric repulsions. Oleic acid could act as capping agent to coordinate the surface of BaTiO₃ nanocubes [18, 22-25], where the COO⁻ group is bonded to barium ions (Ba²⁺). The adsorption is considered to occur at the surface of tiny crystalline BaTiO₃ nuclei at the beginning stage of the hydrothermal reaction. As well known, the shapes and surface morphology of final BaTiO₃ cubic crystals were determined by the ratio of the growth rate along the <100> directions to another crystal directions. The preferentially selective adsorption of oleic acid on {100} crystal surfaces could play a crucial role in the shape control of nanocubes [22, 26-28]. When the amount of oleic acid varied from 3 times to 8 times of that of Ba(OH)₂, it first interacted with the {100} planes of BaTiO₃ nanocrystal and the preferential adsorption on the {100} faces confined crystal growth along the directions.

Thus, the cubic-like BaTiO₃ nanocrystals were synthesized, as shown in Figure 2 (b) and (c). Due to the low concentration of oleic acid (Figure 2 (a)), some aggregation phenomenon existed in the final products. When the concentration of oleic acid was increased step-by-step and reached to an optimal value, the ratio of the growth rate of BaTiO₃ nanocrystals along the <100> directions to another crystal directions decreased gradually and the {100} faces were protected well in final products. So, the nanocubes showed the standard cubic structure and neat surface morphology, as shown in Figure 2 (c). When the molar ratios of oleic acid continued to be increased, the oleic acid presented dominantly in the form of a dimer rather than in carboxylate anions because of the hydrogen-bonding interaction [29-30]. The absence of carboxylate anions led to a weaker interaction between the surfactant and the surfaces of nanocrystal. This phenomenon influenced the role of oleic acid and resulted in the formation of larger-sized nanoparticles with convex morphology. In addition, based on previous reports, when a large excess of oleic acid was employed, the adsorption of oleic acid on {100} faces was saturated and another faces were also capped by oleic acid [31]. This situation could inhibit the growth in the capped direction and influence the final shape of nanocrystals. Thus, it is considered that the transformation on the morphology of BaTiO₃ nanocubes in Figure 2 is attributed to the molar ratios of oleic acid in reaction

system.

Figure 3 showed the HRTEM images of BaTiO₃ nanocubes, synthesized by using corresponding molar ratios of Figure 2. All of high resolution TEM images revealed that the nanocubes were single-crystalline. Four (100) and (110) planes in all of BaTiO₃ nanocubes were identified from the fast fourier transform (FFT) profiles of the HRTEM image. The FFT patterns further indicate the high phase purity and crystallinity of as-synthesized BaTiO₃ nanocubes. Careful examination of Figures 3 (b) and (c) elucidated that the nanocrystals were cubic and have sharply faceted edges. The lattice fringes were parallel with or made an angle of 90° with the edge of the nanocubes and went across the nanocubes without any distortion. As shown in Figures 3 (d) and (e), the sharp edges and smooth surface of BaTiO₃ nanocubes disappeared. Especially, it can be observed from Figure 3 (f) that the step and terrace structure were developed at the {100} surface of the nanocrystals with convex structure. The distances of the lattice fringes on surface area of Figure 3 (f) were 0.398nm and 0.282nm, which were close to the {100} and {110} lattice spacing of cubic phase of BaTiO₃, respectively. It was considered that the co-existence of different crystal planes on the surface area resulted in the formation of BaTiO₃ nanocrystals with convex shape.

Tert-butylamine has been widely used as reducing agents to produce novel metal

nanoparticles [32-33]. Meantime, tert-butylamine is also an effective additive for synthesizing metal oxide nanomaterials [18, 31]. Figure 4 showed the TEM images of BaTiO₃ nanocubes, which were produced by using hydrothermal method at 220°C with different molar ratios of tert-butylamine /oleic acid. When the molar ratio varied from 1: 3 to 1: 1 (tert-butylamine: oleic acid), the shape of BaTiO₃ nanocrystals changed from convex structure to cubic structure (Figure 4 (a) and (b)). However, comparing the TEM and high-resolution images in Figure 4 (b) and (c), the surface of BaTiO₃ nanocubes became rough as the molar ratio changed from 1: 1 to 4: 3. The results indicated that a suitable tert-butylamine /oleic acid combination was critical for the highly cubic-shape structure. In our synthesis procedure, tert-butylamine showed one triple-positive-role at least on the formation of nanocubes. Firstly, the molecular of tert-butylamine can stabilize the hydroxyl group of Ti octahedral, and secondly, the strong polarity of tert-butylamine is critical for the formation of BaTiO₃ phase [18, 21-22]. Thirdly, tert-butylamine can enhance the deprotonation of oleic acid, as mentioned above. It has been reported that the amine can promote the deprotonation of OLA [26]. Tert-butylamine will react with oleic acid with the follow process:

The deprotonated process of oleic acid molecular can improve the connection between

oleic acid and barium ions, which is crucial for the shape of BaTiO₃ nanocubes. When the molar ratio of tert-butylamine /oleic acid was increased from 1 : 3 to 1 : 1 (Figure 4 (a) and (b)), the strong deprotonation of oleic acid in aqueous solution could be promoted and the formation of the dimer was prevented. The deprotonated oleic acid may cap the {100} faces of BaTiO₃ nanocrystals and enhance the growth probability of cubic structures. However, if a huge amount of tert-butylamine existed in the synthesis system, as shown in Figure 4 (c), the excess tert-butylamine molecular were also connected the crystal faces and influence the growth speed along these directions [31-32]. So, the roughness of surface morphology of BaTiO₃ nanocubes was attributed to the huge concentration of tert-butylamine in aqueous system.

The reaction time of hydrothermal synthesis process showed obvious influence on the morphology of BaTiO₃ nanocubes. Figure 5 demonstrated the relationship between the morphology of nanocubes and the reaction time. As the reaction time increased from 48hours to 72hours (Figure 5 (a) and (b)), the quality of the shape of BaTiO₃ nanocubes was improved. However, as the reaction time was 88 hours and 96 hours (Figure 5 (c) and (d)), the surface morphology of nanocubes became rough. This result indicated that over-long hydrothermal time played a negative role on the shape and surface morphology of nanocubes. The connection between the oleic acid and the barium ions

on the surface of BaTiO₃ nanocubes was influenced by the long-time heating treatment. During the long time of hydrothermal treatment, part of the oleic acid was stripped from the surface of BaTiO₃ nanocrystals and re-dissolved into the solution. This phenomenon resulted in the change on the growth speeds along <100> crystalline direction of nanocrystals. The surface of BaTiO₃ final nanocrystal was not only consisted by six {100} faces. So, the morphology of final product was not the cubic-like structure but irregular structure. In our case, the 72-hours hydrothermal treatment was the relative better choice for the formation of BaTiO₃ nanocubes.

The alkalinity of the aqueous solution was an important parameter in wet chemical method, which could affect obviously the size and morphology of nanomaterials [34-38]. In our case, the total concentration of hydroxide ions (OH⁻) present in the solution (mainly coming from NaOH) was responsible for the formation of [Ti(OH)₆]²⁻ and played an important role on the formation of crystalline BaTiO₃ [18, 22, 39]. The FE-SEM images of BaTiO₃ nanocrystals synthesized by hydrothermal method with different concentrations of NaOH were shown in Figure 6. The convex-structured BaTiO₃ nanocrystals were synthesized when 0.6M NaOH was employed. As the concentration of NaOH increased 1.0 and 1.2 M, the shape of BaTiO₃ nanocrystals showed the cubic-like morphology. In contrast, when the concentration of NaOH was

1.5M, the irregular BaTiO₃ nanocrystals were produced. The results indicated that the concentration of NaOH in the solution was crucial for the shape and surface morphology of BaTiO₃ nanocrystals.

We showed the arrangement of BaTiO₃ nanocubes with different surface morphology (Figure 7). Due to the surface roughness of nanocubes, only the orderly arrangement of BaTiO₃ nanocubes could be achieved in several tens micrometers scale by using simple drop-casting method, as demonstrated in Figure 7 (a). However, BaTiO₃ nanocubes with convex or terrace structure only showed an irregular arrangement, as shown in Figure 7 (b). The results show the positive role of cubic structures on the self-arrangement of BaTiO₃ nanocubes. The orderly arrangement of larger-sized nanocubes indicates the possibility of their application on the study of ferroelectric science and the development of next generation devices. The XRD pattern in the inset of Figure 7 (a) showed (100) and (200) diffraction peaks with high intensities. Other diffraction peaks, which belong to BaTiO₃, showed weak intensities or could not be detected. The peak around 33° was attributed to the influence of silicon substrate. On the contrary, the XRD pattern in the inset of Figure 7 (b) demonstrated several diffraction peaks with high intensities, (100), (110), (111), (200), (210) and (211). The results provided the evidence to confirm the orderly arrangement of BaTiO₃ nanocubes with standard cubic structure by utilizing a

simple method of drop-casting instead of very low speed dip-coating method.

4. Conclusion:

In this work, the shape and surface morphology of BaTiO₃ nanocubes showed a strong relationship with the molar ratio of precursor solution. High quality 25 nm-sized BaTiO₃ nanocubes with standard cubic shape and smooth surface morphology were produced by using low molar ratio of Ba²⁺: tert-butylamine: oleic acid. As the molar ratio of oleic acid was increased step by step, the shape of BaTiO₃ nanocrystals were changed from cubic structure to convex structure and the terrace structure were developed at the {100} surface of them. On the other hand, the shape and surface morphology of nanocrystals were sensitive to the increase of the molar ratio of tert-butylamine /oleic acid.

In addition, the roles of the reaction time and the molar concentration of NaOH on the shape of BaTiO₃ nanocrystals were investigated. When the value of the concentration of NaOH varied from 1.0M to 1.2M, the cubic-like BaTiO₃ nanocrystals could be synthesized successfully. And the 72-hours hydrothermal treatment was a suitable choice for the formation of 25 nm-sized BaTiO₃ nanocubes. This work suggests the possibility of synthesizing high quality BaTiO₃ nanocubes for their industrial applications.

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Figure 1 (a) FE-SEM image, (b) TEM image, (c) high-resolution TEM image and (d) XRD pattern of BaTiO₃ nanocubes, which were synthesized by the oleic acid/tert-butylamine assisted hydrothermal process.

Figure 2 TEM images of BaTiO₃ nanocubes, synthesized by using the hydrothermal method at 220°C with different molar ratios of Ba(OH)₂ : tert-butylamine: oleic acid : (a) 1: 6: 3; (b) 1: 6: 6; (c) 1: 6: 8; (d) 1: 6: 10; (e) 1: 6: 12; (f) 1: 6: 18.

Figure 3 HRTEM images and FFT patterns of BaTiO₃ nanocubes, synthesized by the hydrothermal method with different molar ratios of Ba(OH)₂ : tert-butylamine: oleic acid : (a) 1: 6: 3; (b) 1: 6: 6; (c) 1: 6: 8; (d) 1: 6: 10; (e) 1: 6: 12; (f) 1: 6: 18.

Figure 4 TEM images of BaTiO₃ nanocubes, which were produced by using the hydrothermal method at 220°C with different molar ratios of tert-butylamine/oleic acid: (a) 1 : 3; (b) 1 : 1; (c) 4 : 3.

Figure 5 TEM images of BaTiO₃ nanocubes, which were synthesized by the hydrothermal process at 220°C for different reaction time: (a) 48 hours; (b) 72hours; (c) 88hours and (d) 96hours.

Figure 6 FE-SEM images of BaTiO₃ nanocrystals, which were synthesized by the hydrothermal process at 220°C with different concentration of NaOH: (a) 0.6M; (b) 0.8M; (c) 1.0M; (d) 1.2M and (e) 1.5M.

Figure 7 (a) The orderly arrangement of BaTiO₃ nanocubes (the inset is the corresponding XRD pattern); (b) the random arrangement of BaTiO₃ nanocubes with irregular structures (the inset is the corresponding XRD pattern).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Graphical Abstract

Nanocrystal with
terrace structure

Quasi-cube

Nano-cube