研究简报

简捷水热前驱物技术制备钛酸钡纳米棒与纳米球

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Facile Hydrothermal Single-source Approach to Barium Titanate Nanorods and Nanospheres Preparation

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Abstract：A facile synthesis route has been developed to prepare barium titanate nanoparitcles *via* a low temperature (120 ℃) hydrothermal decomposition of single-source metal-organic precursor. A mixture of tetramethylammonium hydroxide (TMAH) and distilled water was used as reaction media, and Barium titanium ethyl-hexanoisoproxide [$BaTi(O_2CC_7H_{15})(OC_3H_7)_5$] was used as precursor. The architecture of products can be selectively controlled from nanorods to nanospheres by adjusting the precursor's concentration in the reaction system. Powder X-ray diffraction (XRD) analysis indicated that the products were in cubic phase. Transmission electronic microscopy (TEM) observation showed that the nanospheres were 30~50 nm in diameter, and the nanorods were 5~10 nm in diameter and 100~600 nm in length, respectively. Phase transformation behavior of the as-prepared products was also investigated.

Key words: barium titanate；hydrothermal technique；precursor；nanoparticles

0   Introduction

Nanoscale structures,   such as nanoparticles, nanorods, nanowires, nanocubes, and nanotubes have attracted extensive synthetic attention,   as a result of their novel size-dependent properties[1]. The physical properties of materials, as they progress from the bulk to the nanoscale regime, (1~100 nm) continue to be of mmense interest and increasing importance for future technological applications. Nanocrystals display properties generally found to be scientifically different from the bulk materials or the atomic or molecular species from which they can be derived.   Examples of this phenomenon are manifold[2-4]. The study of semiconductor nanocrystals is a well-established field, yielding rich,   useful and application-oriented research[5].

Understanding the behavior of ferroelectric mate-

rials at the nanoscale is of importance to the development of molecular electronics, in particular for random access memory and logic circuitry. Perovskite-phase mixed-metal oxides exhibit outstanding chemical and physical properties, which include catalytic, oxygen-transport, ferroelectric, pyroelectric, piezoelectric and dielectric behavior[6~8]. These properties mainly depend on the crystal size, shape, defects, surface and interface properties. Therefore, the preparation of pure, stoichiometric, homogeneous and crystalline perovskite materials with controllable size and shape is of high interest.

Barium titanate ($BaTiO_3$) is probably the most investigated perovskite material, because of its high dielectric constant[9~11] and ferroelectric properties[12,13], which are essential for the use in eclectro-ceramic[8,14~17] and optical materials[18]. $BaTiO_3$ exists in various crystallographic modifications, of which the tetragonal and cubic polymorphs are the most studied. The tetragonal ferroelectric structure forms in the temperature ranges from 0 to 130 ℃, whereas the paraelectric cubic modification is stable above the Curie temperature of 130 ℃. In the tetragonal polymorph, the titanium ions are distorted from the centro-symmetric position within the TiO_6 octahedral, giving rise to spontaneous polarization[19].

Although tetragonal polymorph is the thermodynamically stable form at room temperature, most low-temperature synthesis routes result in the formation of the cubic structure. A high-temperature treatment at around 1 000 ℃ is necessary to induce phase transformation from the cubic to the tetragonal structure upon cooling again to room temperature[10,11,19]. In view of the importance of titanates, it is not surprising that a wide variety of approaches for their synthesis have been reported. Wong et al. reported a solid-state reaction as a means of preparing single-crystalline $BaTiO_3$ and $SrTiO_3$ nanostructures in a NaCl medium at 820 ℃ in the presence of nonionic surfactant[20]. O′Brien and coworkers developed a method of injection-hydrolysis of organometallic precursor to synthesize monodispersed nanoparticles of barium titanate[21]. Nanorods of $BaTiO_3$ and $SrTiO_3$ have been prepared by Hongkun

Park et al. via a solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands[22]. On the other hand, hydrothermal and sol-gel method have also been extensively explored to prepare perovskite nanocrystals [23~26]. Recently, Niederberge et al. developed a non-aqueous and halide free route to prepare perovskite nanoparticles [27]. However, the development of a simple and convenient route to synthesize $BaTiO_3$ nanocrystals with controlled size and shape is still a challenge to chemists and material scientists.

Herein, we report a controlled preparation of $BaTiO_3$ nanoparticles through hydrothermal decomposition of bimetallic alkoxide precursor, using a mixture of tetramethyl ammonium hydroxide (TMAH) (20% in water) and distilled water as reaction media. In the present solution route, we can selectively prepare $BaTiO_3$ nanorods or nanospheres by varying the precursor′s concentration in the system.

1　Experimental section

Barium titanium ethyl-hexano-isoproxide [$BaTi(O_2CC_7H_{15})(OC_3H_7)_5$] in isopropanol was purchased from Alfa Aesar Company. 20% TMAH aqueous solution was from Aldrich. In a typical procedure, 1 mmol $BaTi(O_2CC_7H_{15})(OC_3H_7)_5$ was added to a Teflon-lined autoclave with the capacity of 60 mL, which was filled with appropriate amount of mixture of TMAH and distilled water. In order to remove CO_2 dissolved in the solution, the autoclave was bubbling with argon for 10~15 min. The autoclave was sealed quickly and put in an oven, maintained at 120 ℃ for 10~12 h. After the heating treatment, the autoclave was allowed to cool to room temperature naturally. The precipitates were filtered and washed with distilled water, absolute alcohol several times. After being dried in vacuum at 50 ℃ for 4 h, white powders were collected for characterization.

The obtained samples were characterized by X-ray powder diffraction (XRD), operating on a Rigaku/D-Max γA X-ray diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ =0.154 06 nm). The morphology and particle size of the final products were

determined by transmission electronic microscopy (TEM), taken on a JEM JEOL-2010 with an energy-dispersive X-ray (EDX) spectroscopy.

2 Results and discussion

2.1 Characterization of the as-prepared products

Fig. 1 shows a typical XRD pattern of the sample prepared in a mixture of 20 mL distilled water and 25 mL TMAH. All the diffraction peaks can be indexed to cubic perovskite phase of $BaTiO_3$. The unit cell parameter has been determined to be 0.399 5 nm, which is very close to the reported value (JCPDS Card 75-0461). No evidence of other impurities such as barium carbonate, titanium oxide and other compounds can be detected in the pattern. Scherrer analysis indicated that the crystal size was about 40 nm, similar to the value obtained from TEM (30~50 nm). The related
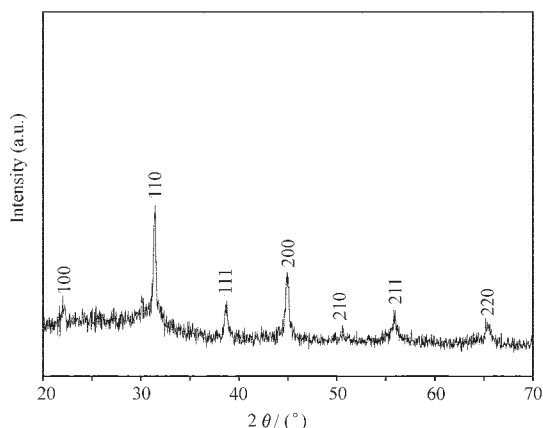

Fig.1 Typical XRD pattern of the sample prepared
in a mixture of 20 mL distilled water and
25 mL TMAH

EDX analysis shown in Fig. 2 indicated that the product could be obtained in a stoichiometric ratio. Due to the possible overlap of Ba and Ti in position, we also perform chemical analysis of the sample. The results revealed that the barium titanate had a Ba/Ti ratio of 0.996.
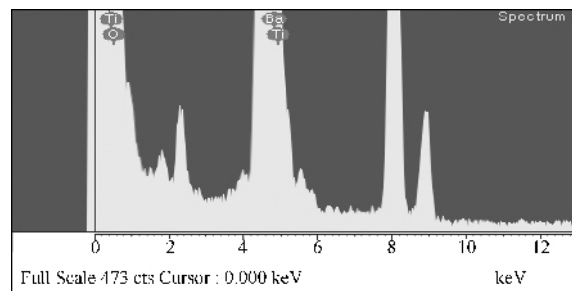

Fig.2 EDX spectrum of the as-prepared product

Fig.3a shows the TEM images of the sample prepared in a mixture of 25 mL distilled water and 25 mL TMAH. It can be seen that the obtained sample is nanospheres with diameters of 30~50 nm. If the water content was changed to 20 mL, rohile kept the other conditions constant, TEM images as shown in Fig.3b, c revealed that the product was abundant nanorods with diameters of 5~10 nm and length of 100~600 nm. The electronic diffraction pattern (ED) shows that products were polycrystalline. The diffraction rings could be easily assigned to the cubic phase of $BaTiO_3$. TEM observation proved that the shape of the BaTiO3 nanoparticles can be selectively controlled by varying the precursor concentration (or water content) of the reaction system.
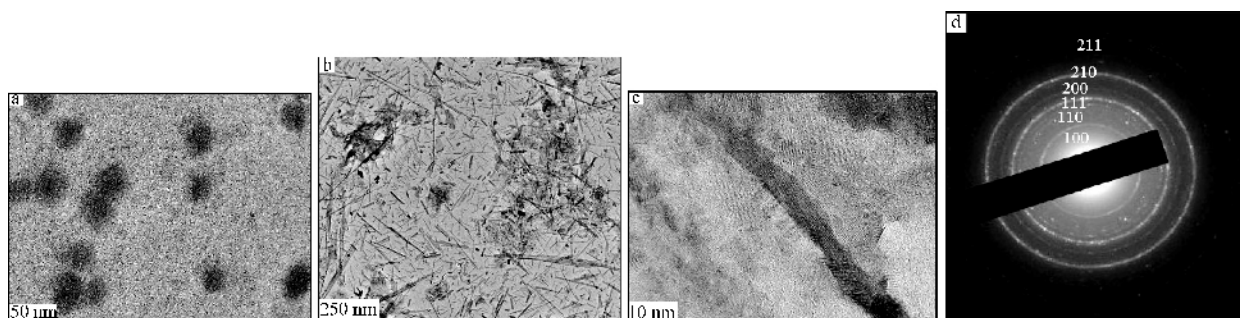
(a) the sample prepared in a mixture of 25 mL distilled water and 25 mL TMAH;

(b, c) the sample prepared in a mixture of 20 mL distilled water and 25 mL TMAH

(d) SAED pattern of the nanorods

Fig.3 TEM images of the as-prepared products

2.2 Phase transformation of the BaTiO₃ nano-paritcles

In order to investigate the phase transformation behavior of the BaTiO₃, the as-prepared sample was annealed under nitrogen atmosphere at 1 100 ℃ for 1 h. XRD pattern of the annealed product as given in Fig.4a showed that there was a splitting of the (200) reflection in the tetragonal form, with the lower angle shoulder indexed at (002). In the cubic form this peak remains unsplit[28]. All the diffraction peaks in the pattern can be indexed to the tetragonal unit cell of BaTiO₃ with lattice parameters of a=0.399 5 nm, b=0.403 4 nm, which were very close to the reported data (JCPDS Card 42-1393). No characteristic peaks of impurities, such as $BaCO_3$ or TiO_2, were detected in the pattern. Elemental analysis for the composition of the as-prepared product indicates that the target compounds are formed in a stoichiometric ratio, which is consistent with the analysis of XRD. The related TEM image (Fig.4b) shows that the annealed sample was plate-like with the average diameter of 120~200 nm.
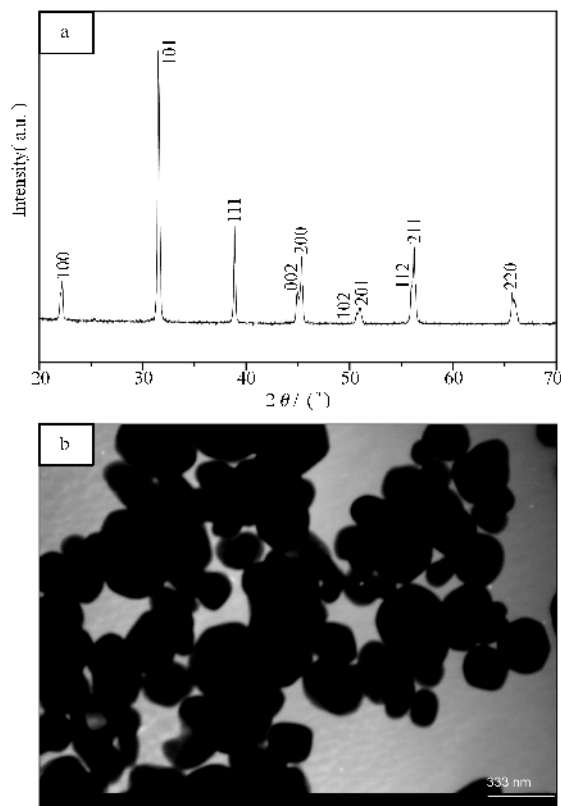

Fig.4 (a) XRD pattern of the annealed product
(b) TEM image of the annealed product

2.3 Possible of reaction mechanism

In this approach, the hydrolysis is performed in the presence of excess water and a base is employed to catalyze the complete hydrolysis of all O-R groups[29]. The hydrolysis and condensation of titanium alkoxide or titanium cations in solution has been the subject of a great deal of attention[30]. Previous studies particularly relevant to the present results is the theoretical work by Henry and Livage, developed based on the partial charge model to understand and predict inorganic polymerization of transition metal oxide precursors[30b], as well as the work by Bradley on the hydrolysis of titanium alkoxides in the presence of a base[31]. According to these reports, the presence of a base influences the condensation by favoring the formation of the highly nucleophilic TiO^- species. These reactive condensation precursors react with the positively charged titanium, leading to the formation of polymeric materials[30a]. In the present route, the hydrolysis of $BaTi(OR)_6$ may be similar to that of $Ti(OR)_4$[29]. The role of H_2O is believed to first hydrolyze the alkoxide by forcing out the alkoxide ligands *via* nucleophilic substitution

Hydrolysis: $H_2O + L\text{-}OR \rightarrow L\text{-}OH + ROH$ (1)
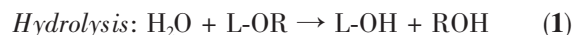
where L=hydrolyzed alkoxide oligomer, Ba or Ti, and $R=(O_2CC_7H_{15})(OC_3H_7)_5$, whereas the role of the alkaline condition was to produce strong nucleophiles $(L\text{-}O:^-)$ *via* deprotonation of hydroxo ligands

Condensation: $L\text{-}OH + :B \rightarrow L\text{-}O:^- + BH^+$ (2)

where L = hydrolyzed alkoxide oligomer, Ti or H, and $B =:OH^-$, so that condensation between $L\text{-}O:^-$ and L-OH species could take place[32,33]. And finally the BaTiO₃ resulted by condensation of $(Ba\text{-}O\text{-}Ti)_n$ clusters. Our present understanding of the mechanism for the formation of BaTiO₃ nanoparticles is still limited, and more in-depth studies are still needed.

3 Conclusion

Crystalline BaTiO₃ nanorods and nanospheres with a cubic perovskite structure have been selectively synthesized by hydrothermal decomposition of single-source bimetallic alkoxide precursors. The obtained nanoparticles should provide an ideal candidate

for fundamental studies of nanoscale ferroelectricity, piezoelectricity and paraelectricity. The synthetic strategy, a base catalysis-hydrolysis method, presented here may offer the possibility of a generalized approach to the production of other cubic perovskite nanoparticles with different chemical composition by choosing appropriate bimetallic precursors.

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