Investigation on the synthesis procedure of ultrafine monodispersed BaTiO₃ powders by solvothermal method

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Monodispersed BaTiO₃ nanoparticles with an average grain size of 3–5 nm were obtained by a convenient one-step solvothermal method. In this method, the crucial step to achieve ultrafine BaTiO₃ nanoparticles is the control of hydrolysis of Ti(OC₄H₉)₄ by Diethylene glycol (DEG). DEG can strongly inhibit the hydrolysis procedure and prevent the grain growth of BaTiO₃ nanoparticles. Ba(OH)₂·8H₂O provides H₂O source and alkaline environment. Polyvinyl pyrrolidone (PVP) is used as surfactant. The as-prepared monodispersed BaTiO₃ nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), BET-specific surface area measurement, fouriertransform infrared (FT-IR) spectrum and X-ray photoelectron spectroscopy (XPS). The influence of concentration, temperature, time and the importance of PVP were explored to investigate the growth-up mechanism of the BaTiO₃ nanoparticles.

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1. Introduction

Barium titanate, with a perovskite ABO₃ crystal structure, is known to have outstanding dielectric, ferroelectric, thermoelectric, and piezoelectric properties.¹⁾ It can be applied in the electronic devices such as multilayer ceramic capacitors, printed circuit boards, dynamic random access memory, positive temperature coefficient of resistance thermistors, piezoelectric sensors, and actuators.^{1)–3)} Nowadays, the development tendency of most devices is getting smaller and smaller, which requires a decreasing grain size of ferroelectric materials.¹⁾ Therefore, it is very important to study the synthesis of ultrafine barium titanate powders with well crystallinity, high purity and well morphology, especially in investigating size effect.⁴⁾

BaTiO₃ is generally synthesized by either solid-state reaction methods or wet-chemical methods. BaCO₃ and TiO₂ are chose as raw materials in conventional solid-state reaction methods, BaTiO₃ is obtained after long-time high-temperature calcination.⁵⁾ Solid-state reaction has been adopted as the main synthesis route in practice due to its simple equipment and cheap raw materials. However, this method is of high energy-consumption, and the other disadvantages include inevitable formation of coarse grains, a nonuniform grain size distribution, and low purity. Recently, high-energy ball milling is introduced in barium titanate fabrication to lower the reaction temperature, which is ascribed to the defects in the reagent caused by mechanical forces. Using Ba(OH)₂ and Ti(OC₄H₉)₄ as reagents, Qi et al. prepared 7 nm BaTiO₃ powders at room temperature with the mixture resealed for 18 h milling at the rate of 200 rpm.⁶⁾ Other new solid-state reactions such as self-propagating method,⁷⁾ low-temperature combustion method⁸⁾ have also been reported.

Wet-chemical methods, including microwave heating, sol–gel method, coprecipitation, solvothermal, hydrothermal, microemulsion, etc. can achieve uniform grain size distribution of fine barium titanate particles. Viswanath R N et al.⁹⁾ dispersed Ba(OEt)₂ and Ti(OEt)₄ in ethanol and water at 80°C to obtain gel, then 30 nm barium titanate was achieved after the xerogel was calcinated at 750°C. Although fine powders with high purity could be achieved by sol–gel method, the preparation period is too long, and agglomeration occurs easily due to the high-temperature calcination. Oxalate coprecipitation route¹⁰⁾ is another wet-chemical method that is widely used. But it is hard to get fine-grained powders because the reactants are easily agglomerated. Hydrothermal or solvothermal method is to place precursors and deionized water or solvent in a teflon jar and keep high temperature, high pressure for a period of time, then dry and calcine the product to get powders. X. Wang et al.¹¹⁾ used oleic acid, ethanol and water as solvent, Ba(OH)₂ and Ti(OC₄H₉)₄ as reagents, sodium oleate as surfactant, then kept the mixture of them at 160°C for 12 h to get 6 nm barium titanate powders with narrow size distribution and well crystallinity. Hydrothermal and solvothermal method¹²⁾ can provide high pressure and temperature for reactions. It is easy to control the conditions and the reactant is ultrafine and well crystallized which need not to be calcined. Especially in preparing highly dispersed BaTiO₃ powders with a particle size smaller than 10 nm, solvothermal method has more advantages.

In this work, a convenient one-step solvothermal synthesis route is developed to prepare pure, near spherical, monodispersed, nonporous barium titanate nanoparticles.¹³⁾ The particle size is as small as 5 nm with narrow size distributions, which is very useful in the investigation of size effect and the fabrication of smaller electric devices.

2. Experimental procedure

The main raw materials include barium hydroxide octahydrate [Ba(OH)₂·8H₂O, Sinopharm Chemical Reagent, ≥98%], Tetra-

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n-butyl Titanate [$\text{Ti}(\text{OC}_4\text{H}_9)_4$, Sinopharm Chemical Reagent, $\geq 98\%$, Beijing, China], Diethylene glycol (DEG, Sinopharm Chemical Reagent, $\geq 98\%$) and Polyvinylpyrrolidone (PVP, Beijing Chemical Reagent Company K30, Beijing, China). DEG is used as solvent and inhibitor, PVP is used as surfactant. Controlling of the hydrolysis procedure of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ is crucial for the grain size and morphology, thus the system should be strictly free from water. BaTiO_3 monodispersed nanoparticles were synthesized as follows: $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, PVP, $\text{Ti}(\text{OC}_4\text{H}_9)_4$, and DEG were placed into a 50 ml Teflon cup subsequently. Thereafter, the Teflon cup was sealed tightly into a stainless steel autoclave and transferred into a pre-heated oven for 4 to 12 h. The oven was pre-heated from 140 to 260°C . When finished, the reaction kettle cooled down to room temperature naturally. White precipitations aggregated at the bottom of the Teflon cup. After removing the upper clean solvent, the residuals were washed three times with ethanol to remove the excess organics and small amount impurity BaCO_3 . The products were separated by centrifuge and dried in a vacuum oven at 80°C for one day.

Phase identification and crystal structures of the BaTiO_3 nanoparticles were determined by X-ray diffraction (XRD) (Rigaku 2500, Kyoto, Japan), with $\text{Cu K}\alpha$ radiation of a wavelength of 0.154056 nm operated at 40 kV and 200 mA. The morphology of the nanoparticles was observed by transmission electron microscopy (JEOL-JEM-1200EX, JEOL Ltd., Tokyo, Japan). The high-resolution TEM images were obtained by a high-resolution transmission electron microscope (JEOL-2011, JEOL Ltd.). The Fouriertransform infrared (FT-IR) spectrum was recorded on a FT-IR system (spectrum RX, PerkinElmer, England). The heat loss of the nanocrystals was evaluated with an aid of TG/DTA (TA Instruments Q600, America). The X-ray photoelectron spectroscopy (XPS) was achieved on a XPS system (ESCALAB 250 Xi) to study the surface conditions of the nanoparticles.

3. Results and discussion

The XRD patterns, TEM and HR-TEM images, size distribution histogram, electron diffraction pattern, and Raman spectra of the 5 nm BaTiO_3 nanocrystals synthesized at 180°C for 12 h are all shown in the supporting information.¹³⁾ The reagents react in two steps described with the following two equations:

At the beginning, $\text{Ti}(\text{OC}_4\text{H}_9)_4$ disperses uniformly in a non-aqueous media. With temperature increasing, the crystal water of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is released gradually in DEG solvent and makes $\text{Ti}(\text{OC}_4\text{H}_9)_4$ hydrolyze to ultrafine oxyhydroxide of titanium with

high activity. Then this precursor reacts with $\text{Ba}(\text{OH})_2$ in a controlled rate and forms the 5 nm BaTiO_3 . To synthesize ultrafine BaTiO_3 nanoparticles, DEG, PVP, and limitation of water are key factors.

Using this method, we can achieve a typical perovskite structure of pseudocubic BaTiO_3 with c/a ratio of 1.0069 ± 0.0010 . The grain size is estimated of 7.4, 8.2 and 5 nm by XRD, BET test and direct measure on TEM images respectively. X-ray fluorescence analysis shows the Ba/Ti atomic ratio is 1 ± 0.003 . And Raman spectra indicate a tetragonal phase remnants.

The effect of concentration, temperature, time and PVP are further investigated to explore the nucleation and growth-up mechanism of the BaTiO_3 nanocrystals.

3.1 Effect of concentration

The TEM images of BaTiO_3 nanoparticles prepared with different concentrations (0.75, 1.5, and 3 M) are shown in **Fig. 1**. Combined with the XRD patterns, shown in the supporting information,¹³⁾ all samples are well crystallized in perovskite structure and no other miscellaneous peaks exist. As concentration decreasing, the particle size of BaTiO_3 decreases correspondingly and becomes more uniform, which can be confirmed by the TEM images as well as the broadening of the XRD peaks. The particle size is estimated by Scherrer's equation using the (002)/(200) peaks of the BaTiO_3 nanoparticles and the results are listed in **Table 1**. During the reaction procedure, DEG is a critical factor that can prevent the BaTiO_3 grains from growing up to coarse ones. DEG can strongly absorb the released crystal water and reduce the hydrolysis rate of the Ti resource. And high viscosity of DEG is helpful for the inhibition of the grow-up of particles. In this method, although high concentration will introduce large numbers of nuclei, contact probability among nuclei and particles will increase with the high concentration, which will induce the growing up of the particles, due to high surface energy. Besides, high concentration involves more water, which will lower the viscosity and facilitate the growth-up of the particles.

3.2 Effect of temperature

Temperature is one of the most important factors that influence

Table 1. Width and grain size calculations of BaTiO_3 nanopowders at different concentrations

Concentration (M)	2θ	FWHM	Dimension (nm)
3	45.1007	0.518	16.2
1.5	45.0739	0.789	13.7
0.75	44.9915	0.963	7.4

Fig. 1. TEM images of the BaTiO_3 nanoparticles synthesized at 180°C for 12 h at the concentration of (a) 3 mol/L, (b) 1.5 mol/L, (c) 0.75 mol/L.

Fig. 2. X-ray powder diffraction patterns of the BaTiO₃ nanoparticles synthesized at different temperatures varies from 140 to 260°C for 12 h of 0.75 mol/L concentration. (a) $2\theta = 20\text{--}80^\circ$; (b) $2\theta = 43\text{--}47^\circ$ (140–180°C); (c) $2\theta = 44\text{--}46^\circ$ (200–260°C).

the reactions. Thermodynamically, the raw materials can only react at a relatively high temperature. Dynamically, the increase in temperature can accelerate the reaction rate and shorten the reaction time. X-ray diffraction patterns of BaTiO₃ nanopowders reacted at different temperatures ranging from 140 to 260°C are shown in **Fig. 2(a)**. All samples present a typical perovskite structure as well as a small amount of BaCO₃ phase. Grain sizes of the BaTiO₃ nanopowders are estimated by Scherrer's equation using data of **Fig. 2(b)**. With increasing temperature, the grain size is calculated to be 7.9, 7.5 and 7.4 nm corresponding to the temperature of 140, 160 and 180°C. To find out the difference in the powders synthesized at different temperatures, more details are shown in **Figs. 2(b) and 2(c)**. There is no feature of typical tetragonal or cubic phase in these samples. The (002)/(200) peaks are all asymmetric. It is supposed that the undersized grain size causes an obvious broadening of the diffraction peaks, which makes it difficult to figure out the phase features.

Figure 3 shows TEM and HR-TEM images of the BaTiO₃ nanoparticles synthesized at 140°C (a1, a2), 160°C (b1, b2), and 180°C (c1, c2), respectively. And **Fig. 4** shows TEM images of the BaTiO₃ nanoparticles synthesized at 200°C (a), 220°C (b), 240°C (c), and 260°C (d), respectively. The BaTiO₃ nanoparticles

synthesized at 140, 160 and 180°C all have an average grain size of 5 nm as well as a spherical and uniform morphology. When the temperature increases to 200°C, the grain size of the reactant reaches 20 nm. Further increasing the temperature to 240 and 260°C drives the grain sizes continue to grow up and become nonuniform. This phenomenon is associated with the boiling point and the viscosity of DEG. The boiling point of DEG is 245°C, and the reaction mixture's boiling point is lower than that. The solvent becomes gasify when the reaction temperature approaches the boiling point. Otherwise, high viscosity of the solvent is helpful for the inhibition of the growth-up of particles, but the viscosity will decrease with the rising of temperature. Accordingly, it fails to prevent the particles from growing up.

3.3 Effect of time

Reaction time is another important factor that can influence the particle morphology and uniformity. X-ray diffraction patterns of BaTiO₃ nanoparticles synthesized at 180°C for 4, 6, 8 and 12 h are shown in **Fig. 5**. BaTiO₃ has already reached a high level of crystallization under the condition of 4 h. With increasing time, the diffraction peaks change very little. **Figure 6** shows TEM and HR-TEM images of the BaTiO₃ nanoparticles synthesized

Fig. 3. TEM and HR-TEM images of the BaTiO₃ nanoparticles synthesized at (a1, a2) 140°C, (b1, b2) 160°C, and (c1, c2) 180°C for 12 h at the concentration of 0.75 mol/L.

Fig. 4. TEM images of the BaTiO₃ nanoparticles synthesized at (a) 200°C, (b) 220°C, (c) 240°C, and (d) 260°C for 12 h at the concentration of 0.75 mol/L.

for different time. From the pictures, we can see that, with the increasing of reaction time, the particles tend to be more uniform and monodisperse, which indicates that the formation of BaTiO₃ includes two processes, one is the reaction of Ti and Ba, and the other is the reorganization of the BaTiO₃ particles to make more uniform. Combined with Fig. 3, when the reaction time reached 12 h, high uniform and monodisperse particles can be got.

Table 2 shows the width at half maximum of (110) peaks of the BaTiO₃ nanoparticles synthesized at different time. It is

Fig. 5. X-ray powder diffraction patterns of BaTiO₃ nanoparticles synthesized at 180°C for different time from 4, 6, 8 to 12 h of 0.75 mol/L concentration.

obvious that the width at half maximum is broadened as the time increases, and meanwhile the particle size decreases. The XRD peaks are broadened when the particles become fine. As time increases, particle size differs little, but still shows a decreasing trend. Combined with the TEM figures, longer time can achieve better crystallinity, morphology and smaller grain size.

3.4 The role of PVP

PVP is a factor that affects the product significantly. As surfactant, PVP has special long chains and function groups, it can coat on the surface of the BaTiO₃ particles to prevent the particles from getting aggregated. **Figure 7** shows the Fouriertransform infrared (FT-IR) spectra of BaTiO₃/PVP, pure BaTiO₃, and pure PVP. The spectrum of pure BaTiO₃ shows an obvious peak at 550 cm⁻¹, which is ascribed to the Ti–O bond stretching vibration. A peak at 1665 cm⁻¹ is found in the spectra of pure PVP, which is caused by C=O bond vibration. Compared with these two spectra, the spectrum of BaTiO₃/PVP shows no peak at 1665 cm⁻¹ but two new peaks at 1574 and 1559 cm⁻¹.¹⁴⁾ The new

Fig. 6. TEM and HR-TEM images of the BaTiO₃ nanoparticles synthesized at 180°C for (a1, a2) 4 h, (b1, b2) 6 h, (c1, c2) 8 h at the concentration of 0.75 mol/L.

Table 2. Width and grain size calculations of BaTiO₃ nanopowders at different time

Time	2 θ	FWHM	Dimension (nm)
4	31.3052	0.9993	9.6
6	31.3052	1.0081	9.5
8	31.3052	1.0884	8.8
12	31.3052	1.2346	7.8

Fig. 7. Fourier transform infrared (FT-IR) spectra of (a) BaTiO₃/PVP, pure (b) BaTiO₃, and (c) pure PVP.

peaks are supposed to be caused by the bonding of N atoms or O atoms of PVP and the surface of BaTiO₃ particles. It indicates that BaTiO₃ nanoparticles have fully reacted with PVP. As a result, the agglomeration of the BaTiO₃ nanoparticles is avoided to a great extent by forming a polymer coating layer of PVP. Thus it can be concluded, proper amount of PVP is important to synthesize monodispersed and uniform BaTiO₃ nanoparticles.

Figure 8 displays the differential thermal analysis and thermogravimetric analysis (TG/DTA) curve of BaTiO₃/PVP. The

Fig. 8. Differential thermal analysis and thermogravimetric analysis (TG/DTA) curve of BaTiO₃/PVP.

weight continues to lose until 750°C. Two platforms in the thermogravimetric curve can be observed: one is at about 100°C, mainly caused by the evaporation of DEG and water; the other is at 320°C around, mainly caused by combustion of PVP. TG/DTA data suggest that organics are almost exhausted around 750°C, which agrees with the FT-IR results.

The valence state of the BaTiO₃ nanoparticles' surface is characterized by XPS, and the results are shown in **Fig. 9**. From the XPS of pure PVP, The main composition, carbon, nitrogen and oxygen exist on the surface of the BaTiO₃ nanoparticles in terms of C (1s), N (1s) and O (1s) by inquiring in XPS database in that the corresponding energy peak is around 280, 400 and 530 eV, which coincides with the structure of PVP. In the XPS of BaTiO₃/PVP, the spectrum peaks for BaTiO₃ fall into two areas: 450 and 780 eV, which respectively indicates the Ti (2p) and Ba (3d) states. The remaining C1s, N 1s and O1s peaks

Fig. 9. X-ray photoelectron spectra of pure (a) PVP, (b) BaTiO₃/PVP, and (c) N1s scan peak of PVP and BaTiO₃/PVP.

illustrate that there are still organic residual on the surface of the BaTiO₃ nanoparticles.

4. Conclusions

Monodispersed BaTiO₃ nanocrystals with well morphology and narrow grain size are synthesized by a one-step solvothermal method. The effect of concentration, temperature, time and PVP are investigated and an optimum condition is obtained. In this method, DEG is the key factor to control the particle size and

uniformity because of its inhibitory action to the hydrolysis of Tetra-n-butyl Titanate and high viscosity. PVP as surfactant also plays an important role to ensure well morphology. This method develops a convenient, low-cost and massproductive way to synthesize ultrafine BaTiO₃ nanocrystals in quantity. And it is very beneficial to the future applications of BaTiO₃ in the electric industry.

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