The barium titanate (BaTiO$_3$) nanoparticles with novel dendrite-like structures have been successfully fabricated via a simple coprecipitation method, the so-called BaTiO$_3$ nanodendrites (BTNDs). This method was remarkable, fast, simple, and scalable.

The growth solution is prepared by barium chloride (BaCl$_2$), titanium tetrachloride (TiCl$_4$), and oxalic acid. The shape and size of BaTiO$_3$ depend on the amount of added BaCl$_2$ solvent. To investigate the influence of amount of BaCl$_2$ on BTNDs, the amount of BaCl$_2$ was varied in the range from 3 to 6 mL. The role of BaCl$_2$ is found to have remarkable influence on the morphology, crystallite size, and formation of dendrite-like structures. The thickness and length of the central stem of BTND were $\sim$300 nm and $\sim$20 $\mu$m, respectively. The branchings were found to occur at irregular intervals along the main stem. Besides, the formation mechanism of BTND is proposed and discussed.

1. Introduction

Over the past few years, the unique ferroelectric, piezoelectric, and thermoelectric properties of barium titanate (BaTiO$_3$) nanoparticles have become increasingly important in the electronic ceramics industry. The BaTiO$_3$ nanoparticles have been extensively applied in various fields such as multilayer ceramic capacitors (MLCCs), integral capacitors in printed circuit boards (PCB), dynamic random access memories (DRAM), resistors with positive temperature coefficient of resistivity (PTCR), temperature-humidity-gas sensors, electrooptic devices, piezoelectric transducers, actuators, and thermistors [1–9]. Among these applications, performance and characteristics are strongly influenced by size, shape, composition, morphology, spatial ordering, and impurities of the BaTiO$_3$ nanoparticles. Thus, effectively controlling their shape and size is of high importance and is a challenging task for researchers and the industry. In this work, we have developed BaTiO$_3$ with novel dendrite-like structures. Very recently, nanoparticles with dendrite-like structures have received much attention because of their potential application in device [10, 11]. However, finely controlling the morphology of the BaTiO$_3$ nanoparticles is extremely dependent on preparation method and synthesis procedure.

Traditionally, the BaTiO$_3$ particle is prepared by the solid-state reaction method through heating BaCO$_3$ and TiO$_2$ at high temperature as 1200$^\circ$C [12, 13]. The disadvantage of this method is that high calcinations temperature may strongly cause aggregation between the particles, and it takes a long time to produce submicrometer particles (1~2 $\mu$m). Up to now, various new preparation methods have been developed and reported in fabricating BaTiO$_3$ nanoparticles with high quality, well-controlled shape, and small size, such as the sol-gel method [14, 15], the hydrothermal method [16, 17], the Pechini processing using a citric or oxalate complex as the precursor [18, 19], the ball-milling method [20, 21],
the polymeric precursor method [22], the soft chemical process [23], the glycolthermal method [24], and the coprecipitation method [25]. Among these, the coprecipitation method is superior to other methods in terms of the following characteristics: high growth rate, modest equipment, low processing temperature, ease of controlling the yield, low cost, large amount synthesized, and high quality [26].

In the coprecipitation method, the preparation of BaTiO₃ nanoparticles through the coprecipitation of barium and titanium hydroxides from aqueous solutions has been reported since the early Flaschen research work [27]. Synthesis of BaTiO₃ nanoparticles as the decomposition product of barium titanyl oxalate or barium titanyl citrate is a multistage process, depending on the gaseous medium, the dispersion of the starting reagents and intermediate phase (the degree of branching of the interphase surface), the regime in which the reaction occurs (kinetic or diffusion), the growth temperature, and the heating rate [28–32]. Although these previous studies succeeded in fabricating BaTiO₃ nanoparticles, the procedure is quite complicated. Furthermore, these procedures also require special conditions, such as judicious choice of the stabilizer, heat treatment, and time duration. Therefore, it will be a significant challenge to simplify the procedure for the fabrication of BaTiO₃ nanoparticles.

In our laboratory, we developed a simple procedure by slightly modifying the multistage process so it could be applied to fabricate BaTiO₃ nanoparticles with well-controlled size. In this simple procedure, appropriate amount of stock solution of titanium tetrachloride (TiCl₄), barium chloride (BaCl₂), and oxalic acid was added in deionized water to form growth solution. The BaTiO₃ nanoparticle was formed by coprecipitation of both barium and titanium precursor. During the coprecipitation process, titanium acted as the seed in the growth solution so that the barium could nucleate and precipitate onto the surfaces of titanium via the heterogeneous nucleation process. More importantly, it is found that the amount of added BaCl₂ can be critical for shape and size of BaTiO₃ nanoparticles.

In this study, we first reported the fabrication of BaTiO₃ nanoparticles with novel dendrite-like structures through the coprecipitation method, the so-called BaTiO₃ nanodendrites (BTNDs). It can be observed that the various amounts of added BaCl₂ during nucleation and growth process caused the alteration of the BaTiO₃ nanoparticles shape, forming the branch-like structures. Until now, to our knowledge, there are no reports yet on the synthesis of the BTNDs by coprecipitation method. A good understanding of the microstructure properties is a very important issue for the potential application of the BTNDs. Thus, a detailed model for the newly observed novel BTNDs is also proposed to explain their possible formation mechanism.

2. Experimental Details

Barium chloride (BaCl₂·2H₂O, 99%) and oxalic acid (C₂H₂O₄·2H₂O, 99%) were obtained from Riedel-deHaën (Sigma-Aldrich, USA). Titanium tetrachloride solution (TiCl₄, 99%, 0.1M) was purchased from Fluka (Sigma-Aldrich, USA). All chemicals and materials were used without further purification. The distilled water used throughout the experiments was purified by a Milli-Q system (Millipore resistivity 18.2 MΩ cm). The BTNDs were fabricated by first dissolving BaCl₂ in distilled water at 50–70°C. Separately, oxalic acid was dissolved in distilled water at 65°C in an ultrasonic tank with titanium tetrachloride slowly added. The two solutions were mixed in an ultrasonic bath at 65°C. Nanometer-sized BaTiO₃ particles were formed at this stage. Finally, the growth time was 20 min.

The size and shape of the BTNDs were measured and analyzed by transmission electron microscopy (TEM, JEOL JEM-1230) at an accelerating voltage of 80 kV. The microstructure of the BTNDs was observed by high-resolution transmission electron microscopy (HRTEM, Philips Tecnai G2 F20) with an accelerating voltage of 200 kV. The HRTEM was equipped with selected area electron diffraction (SAED) and an energy-dispersive X-ray (EDX) spectrometric element analyzer. The samples for TEM, SAED, and EDX were prepared by drop coating onto a standard 200-mesh, 3 mm, carbon-coated copper grid (Agar Scientific, UK).

3. Results and Discussion

Figures 1(a)–1(d) show the TEM images of BaTiO₃ nanoparticles obtained by adding 3, 4, 5, and 6 mL of BaCl₂. The results clearly show that the shape of the BaTiO₃ nanoparticles can be changed by altering the amount of BaCl₂. When the amount of BaCl₂ was 3 mL, the BaTiO₃ nanoparticles with large quantities were almost spherical in shape and were small in size, as shown in Figure 1(a). The inset of Figure 1(a) shows the TEM image of BaTiO₃ nanoparticles at higher magnification, indicating that the particle size is about 20 nm. When the amount of BaCl₂ was increased from 4 to 5 mL, the shape of BaTiO₃ nanoparticles began to change from spherical to dendrite-like, as shown in Figures 1(b) and 1(c). When the amount of BaCl₂ was 6 mL, the BaTiO₃ nanoparticles were almost dendrite-like in shape, as shown in Figure 1(d). Even after sonication for TEM sample preparation, the branches of the dendrites were intact, indicating strong bonding between the grains. Thus, there is not any isolated spherical BaTiO₃ particles in TEM image. However, the role of BaCl₂ may be to act as shape-modifier to change BaTiO₃ nanoparticles’ shape from spherical to dendrite-like structure when the BaCl₂ with high amount was added to growth solution during coprecipitation process. Besides, these results also show that the size of BaTiO₃ nanoparticles increased as the amount of BaCl₂ increased, as revealed TEM analysis (Figure 1).

Figure 2 shows the low-magnification TEM images of single BTND prepared with 6 mL of BaCl₂. As can be seen in Figure 2(a), the BTND described as dendritic structures has a large area of several square micrometers. The thickness of the central stem of BTND was ∼300 nm. Along the central stem (with length of ∼20 μm), branching was seen for every ∼300 nm. The lengths of the side branches were found to be different for the same BTND. Also the angle between the main stem and the branch was not constant.
Table 1: Preparation of BaTiO$_3$ particles using oxalate process.

**Step 1: synthesis of mixed oxalate**

$$
\text{TiCl}_4 + \text{H}_2\text{O} \rightarrow \text{TiOCl}_2 + 2\text{HCl} \quad (1)
$$

$$
\text{BaCl}_2 + \text{TiOCl}_2 + 2\text{H}_2\text{C}_2\text{O}_4 + 4\text{H}_2\text{O} \rightarrow \text{BaTiO(C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O} + 4\text{HCl} \quad (2)
$$

**Step 2: thermal decomposition**

$$
\text{BaTiO(C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{BaTiO(C}_2\text{O}_4)_2 + 4\text{H}_2\text{O} \quad (3)
$$

$$
\text{BaTiO(C}_2\text{O}_4)_2 \rightarrow 0.5\text{BaTi}_2\text{O}_5 + 0.5\text{BaCO}_3 + 2\text{CO} + 1.5\text{CO}_2 \quad (4)
$$

$$
0.5\text{BaTi}_2\text{O}_5 + 0.5\text{BaCO}_3 \rightarrow \text{BaTiO}_3 \downarrow + 0.5\text{CO}_2 \quad (5)
$$

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**Figure 1**: Transmission electron microscopy (TEM) images of the BaTiO$_3$ nanoparticles prepared by (a) 3, (b) 4, (c) 5, and (d) 6 mL of barium chloride.

for all the cases, as shown in Figure 2(b). The aggregated crystallites may form a BTND by oriented attachment of the crystallites. The inset of Figure 2(b) shows the SAED pattern of the individual grain from the BTND. The characteristic ring in the polycrystalline diffraction pattern confirmed that the BTNDs are polycrystalline structures. Figure 2(c) shows high-magnification TEM image of stem of single BTND, which clearly shows that the dendrite-like structure consisted of eleven large BaTiO$_3$ particles and many small BaTiO$_3$ compounds between the particles. Figure 2(d) schematically
shows the formation mechanism of BTNDs. The BTNDs were formed by aggregation of many small BaTiO$_3$ compounds between the large BaTiO$_3$ particles during the growth process, indicating that small BaTiO$_3$ compounds linked the large BaTiO$_3$ particles to form the dendrite-like shape. However, the present study is to show that the amount of BaCl$_2$ is a key parameter in the formation of BaTiO$_3$ nanoparticles with various sizes and shapes.

The BaTiO$_3$ nanoparticles produced using the coprecipitation method were analyzed by using EDX for studying the composition of BaTiO$_3$ nanoparticles, as shown in Figure 3. The elements detected should be carbon, oxygen, titanium (Ti), and barium (Ba) in the present method. No other elements were detected, indicating that the sample is purely BaTiO$_3$. The peaks of copper (Cu) and carbon in this chart correspond to the Cu grid coated with a thin carbon film as a carrier of the BaTiO$_3$ nanoparticles during the test. The above findings support the hypothesis that the formation of BTNDs process is as follows. The relationship between the formation of BTNDs and the amount of BaCl$_2$ can be easily explained through the chemical formation of BaTiO$_3$ particles during oxalate process [33], as shown in Table 1.
The precipitation of monodisperse BaTiO$_3$ particles is generally formed with the synthesis of mixed oxalate (Step 1) and the thermal decomposition (Step 2). According to (1) of Step 1, Ti (IV) hydroxo complexes or Ti (IV) polyanions are produced by hydrolysis and condensation reactions. According to (2) of Step 1, starting materials TiCl$_4$ and BaCl$_2$ are reacted with water and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) to precipitate a double oxalate (BaTiO(C$_2$O$_4$)$_2$·4H$_2$O) precursor. This precursor was obtained by the reaction which proceeds in two steps: (i) initial rapid formation of a Ti-rich gel phase and (ii) slower reaction between the gel phase and the Ba$^{2+}$ left in solution. According to Step 2, this precursor during growth process then results in formation of small BaTiO$_3$ compounds (at atomic- or molecular-level compositional homogeneity) through thermal decomposition. Finally, the aggregation and the agglomeration of many small BaTiO$_3$ compounds lead to the formation of crystalline BaTiO$_3$ particle, and a white BaTiO$_3$ particle precipitate can be readily observed. According to (2), the amount of double oxalate precursor is increased as the amount of BaCl$_2$ increases when the TiCl$_4$ is enough amounts. In other words, the amount of small BaTiO$_3$ compounds is increased with the increase in amount of double oxalate precursor, as shown in Table 1. Thus, the aggregation of small BaTiO$_3$ compounds is enhanced when the amount of small BaTiO$_3$ compounds increases, resulting in the growth of BaTiO$_3$ nanoparticles being enhanced and causing the size of the BaTiO$_3$ nanoparticles to be increased. However, the size of BaTiO$_3$ nanoparticles is directly proportioned to amount of BaCl$_2$, with the results being consistent with TEM analysis of Figure 1.

In this study, we propose that the addition of BaCl$_2$ causes the possible mechanism of BTNDs formation. It is found that a high amount of BaCl$_2$ led to formation of large BaTiO$_3$ particles and small BaTiO$_3$ compounds during the coprecipitation growth that caused particle agglomeration to form BTNDs in the growth solution, as shown in Figure 2. The small BaTiO$_3$ compounds aggregated onto the surface of the large BaTiO$_3$ particles by the van der Waals attractions forces during growth process. It is considered to comprise mainly two processes: (i) the formation of small BaTiO$_3$ compounds at the growth process and (ii) the subsequent anisotropic coalescence of these small BaTiO$_3$ compounds leading to the BTNDs formation; that is to say, these small BaTiO$_3$ compounds with an unstable state show a tendency to undergo fusion into dendrite-like structures. Hence, the amount of BaCl$_2$ definitely plays a critical role in the formation of the BTNDs. However, formation mechanism for BTNDs using the coprecipitation method via BaCl$_2$ addition is still under investigation.

4. Conclusions

In summary, this study prepares polycrystalline BTNDs by a simple coprecipitation method. It has been observed that the amount of BaCl$_2$ plays an important role in the formation of BTNDs. Change in the amount of BaCl$_2$ from 3 to 6 mL strongly affected the shape of particles from sphere to dendrite-like shape. The formation of BTNDs was induced by aggregation of many small BaTiO$_3$ compounds between the several large BaTiO$_3$ particles during growth, causing the small BaTiO$_3$ compounds to link to the large BaTiO$_3$ particles forming dendrite-like structures. Further measurements are now necessary to get a better understanding of these BTNDs. This preparation of BTNDs is proven to be a simple and effective synthesis method.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


