Facile microwave synthesis and photocatalytic activity of monodispersed BaTiO₃ nanocuboids

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Abstract A facile microwave hydrothermal method for preparation of monodispersed barium titanate (BaTiO₃) nanocuboids with average size of 13 nm is developed, and the effects of synthesis parameters, such as molar composition of the precursor, synthesis time and temperature, on the morphology of BaTiO₃ nanocrystals are systematically evaluated. The resulting products are characterized by X-ray diffraction (XRD), Raman spectrum, infrared spectrum (IR), UV-vis diffuse reflectance spectrum, water contact angle, thermogravimetry (TG), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), and selected area electron diffraction (SAED). A possible formation mechanism of BaTiO₃ nanocuboids is proposed. The BaTiO₃ nanocuboids show high photocatalytic activity for the degradation of Rhodamin B under UV irradiation.

Keywords monodispersed, BaTiO₃, nanocuboids, preparation, photocatalysis

1. Introduction

Barium titanate (BaTiO₃) is well-known electroceramic material and widely used in the electronic industry [1]. Recently, monodispersed BaTiO₃ nanocrystals have attracted more and more attentions than BaTiO₃ bulk materials [2], due to their excellent properties, such as high bioimaging [3] improved

dielectric properties, potential for device miniaturization, ~~photocatalytic activity~~, and so on. Furthermore, ~~Because the~~ band gap of BaTiO₃ ~~nanocrystal is~~ close to that of TiO₂ [4] ~~indicates its potentiality in the field of photocatalysis. which make it possible to act as an effective photocatalyst.~~ It has been reported that BaTiO₃ can degrade organic dyes like methyl red [5], crystal violet [6] and methyl orange [7] under super-band-gap irradiation. Further research shows that the tetragonal phase of BaTiO₃ exhibit better photocatalytic performance than the cubic phase [8], which is contributed to the influence of the ferroelectricity on the carrier separation and stern layer formation. All these results indicate that BaTiO₃ is a very interesting material for photocatalysis. However, BaTiO₃ nanocrystals obtained in these works have large size (>55 nm) and irregular shape. It is well known that BaTiO₃ nanocrystals with small size and special crystal planes show high photocatalytic activity due to their enough active sites. Thus, it is very important to prepare BaTiO₃ nanocrystals with small size and uniform shape.

Until to now, much effort has been given to BaTiO₃ morphology-controlled synthesis including size and shape [9-10], and various shapes, such as nanorods [11], nanotubes [12], nanowires [13], and nanocubes [14], have been successfully prepared. Among them, cube or cuboid nanocrystals have seemly more advantages in acting as building blocks for BaTiO₃ thin film which is desirable for advanced device applications [15], and thus have attracted some attentions.

Some valuable trials have been done on synthesis of cube or cuboid shaped BaTiO₃ nanocrystals. For example, Hou et al. prepared BaTiO₃ nanocubes by solvothermal method [16]. Yan et al. [17] used the BaTiO₃ seeds second growth method under hydrothermal condition to prepare BaTiO₃ nanocubes. Liu et al prepared cube or cuboid shaped BaTiO₃ nanocrystals in a solution of composite-hydroxide eutectic [18]. But BaTiO₃ nanocrystals obtained by these methods have slight large size (30-90 nm) and present cube shape with round-corner. Then smaller size and sharp-edge cube shaped BaTiO₃ nanocrystals are prepared. Adireddy et al successfully prepared regular BaTiO₃ nanocubes with size of about 22 nm by hydrothermal

method under an inert atmosphere using butanol/H₂O as solvent at 135 °C for 18 h [19]. Wada et al prepared BaTiO₃ nanocubes with 12–15 nm via solvothermal method at 240 °C for 18 h, where 2-methoxyethanol/ethanol (40: 60, vol. %) was used as solvent [20]. Zhou et al prepared monodispersed sub-10 nm BaTiO₃ nanocubes by using ethanol as solvent and OA as the surfactant at 160 °C for 12 h [21]. In these literatures, the organic solvent and longer synthetic time than 10 h are necessary to obtain sub-20 nm BaTiO₃ nanocubes. However, organic solvents are costly and unfavorable for environment, and long heating time results in much higher energy consumption.

Hydrothermal microwave method is commonly used to prepare inorganic materials due to its short synthesis time and convenient process, and is a good alternative for conventional hydrothermal synthesis. Until to now, there have few reports on the preparation of BaTiO₃ nanocrystals via hydrothermal microwave method. Recently, Moreira et al have prepared BaTiO₃ nanocrystals at 140 °C for 10 min using hydrothermal microwave method, but the obtained nanocrystals show spherical shape and large size nearly 100 nm [22]. In this study, we present a microwave hydrothermal method to prepare monodispersed BaTiO₃ nanocuboids with average size about 13 nm, which can be achieved at 200 °C for 4 h just using water as solvent. Further, the effects of crystallization temperature, time and the molar composition of the precursor mixture on the morphology of BaTiO₃ nanocrystals are systematically investigated, and then the formation mechanism and photocatalytic activity of the resultant BaTiO₃ nanocubids are studied.

2. Material and methods

Barium hydroxide octahydrate (Ba(OH)₂·8H₂O, purity 98%), barium nitrate (Ba(NO₃)₂, purity 98%), barium chloride (BaCl₂, purity 98%), sodium hydroxide (NaOH, purity 98%), titanium (IV) n-butoxide (TBOT, purity 98%), oleic acid (OA, purity 99%) and Rhodamin B (RhB) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and used without any further purification.

2.1 Synthesis of BaTiO₃ nanocuboids

In a typical procedure for the preparation of BaTiO₃ nanocuboids, 0.45 g of Ba(OH)₂·8H₂O was dissolved in 10 mL of deionized water, to which 0.125 mL of OA was added, and white precipitate of barium oleate immediately occurred. The mixture was stirred for 30 min. And then 0.40 g of TBOT was poured into the mixture. After stirred for another 30 min, the amount of white precipitate increased due to the formation of amorphous titania. The resulting mixture subsequently was transferred to a 60 mL autoclave. The autoclave was then sealed and irradiated at 200 °C for 4 h **under autogenous pressure** in a microwave oven (**MDS-6, Shanghai Sineo Microwave Chemistry Technology Co. Ltd, China**) (with a rotator), which was operated at 2.45 GHz and with output power of up to 1000 W. After the reaction mixture was cooled naturally to room temperature, the solid product was separated from the supernatant solution by centrifugation. No size selection was performed to narrow the size distribution of the nanoparticles. The precipitate was washed with water and ethanol, and then dried at 60 °C for 12 h in vacuum oven. In order to investigate the effect of synthesis parameters, the following synthesis parameters were evaluated: crystallization temperature/time, molar ratios of H₂O/Ba, OA/Ba and Ba/Ti (Table 1).

2.2 Characterization of BaTiO₃ nanocuboids

The crystal structure and purity of the dried products were studied by powder X-Ray diffraction (XRD) (Rigaku, D/Max-3c, Cu K α radiation) and Raman microscope spectrometer (Renishaw inVia Reflex, excitation at 532 nm) at room temperature. The shape, crystal structure and particle size were analyzed by transmission electron microscopy (TEM, JEOL 2100) equipped with selected area electron diffraction (SAD). The presence of OA molecules on the surface of BaTiO₃ nanocrystals was characterized with a Fourier transform infrared spectrometer (FT-IR, Bruker, Tensor27), Thermogravimetry (TG) analyses (TA Q50, heating rate of 10 °C min⁻¹, nitrogen flow of 40 mL·min⁻¹) and contact angle analyzer (OCA 20, Dataphysics). UV-vis diffuse reflectance spectrum was recorded on a UV spectrophotometer (Shimadzu, UV-3600) at room temperature.

2.3 Photocatalytic experiments

The photocatalytic activity of the BaTiO₃ nanocuboids was examined via a model reaction of RhB degradation under UV irradiation. The typical experiment was carried out as follows. A certain amount of the BaTiO₃ powder was added to 30 mL of RhB solution with a certain concentration. In order to investigate the influence of catalyst amount and the concentration of RhB, 10, 20, 40 and 60 mg of BaTiO₃ powder were added into 30 mL of 10 mg/L RhB solution, respectively; and 10 mg of BaTiO₃ powder were added into 30 mL of 5, 10, 15 and 20 mg/L RhB solution, respectively. Prior to irradiation, the suspensions were magnetically stirred for 30 min in the dark to establish the adsorption/desorption equilibrium between dye and BaTiO₃ nanocrystals. Then, the mixed solution was transferred into a 50 mL quartz test tube and irradiated with a 300 W Hg lamp (365 nm) at a distance of about 10 cm (XPA-7 photochemical reactor, Xujiang Electromechanical Plant, Nanjing, China). At a given irradiation time interval, the samples were drawn from the test tube and were immediately centrifuged at 10000 r/min to remove catalyst particles for analysis. The absorption spectra of these solutions were measured by a TU-1901 Ultraviolet–Visible spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, China). The degradation efficiency can be calculated as: efficiency (%) = 100 % * (C₀ - C) / C₀, where C₀ is the initial concentration of RhB, and C is the revised concentration considering RhB adsorption on BaTiO₃ after photoirradiation. The concentration of RhB is calculated by a calibration curve. The maximum absorption of RhB is at wavelengths of 554 nm.

3. Results and discussions

3.1 Characterization of BaTiO₃ nanocuboids

The products, which are prepared ~~BaTiO₃ nanocuboids are successfully prepared~~ after microwave heating the precursor solution with a molar composition of Ba (OH)₂: 0.83 Ti (OBu)₄: 0.3 OA: 394 H₂O at 200 °C for 4 h, are characterized by ~~and~~ XRD ~~pattern~~, Raman ~~spectrum spectrometer~~ and TEM ~~image are~~

~~shown in Fig.1.~~ From XRD pattern (Fig. 1a); it is found that the product is single perovskite structure. In addition, a very weak peak at $2\theta = 23.9^\circ$ assigned to barium carbonate is also observed, which might originate from the carbonate impurities contained in the raw materials and can be easily removed by washing with 0.1 mol/L formic acid solution. The average crystal size calculated from the Debye-Scherrer equation by taking account of the peak broadening at [111] diffraction is about 20 nm. In addition, the diffraction pattern in the 2θ region of $40\text{--}50^\circ$ is usually characteristic of the presence of either cubic or tetragonal BaTiO₃ structure. In this case, no splitting of cubic (200) into tetragonal (200) and (002) reflections at about 45° can be observed due to line broadening resulted from the size effect [19]. Therefore, it is difficult to assign the crystal symmetry of BaTiO₃ nanocrystals to either cubic or tetragonal symmetry using conventional x-ray diffractometers. ~~Because the pronounced broadening of X-ray peak at about 45° , which are attributed to the small particle size of BaTiO₃ crystals, Because nanoparticles cause the peak line broadening and results in thus the peak splitting is hidden [19], it is difficult to assign the crystal structure of BaTiO₃ to either cubic or tetragonal symmetry, although no obvious splitting of the (200)/(002) diffraction peaks is observed from XRD pattern.~~

It is well known that Raman spectroscopy is a useful technique for probing the phase structure of the BaTiO₃ nanoparticles at the atomic scale, on the basis of vibrational symmetry. Cubic phase BaTiO₃ inherently has no Raman active modes because of the isotropic distribution of the electrostatic forces, however Raman active modes are expected for the noncentrosymmetric tetragonal structure [23]. The bands at 183, 247, 305, 514, and 715 cm^{-1} observed in Fig. 1(b), are attributed to the A₁ (LO), A₁ (TO), B₁+E (TO+LO), E (TO) +A₁ (TO), and the A₁ (LO) +E (LO) modes respectively, which is typical tetragonal structure [18]. These results indicate that the obtained BaTiO₃ ~~nanocuboids~~ are whether single phase of tetragonality or mixed phase of cube and tetragonality.

Scanning electron microscopy (SEM) and TEM are powerful techniques for morphology

characterization. SEM image has not been obtained due to the too small size of nanoparticles to be clearly observed by our low resolution scanning electron microscope. As shown in Fig. 1e, The TEM images (Fig. 1c) reveal that the products are cuboid shaped nanoparticles and well-dispersed without aggregation. In addition, a uniform diffraction contrast across these single crystals is also observed, indicating that the crystals have a low strains. SADE pattern (Fig. 1d) recorded on these particles shows polycrystalline diffraction rings with discrete diffraction spots, which can be ascribed to either cubic or tetragonal BaTiO₃. Although the crystallite size calculated from XRD is around 20 nm, the particle size distribution (Fig. 1e) derived from TEM image shows an average particle size of 13.5 nm along the longer edge of BaTiO₃ nanocuboids. HRTEM (Fig. 1f) shows that BaTiO₃ nanocuboid possesses {100} faceted edges and is free of defects such as stacking faults and dislocations. The measured fringe spacing is 0.40 nm, which is corresponded to the (100) and (010) lattice spacing of cubic BaTiO₃ [18], indicating that some of BaTiO₃ nanocuboids have perovskite cubic phase. The fast Fourier transform (FFT) pattern (Fig. 1g) of HRTEM further demonstrates that the exposed surface belongs to the (001) plane of BaTiO₃. The images of TEM and HRTEM and the FFT pattern are well agreement with the literatures [14], and suggesting that BaTiO₃ nanocuboids have been successfully prepared. Hence Moreover, according to the results of HRTEM, XRD and Raman spectrum, it can be drawn that the obtained BaTiO₃ nanocuboids are mixed phase of cube and tetragonality.

For BaTiO₃ nanocrystals prepared with OA as surfactant, it can be found that OA molecules moleculars are generally absorbed adsorbed on their nanocrystal surfaces [21]. Fig. 2a shows FT-IR spectra of the BaTiO₃ nanocrystals prepared with and without OA, respectively. The FT-IR peaks ranging from 3200 to 3500 cm⁻¹ can be ascribed to H₂O adsorbed by surface-hydroxyl groups of BaTiO₃ crystals—the surface-hydroxy adsorbed water or OH defects in BaTiO₃ crystals. The peaks ranging from 2925 to 2858 cm⁻¹ belonging to the C–H stretching mode of methyl and methylene groups are observed in both cases of

OA and BaTiO₃ nanocrystals prepared with OA. Instead of the appearance of C=O stretching vibration at 1718 cm⁻¹ in case of OA itself, two characteristic peaks at 1558 and 1432 cm⁻¹ associated with asymmetric and symmetric COO-stretching vibrations are found in the spectrum of BaTiO₃ nanocrystals prepared with OA, evidently indicating that the chemical bonds between the surface of BaTiO₃ nanocrystals and OA are formed [14, 24].

Compared with the static contact angle image between Fig. 2b and 2c, it is clearly observed that the water contact angle on the thin film compressed with BaTiO₃ nanocrystals, which were prepared with OA, is 117.9 °. In contrast, in the case of without OA, the contact angle dramatically decreased to 14.5 °. This result indicates that the OA molecules exist on the external surface of BaTiO₃ and convert the hydrophilic surface of BaTiO₃ to a hydrophobic one.

TG curve (Fig. 2d) further demonstrates the presence of OA molecules on the surface of BaTiO₃ nanocrystals. Except for the weight loss of approximately 2.6 % before 250 °C deriving from the adsorbed water or the OH defects in crystals [25], the other two weight loss steps ranging from 250 to 550 °C are attributed to the releases of OA molecules attaching on the outer and inner surface layers of BaTiO₃ nanocrystals, respectively [26], as shown in the suggested OA adsorption model in Fig. 2d. Moreover, the total amount of OA is high to 23 wt%, which should be important in controlling the particle size and the monodispersity of BaTiO₃ nanocrystals.

3.2 Reproducibility of preparation of BaTiO₃ nanocuboids

It is known that some reported experiments with microwave heating technology are difficult to be repeated and compared by other researchers. The reason behind this phenomenon has been pointed out by Zhu et al in their review article [27], that is, the microwave oven is not in the same type for different laboratories, which causes the variance in heating/cooling rate, measuring and controlling the temperature, and thus the low reproducibility. In this work, a commercial research-type microwave oven with one

sample-tube was used, which can operate in temperature control mode under autogenous pressure. Although $\pm 1^\circ\text{C}$ of precise temperature control can be realized in range of 0-250 $^\circ\text{C}$, the heating rate is uncontrollable.

In order to investigate the reproducibility of preparation of BaTiO_3 nanocuboids with microwave heating, four repeated experiments have been carried out with precursor of $\text{Ba}(\text{OH})_2$: 0.83 $\text{Ti}(\text{OBu})_4$: 0.3 OA: 394 H_2O at 200 $^\circ\text{C}$ for 4 h, and the morphology of the products are characterized by TEM. Just as shown in Fig.3, these products have similar morphology and are mainly nanocuboid shape, suggesting a good reproducibility.

3.23 Effects of synthesis parameters

3.23.1 Effect of $\text{H}_2\text{O}/\text{Ba}$ and OA/Ba molar ratio.

In order to clarify the role of water in the formation of BaTiO_3 nanocuboids, the molar ratio of $\text{H}_2\text{O}/\text{Ba}$ was varied from 99 to 495 (Table 1), and the XRD patterns and TEM images of the resultant products are shown in Fig. 3. Independent of the molar ratio of $\text{H}_2\text{O}/\text{Ba}$, all the XRD patterns demonstrate that the resultant BaTiO_3 have perovskite structures. TEM images show that the particle size of BaTiO_3 nanoparticles slightly increases with the increase of $\text{H}_2\text{O}/\text{Ba}$ molar ratio, and in all the cases the particle sizes are less than 20 nm. In addition, the number of BaTiO_3 nanocrystals with cuboid shape gradually increases with the increase of the molar ratio of $\text{H}_2\text{O}/\text{Ba}$. In case of $\text{H}_2\text{O}/\text{Ba}$ ratio of 99, the nanoparticles mainly are nearly spherical apart from few cubic shapes. This can be attributed to the high concentration of OA, which weakens the selective adsorption of OA on special faces of BaTiO_3 nanocrystals. As $\text{H}_2\text{O}/\text{Ba}$ ratio increasing to 197, 395 and 495, OA concentration decreases gradually, and they are preferentially adsorbed on the crystal planes with higher surface energy, thus controlling the morphology of nanocrystals. Just as shown in Fig. 3b-3d, in which the main morphology is cubic. Especially in Fig. 3c, nearly 90% of the nanoparticles exhibit the cuboid shapes.

To further test the effect of OA concentration on the morphology of BaTiO₃ nanocrystals, the molar ratio of OA/Ba was varied under the condition of fixed other synthesis parameters.

XRD patterns (Fig. 45a) show that the intensity of all the diffraction peaks dramatically decreases and the half height width increases with increasing the molar ratio of OA/Ba in precursor. When the OA/Ba molar ratio increases up to 1.09 the diffraction peaks nearly disappear. A reasonable explanation for this phenomenon as follows. OA can not only reacts with titanium to form the complex [27 28] but also damages the alkalinity of synthesis system, leading to a reduced concentration of active monomer of [TiO₆]⁸⁻ [28 29] and then to a low degree of super saturation [29 30]. Hence, it is difficult for nanocrystal to grow into the large particles due to lack of active monomer as nutrient. Furthermore, once the nuclei form in synthesis system, the excess OA can cap them rapidly and then reduce their growth rate, too. Therefore, the particle size of BaTiO₃ nanocrystal decreases with the increase of OA/Ba molar ratio. TEM images (Fig. 4b-4d5b-5d) also proved this opinion.

In addition, the effect of oleic acid on the morphology of BaTiO₃ nanoparticles was clearly shown in TEM images (Fig. 4b-4e5b-5e). Without addition of OA there was no cuboid shaped BaTiO₃ nanoparticles [21] (Fig. 45b), and well defined BaTiO₃ nanocuboids can be obtained in the range of 0.3-0.5 of OA/Ba molar ratio (Fig. 4e-4d5c-5d). However, further increasing OA/Ba molar ratio to 0.83 (Fig. 45e), only the ~~nearly spherical~~ ~~torispherical~~ BaTiO₃ nanoparticles with smaller size were observed. This result confirmed further that the excessive OA in precursor solution were not only adsorbed preferentially on special crystal faces of BaTiO₃ nanocrystals, but also ~~absorbed~~ ~~adsorbed~~ on other crystal faces, and resulting in spherical BaTiO₃ nanoparticles.

3.2.3.2 Effect of Ba/Ti molar ratio and barium source

Some researchers [30-3131-32] suggest that increasing Ba/Ti molar ratio in precursor favors to form the frame cubic growth units, and these growth units are easy to pile up on the faces of the same equiaxial

family ~~equiaxially~~ along the three crystal axes, and thus to form BaTiO₃ crystal with cubic shape. To obtain BaTiO₃ nanocrystals with more uniform morphology, Ba/Ti molar ratio in precursor is increased from 1:0.83 to 1.66:0.83. However, TEM images (Fig. ~~56b~~) give unexpected results. Instead of regular cuboid shape, irregular shapes are obtained, although the perovskite structure of the product has no change (Fig. ~~56a~~). According to literature [~~34~~32], the main function of Ba²⁺ ions is stabilizing the growth units of [TiO₆]⁸⁻ octahedral. The more the Ba²⁺ ions are ~~absorbed~~-adsorbed, the higher the stability energy of the growth unit becomes, and the easier the cube shaped BaTiO₃ forms. In this work, with increasing Ba/Ti molar ratio, a different result from literature has been obtained, why? In fact, it should be noted that the alkalinity in precursor is increased accompanying with the increase of Ba/Ti molar ratio due to the addition of Ba ions in the form of Ba(OH)₂, and the synthesis system with high alkalinity usually produced ~~nearly spherical~~ ~~torispherical~~ BaTiO₃ nanoparticles [~~32~~ 33]. In order to eliminate the effect of alkalinity, ~~the total Ba/Ti molar ratio is fixed at 1.66:0.83, and~~ Ba(OH)₂ is partly replaced with BaCl₂ or BaNO₃ by a fixed Ba/Ti molar ratio of 1.66:0.83. The ~~final~~ molar ratio of Ba(OH)₂ : BaCl₂ (or BaNO₃): Ti is ~~kept at of~~ 1:0.66:0.83.

TEM images demonstrate that cuboid shape can be well maintained in the case of Ba(OH)₂ : BaCl₂: Ti molar ratio of 1:0.66: 0.83(Fig. ~~56e~~), which is contrast to the case of Ba(OH)₂: Ti=1.66:0.83 (Fig. ~~56b~~). Hence, it is drawn that the shape conversion observed from Fig ~~56a~~ and Fig ~~56b~~ is caused by the change of alkalinity in precursor instead of the molar ratio of Ba/Ti. However, in the case of Ba(OH)₂ : Ba(NO₃)₂: Ti molar ratio of 1:0.66: 0.83, some irregular shapes (Fig ~~56c~~) are found, indicating that the anion species have an influence on BaTiO₃ nanocrystal shape. Ni et al [~~33~~34] also found that the barium source could affect the morphology BaTiO₃ nanostructures. Under their synthesis condition, coral-like BaTiO₃ nanostructures, aggregated BaTiO₃ nanoparticles/rods, and the coexistence of coral-like nanostructures/big grains were obtained in cases of BaCl₂, Ba(CH₃COO)₂ and Ba(NO₃)₂ as barium source, respectively. The

authors suggested that the stronger coordinative ability CH_3COO^- with BaTiO_3 nuclei, the occupation of small amounts of active sites on BaTiO_3 nuclei by Cl^- or NO_3^- ions resulted in different morphology of BaTiO_3 . Dutta et al investigated the influence of barium source in hydrothermal system [3435]. Their results indicated that the anions (such as Cl^- and NO_3^-) of barium source influenced the phase structure of BaTiO_3 , but did not affect the morphology. ~~Perispherical~~ Nearly spherical BaTiO_3 nanoparticles were obtained in all their studied cases. Due to differences in experimental conditions with the literatures, Cl^- obviously helped to the formation of cuboid shaped BaTiO_3 nanoparticles compared with NO_3^- in this work. We speculated that Cl^- could be adsorbed much more strongly on (010) crystal plane of BaTiO_3 than NO_3^- . Under synergetic effects of Cl^- and OA, cuboid shaped BaTiO_3 nanoparticles are obtained. So, it seems that the important factor influencing the morphology of BaTiO_3 is the anion type of barium source rather than the Ba/Ti molar ratio.

3.2.3.3 *Effect of synthesis temperature and time*

It is known that the high temperature and prolonged time can accelerate the formation of BaTiO_3 under hydrothermal conditions. In our work, the XRD patterns in Fig. 67a indicate that the synthesis temperature varying in the range of 140 - 200 °C has little effect on the perovskite structure of BaTiO_3 nanocrystals. But TEM images suggest that the shape of BaTiO_3 nanocrystals remarkably changes with temperature. No cuboid shape but irregular sphere can be obtained when temperature is below 160 °C (Fig. 67b and 67c). Compared with the case of 180 °C (Fig. 67d), the number of BaTiO_3 nanocuboids obviously increase when synthesis temperature is up to 200 °C (Fig. 67e). It can be concluded that high temperature is helpful for the formation of BaTiO_3 nanocuboids.

The synthesis time is varied from 2 h to 6 h at a fixed temperature of 200 °C. XRD patterns (Fig. 67a) show that the intensity of diffraction peaks has little change with time, suggesting that the crystallization speed of BaTiO_3 nanocrystals is very fast under microwave irradiation and the crystallization process

nearly completes in 2 h. TEM images (Fig. 6e-6h, 7e-7h) also prove that the BaTiO₃ nanocuboids have been formed at 2 h, and further increasing the synthesis time to 5 h has little effect on the morphology. However, Fig. 6i shows that most of BaTiO₃ nanocuboids lose their shape and become to be spherical when the synthesis time was prolonged to 6 h, although the XRD diffraction intensity of this sample is comparative with that of 5 h. A reasonable explanation is that a dissolution-recrystallization process maybe occurs when the BaTiO₃ nanocuboids are heated in their ~~alkalie~~ alkaline mother liquor for prolonged time. And thus the spherical BaTiO₃ nanocrystals with size of 10-15 nm may be the remnants of BaTiO₃ nanocuboids after partly dissolving, and those with small size (< 10 nm) are new-formed by recrystallization.

3.2.3.4 Growth mechanism of the BaTiO₃ nanocuboids

To investigate the formation and shape evolution of BaTiO₃ nanocuboids, time-dependent experiments were carried out and the products collected at different stages were analyzed by XRD, TEM and HRTEM (Fig. 78). The XRD patterns of the samples synthesized for 5, 10, 15 and 30 min are inserted in the corresponding TEM images. Obviously, except of the presence of little amount of BaCO₃, the products are single perovskite in structure. The intensity of the diffraction peaks increases with prolonging the reaction time, which imply the growing particle size and better crystallinity of BaTiO₃ nanocrystals [35 36].

TEM image in Fig. 78a shows that the solid quenched at 5 min are aggregated particles with irregular shape and wide size distribution. The large particles (Fig. 78c) are amorphous, which should be TiO₂ or barium oleate gels formed in the process of precursor preparation. However, the small particles with size less than 10 nm are fully crystallized and single-crystal in nature (Fig. 78b). In case of 10 min (Fig. 78d), the particle aggregation is slightly weakened and the average particle size reduces. Compared with the case of 5 min, the number and size of nanocrystals (Fig. 7d-7e, 8d-8e) increase. In addition, the sizes of amorphous particles (Fig. 78f) reduced, too. These phenomena indicate that the growth of BaTiO₃ follows the dissolution–crystallization mechanism [36 37].

When synthesis time is prolonged to 15 min, the amorphous particles disappear due to complete dissolution, and the obtained particles with irregular morphology are monodispersed and crystallized (Fig. ~~7e-7i~~8g-8i). Prolonging time to 30 min, the particle size slightly increases and small nanocrystals disappear (Fig. ~~7j~~8j), which results from the Ostwald ripe mechanism. In addition, more and more particles exhibit cubic or cuboid shape. The distinct and consistent lattice fringes observed from HRTEM images (Fig. ~~7k~~8k and ~~7l~~8l) suggest a better crystalline of these particles.

According to the research of Wei et al [~~37~~ 38], to minimize the surface area, BaTiO₃ particles remain approximately spherical shape in the early stage of crystal growth. And then, following crystallographic growth causes the spherical shape to develop into cube shape due to the lowest energy of the {1 0 0} planes. But the faceted edges of {1 0 0} planes are high energy and are subjected to preferential dissolution, leading to a final morphology of spherical shape. In this work, OA molecules existing in synthesis system should be ~~absorbed~~ adsorbed on these high energy edges and thus stabilize the cube or cuboid shape of BaTiO₃. A similar result is reported by Adireddy et al [19], although their synthesis conditions are different from this work.

On the basis of morphological features observed in the present study, a growth mechanism of the BaTiO₃ nanocuboids is proposed, where the formation of BaTiO₃ nanocuboids is governed by the dissolution - crystallization mechanism, followed by the Ostwald ripening process in which the lowest energy of the planes are exposed and the high-energy faceted edges are stabilized by ~~absorbing~~ adsorbing OA molecules, and thus the cuboid morphology is preserved.

3.~~2~~3.5 Photocatalytic property of BaTiO₃ nanocudoids

It is known that BaTiO₃ is an insulator with a large energy gap. Suzuki et al [38] revealed that the particle size of BaTiO₃ ~~nanocrystallites~~ nanocrystals has influence on the band gap, and the indirect band gap is in the range of 3.22-3.28 eV for BaTiO₃ nanocrystals with sizes of 11.5-15.3 nm. In this work, the

direct and indirect optical band gaps of BaTiO₃ nanocuboids prepared with the precursor molar composition of Ba(OH)₂:0.83 Ti:0.3 OA:394 H₂O at 200 °C for 4 h are 3.75 eV and 3.15 (inset of Fig. 89a), respectively, which are calculated using the equations of Kubelka-Munk based on UV–Vis diffuse reflectance spectrum (Fig. 89a). The size of BaTiO₃ nanocuboids obtained in this work is about 13 nm, so the indirect band gap of 3.15 eV is more reasonable and seems to be the preferred one. In addition, this value is in agreement with literature result [19] where a band gap 3.2 eV is gotten for cube shaped BaTiO₃ nanocrystals with size of about 22nm.

From the calculated band gap of 3.15 eV ~~ev~~, it is deduced that BaTiO₃ nanocuboids should possess photocatalytic activity. And thus, the experiment of RhB photodegradation was carried out under UV light irradiation as a model reaction. Because adsorption of RhB molecules on catalyst is an important step in the decolorization process, prior to exposure UV light irradiation, the time getting to the stable adsorption equilibrium situation in dark is measured. The results are shown inset of Fig. 89b. It is clearly observed that the adsorption amount of RhB increase with increasing the amount of catalyst. But the time getting to the adsorption equilibrium is independent on the amount of catalyst and is about 30 min. So, the **photocatalysis** ~~photocatslysis~~ experiment is started after the solution has been stirred for 30 min in dark.

Fig. 89b shows the **photodegradation** ~~photogradation~~ efficiency of RhB with different amount of BaTiO₃ nanocuboids for different exposure time. As the exposure time increases, the degradation of RhB also increases. After UV irradiation 220 min, RhB degradation has completed. It is noted that the degradation rate decreases with catalyst amount increasing from 10, 20, 40, 60 mg, the possible reason is that the excess catalysts enhance light scattering, which results in a reduced light utilization [39 40]. Fixing the catalyst at 10 mg, the effect of RhB concentration is investigated. As shown in Fig. 89c, the degradation rate decreases with the increase of RhB concentration. When the concentration of RhB is 5 mg/L, the fastest degradation rate is achieved, and nearly complete degradation is gotten at 180 min, which is proved by the inset of Fig.

There are few studies on the photo ~~degration~~ degradation of RhB ~~Rh-B~~ with BaTiO₃ as ~~catalyst~~ catalyst, and their results are listed in Table 2. Recently, some researches show that BaTiO₃ with tetragonal phase exhibits better photocatalytic performance than the cubic phase due to the ferroelectricity promoting the carrier separation and stern layer formation [45]. However, the degradation efficiency of RhB ~~Rh-B~~ in Table 2 is remarkably different, although all the BaTiO₃ used in literature [~~40~~ 41], [~~41~~ 42] and [4] have the same crystal structure. So, the ferroelectricity should not be the key factor to determine the photocatalytic activity of BaTiO₃, if without considering the influence of other experiment parameters. In fact, the dipolar fields associated with the ferroelectric domains in small particles can separate photo-generated charge carriers and spatially localize reaction products, which results in the relative reactivity of the faces is different [46]. But for literatures [~~40~~ 41], [~~41~~ 42] and this work, the exposed faces of BaTiO₃ nanocrystals are the same type of {100}, indicating that the main factor influencing the photocatalytic activity of BaTiO₃ is not the exposed face. In addition, it is known that particle sizes of a catalyst have a significant impact on the catalytic efficiency of a system [43]. When all other conditions are equal, it is anticipated that a smaller particle size will lead to better catalytic performance, due to a larger surface area with more active sites and a shorter migrating time of photoexcited electrons from the inner to surfaces [44]. Although there is no a linear relationship between particle size and RhB ~~Rh-B~~ degradation efficiency in Table 2, a general trend can still be derived, that is, BaTiO₃ with size less than 20 nm represents a relatively high photocatalytic activity. However, compared with the 7.5 nm BaTiO₃ nanoparticles with pure tetragonal phase (Table 2), the BaTiO₃ nanocuboids prepared in our work exhibit much higher photo catalytic activity, even though they have larger size and are a mixture of tetragonal and cubic phase. A possible reason is that the amount of BaTiO₃ added into RhB ~~Rh-B~~ solution is too much in literature (1 g·L⁻¹) than this work (0.3 g·L⁻¹), which results in stronger light scattering, and then lower the light utilization efficiency, just as observed in Fig.

89b. Based on the above, the high degradation efficiency of RhB ~~Rh-B~~ obtained in this work is mainly attributed to the small size and the appropriate dosage of BaTiO₃ nanocuboids. Certainly, the contribution of the exposed {100} planes and the ferroelectricity ~~can not~~ cannot be ignored.

3.6 Role of OA in photocatalysis

In fact, the adsorbed OA on the surface of BaTiO₃ nanocuboids may play a role in the photocatalysis process. In order to figure out its function, OA is burned off in muffle oven at 500 °C for 2h. This treatment results in a remarkable increase of particle size (Fig.10a), and thus losing the qualification as a reference in comparative experiment. And then, we have tried to remove OA away by repeated washing with ethanol. This treatment causes severe agglomeration, but has little influence on the particle size (Fig.10b). IR results (Fig.10c) show that the adsorption bands attributing to OA at 2925, 2858 and 1558cm⁻¹ have almost disappeared after ethanol washing, meaning that most of OA have been washed away from the surface of BaTiO₃ nanoparticles. Although both the photocatalytic activity and the adsorption for RhB in the dark are lower compared to the untreated BaTiO₃ (Fig. 10d), attributing it to the loss of OA is arbitrary, because the effective surface area also decreases due to the severe agglomeration, which should not be neglected in evaluation of photocatalytic activity. And thus, it is necessary to develop effective method of removing OA and preventing aggregation, and some work is proceeding.

4. Conclusions

Monodispersed BaTiO₃ nanocuboids are prepared by microwave hydrothermal methods at 200 °C for 4 h. The synthesis parameters, such as temperature, time, and molar ratio in the precursor mixture, have great influence on the shape, crystalline and aggregation of BaTiO₃ nanocrystals. The achieved BaTiO₃ nanocuboids are consisted of cubic and tetragonal phases and show high hydrophobic surface property. Based on TEM images of solid extracted from the synthesis system quenched at different time, it is drown that the growth of BaTiO₃ nanocuboids follows the dissolution-recrystallization mechanism and the

Ostwald ripening process, in which the OA ~~molecules~~ ~~molecular~~ play important role in controlling the shape of BaTiO₃ nanocrystals. Compared with literatures, the present BaTiO₃ nanocuboids exhibit higher photocatalytic activity for RhB degradation under UV irradiation. Nearly complete degradation can be achieved in 180 min for 5 mol/L RhB solution.

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Table captions

Table 1 Synthesis parameters for monodispersed BaTiO₃ nanocuboids

Table 2 Comparing the photocatalytic activity of BaTiO₃ nanocuboids with literatures

Figure captions

Fig. 1 XRD pattern (a), Raman spectrum (b), TEM image (c), SADE pattern (d), particle size distribution histograms pattern (e) obtained by counting 100 nanoparticles, **the fast Fourier transform (FFT) profile (g) of the high-resolution TEM image (f) and scheme of the shape (h)** of BaTiO₃ nanocrystals prepared by microwave hydrothermal method using the precursor with molar composition of Ba(OH)₂ : 0.83 TBOT : 0.38 OA : 394 H₂O at 200 °C for 4 h. ▼ indicates trace amounts of barium carbonate phase.

Fig. 2 (a) FT-IR spectra, static contact angle images of water droplets on the thin film compressed with BaTiO₃ nanocrystals prepared with (b) and without (c) OA, and TG-DTG curves (d) of BaTiO₃ nanocrystals prepared with OA.

Fig. 3 TEM images of the products from four repeated experiments.

Fig. 34 (a) XRD patterns of BaTiO₃ nanocrystals prepared with different molar ratio of H₂O/Ba; TEM images of BaTiO₃ nanocrystals prepared with H₂O/Ba molar ratio of (b) 99, (c) 197, (d) 394 and (e) 495. ▼ indicates trace amounts of barium carbonate phase.

Fig. 45 (a) XRD patterns of BaTiO₃ nanocrystals prepared with different molar ratio of OA/Ba; TEM images of BaTiO₃ nanocrystals prepared with OA/Ba molar ratio of (b) 0, (c) 0.30, (d) 0.56 and (e) 0.83.

Fig. 56 TEM images of BaTiO₃ nanocrystals prepared with molar ratio of Ba(OH)₂ : Ti of (a) 1.0 : 0.83, (b) 1.66 : 0.83, (c) Ba(OH)₂ : Ba(NO₃)₂ : Ti = 1.0 : 0.66 : 0.83, and (d) Ba(OH)₂ : BaCl₂ : Ti = 1.0 : 0.66 : 0.83.

Fig. 67 (a) XRD patterns of BaTiO₃ nanocrystals prepared with different temperature and time; TEM images of BaTiO₃ nanocrystals prepared at (b) 140°C/4h, (c) 160°C/4h, (d) 180°C/4h, (e) 200°C/4h, (f) 200°C/2h, (g) 200°C/3h, (h) 200°C/5h, and (i) 200°C/6h.

Fig. 78 XRD patterns (a) and HRTEM images of the solid separated from the mother liquor which is microwave hydrothermally treated for (b-c) 5 min, (d-e) 10 min, (f-g) 15 min and (h-i) 30 min.

Fig. 89 (a) UV-vis diffuse reflectance spectrum of BaTiO₃ nanocuboids (the inset represents the indirect band gap); ~~Photo-catalytic degradation~~ C/Co values of RhB ~~C/C₀ values respect to~~ vs. time under UV irradiation: (b) effect of the quantity of BaTiO₃ nanocrystals. Condition: ~~10, 20, 40 and 60 mg of BaTiO₃ are added into~~ 30 mL of 10 mg/L RhB solution, ~~respectively. with in initial concentration of~~. (c) effect of the initial concentration of RhB solution. Condition: ~~30 mL RhB solution with~~ 10 mg of BaTiO₃ nanocrystals ~~as catalyst~~ are added into 30 mL of 5, 10, 15 and 20 mg/L RhB solution, respectively. Inset (b) presents the adsorption of RhB on BaTiO₃ nanocrystals in dark, and inset (c) is absorption spectra of RhB (5 mg/L) aqueous solution in presence of BaTiO₃ nanocrystals during UV irradiation.

Fig. 10 TEM images of BaTiO₃ after (a) calcined in muffle oven at 500 °C for 2 h and (b) washed several times with ethanol, (c) IR spectra and (d) C/Co values of RhB vs. time under UV irradiation for BaTiO₃ before and after washed several times with ethanol. Photocatalysis is carried out with 10 mg of BaTiO₃ in 30 mL of 5 mg/L RhB solution.

Table 1

No.	Molar ratio						T (°C)	t (h)
	X	y	Z	f	j	k		
S1	1	0	0	0.83	0.30	99	200	4
S2	1	0	0	0.83	0.30	197	200	4
S3	1	0	0	0.83	0.30	394	200	4
S4	1	0	0	0.83	0.30	495	200	4
S5	1	0	0	0.83	0	394	200	4
S6	1	0	0	0.83	0.56	394	200	4
S7	1	0	0	0.83	0.83	394	200	4
S8	1	0	0	0.83	1.09	394	200	4
S9	1.66	0	0	0.83	0.30	394	200	4
S10	1	0.66	0	0.83	0.30	394	200	4
S11	1	0	0.66	0.83	0.30	394	200	4
S12	1	0	0	0.83	0.30	394	140	4
S13	1	0	0	0.83	0.30	394	160	4
S14	1	0	0	0.83	0.30	394	180	4
S15	1	0	0	0.83	0.30	394	200	2
S16	1	0	0	0.83	0.30	394	200	3
S17	1	0	0	0.83	0.30	394	200	5
S18	1	0	0	0.83	0.30	394	200	6

^a Molar composition of the precursor : x Ba(OH)₂ : y Ba(NO₃)₂ : z BaCl₂ : f Ti(OBu)₄ : j OA : k H₂O.

Table 2

Rh B solution		Irraditio n light	BaTiO ₃				Irradiation time (min)	Degradatio n efficiency (%)	Ref.
Volume /mL	Concentration /mg/L		Average size(nm)	Shape	Crystal structure	Amount (mg)			
100	10	UV	7.5	cube	tetragonal	100	40	38	[4041]
20	15	UV	87	cube	tetragonal	20	180	≈ 5	[4142]
50	10	Simulat ed sunlight	622	irregular	cubic /tetragona l	150	60	≈20	[45]
25	10	UV	300	subsphaeroi dal	tetragonal	25	60	≈10	[4]
30	10	UV	13	cube	cubic /tetragona l	10	40 60 220	64 87 ≈100	This work

FIGURES

Fig. 1

Fig. 2

Fig. 3

Fig. 34

Fig. 45

Fig. 56

Fig. 67

Fig. 78

Fig. 89

Fig. 10

Graphical Abstract