Research Article

A Two-Step Method to Synthesize $\text{BaSn}(\text{OH})_6$ Crystalline Nanorods and Their Thermal Decomposition to Barium Stannate

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A novel two-step technique is introduced to synthesize $\text{BaSn}(\text{OH})_6$ nanorods. The method involves the preparation of precursor $\text{Na}_2\text{Sn}(\text{OH})_6$ crystals in aqueous solution via hydrothermal method and the ion-exchange reaction between $\text{Na}_2\text{Sn}(\text{OH})_6$ crystals and Ba^{2+} solution that followed, assisted by ultrasonic treatment. The $\text{BaSn}(\text{OH})_6$ nanorods array are formed due to the split of plate-formed $\text{Na}_2\text{Sn}(\text{OH})_6$ during the ion-exchange treatment. The influence of the surfactant on the growth of the one-dimensional (1D) $\text{BaSn}(\text{OH})_6$ nanostructures is investigated. In addition, the powder BaSnO_3 has been obtained by thermal treatment at 450°C for 5 h under inert gas protecting condition using $\text{BaSn}(\text{OH})_6$ nanorods as precursor. The 1D shape of $\text{BaSn}(\text{OH})_6$ was retained after thermal treatment.

1. Introduction

As a perovskite-structured ceramic, BaSnO_3 is becoming more and more important in material technology because of its characteristic dielectric properties. It has been recently considered to be a new material for semiconductor gas sensors because of its high selectivity, sensitivity, and stability toward sensor materials for a lot of gases, including CO , H_2 , Cl_2 , NO_x , and humidity [1–4]. The mechanism of the gas sensitivity of this semiconducting oxide is a surface reaction process [5]. Thus, a large surface area of the oxide powder is of importance to its characteristic sensor properties. In the recent papers, nanostructures have demonstrated good sensitivity as sensing materials [6–9]. The 1D nanostructure of BaSnO_3 may improve the sensitivity of gas-sensing materials because of their shape and size. The micrometer BaSnO_3 has been synthesized by solid reaction [10], sol-gel method [11], and hydrothermal method [12]. A modified hydrothermal method was used to prepare $\text{BaSn}(\text{OH})_6$ nanoparticle with diameter of 10 nm as precursor from treating $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ and $\text{Ba}(\text{OH})_2$ solution at 250°C . Then, BaSnO_3 of 27 nm was obtained by recrystallizing $\text{BaSn}(\text{OH})_6$ at 330°C . In this work, the peptization of precursor $\text{BaSn}(\text{OH})_6$ was strictly

dependent on the pH value of the solution and the particle sizes of the $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ sol were necessary to be in the range of less than 20 nm [13]. More recently [14], we reported a new simple two-step technique to synthesize well-defined $\text{CdSnO}_3 \cdot 3\text{H}_2\text{O}$ nanocubes where their shape and size can be controlled by adjusting the experimental factors. The method involved the preparation of $\text{Na}_2\text{Sn}(\text{OH})_6$ as starting materials via a hydrothermal method in solution, followed by the ion-exchange reaction between solid $\text{Na}_2\text{Sn}(\text{OH})_6$ and Cd^{2+} solution, assisted by ultrasonic treatment. Our other works that followed revealed that the method could be extended to fabricate other kinds of stannate. In the present work, we applied this method to synthesize $\text{BaSn}(\text{OH})_6$ nanostructure, and the morphology of the obtained product was nanorod array. The influences of reaction conditions, including surfactant and reaction time, on the growth of $\text{BaSn}(\text{OH})_6$ nanorod array were investigated.

2. Experimental

5.0 g of SnCl_4 and 0.5 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 50 mL of deionized water. 30 mL of 12.5 mol/L NaOH aqueous solution was then added

dropwise into the solution under vigorous stirring. The resulting slurry was transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL treated under hydrothermal conditions at 180°C for 24 h. After the vessel was cooled to room temperature, the precursor $\text{Na}_2\text{Sn}(\text{OH})_6$ was obtained.

1.5 mmol of BaCl_2 was dissolved in 300 mL of deionized water to obtain an aqueous solution. The precursor obtained in the hydrothermal process was rapidly introduced to the Ba^{2+} aqueous solution. The slurry was ultrasonically treated for 30 min. The resultant $\text{BaSn}(\text{OH})_6$ was filtered, washed with distilled water and ethanol, and then dried at room temperature. The as-prepared $\text{BaSn}(\text{OH})_6$ was subsequently calcined at 450°C for 5 h under inert gas protecting conditions (99.9% Ar).

The crystallinity and phase purity of the product were examined by a Bruker D8 advanced X-ray diffractometer (XRD) with monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology and structure of the product were characterized using a JEOL JEM-2010 transmission electron microscope (TEM) operating at 200 kV and a JEOL JSM-6700F scanning electron microscope (SEM).

3. Results and Discussion

Figure 1(a) shows the XRD patterns of the product prepared by hydrothermal method. All the detectable peaks in Figure 1(a) can be assigned by their peak position to the hexagonal structure of $\text{Na}_2\text{Sn}(\text{OH})_6$ with lattice parameters of $a = 5.94 \text{ \AA}$ and $c = 14.1 \text{ \AA}$. These parameters match well with the information for JCPDS file card 24-1143. Figure 1(b) shows the XRD patterns of the sample obtained from the reaction between solid $\text{Na}_2\text{Sn}(\text{OH})_6$ and the BaCl_2 aqueous solution. The peak positions are consistent with the standard diffraction pattern of $\text{BaSn}(\text{OH})_6$ (JCPDS 09-0053), with no other crystalline phase observed.

Scanning electron microscopy (SEM) analyses were used to explore the morphology of the products. Figure 2(a) shows the image of the precursor $\text{Na}_2\text{Sn}(\text{OH})_6$, which clearly displays that the product is composed of sheets in different sizes. The SEM image in Figure 2(b) reveals that the $\text{BaSn}(\text{OH})_6$ consists of nanorod arrays with diameters of 90–110 nm and lengths up to several micrometers. The most of the nanorods are aligned in the same direction. To provide further insight into the nanostructures of the rods, TEM investigations are also performed. As shown in Figure 3(a), the $\text{BaSn}(\text{OH})_6$ nanorods are straight, uniform, and tightly packed as a bundle array. The selective-area electron diffraction (SAED) (Figure 3(b)) reveals that the nanorods are crystalline in structure.

From a great deal of experimental work, we find that the surfactant plays an important role in controlling the morphology of the sample. The use of CTAB is crucial to the formation of $\text{BaSn}(\text{OH})_6$ nanorod arrays. Nanosheets were obtained when CTAB was replaced by polyethylene glycol (PEG), and nondirectional nanorods were obtained in the presence of polyvinylpyrrolidone (PVP), which were shown in Figures 4(a) and 4(b). On the basis of our detailed examination and the information we have gathered [15], a

FIGURE 1: XRD patterns of the products: (a) $\text{Na}_2\text{Sn}(\text{OH})_6$ and (b) $\text{BaSn}(\text{OH})_6$.

formation process of the $\text{BaSn}(\text{OH})_6$ nanorods array can be proposed. An illustration of the $\text{Na}_2\text{Sn}(\text{OH})_6$ formation process is shown in Figure 5. When NaOH solution was added dropwise into the SnCl_4 and CTAB mixture solution, the precipitation of $\text{Sn}(\text{OH})_4$ was obtained immediately. By keeping on adding NaOH, the $\text{NaSn}(\text{OH})_6$ was formed (Figure 5(a)). On the other hand, it was reported that the anionic surfactant CTAB can be made to form micelles [16]. In this system, single-chain surfactant molecules CTAB reacted preferentially with $\text{Sn}(\text{OH})_4^{2-}$ polyanions which displace the original surfactant monoanions (Figure 5(b)). Then anionic surfactant CTAB formed sandwich micelles due to the anion charge density and shape requirement (Figure 5(c)). The condensation of $\text{Sn}(\text{OH})_4^{2-}$ absorbed by CTAB is minimal at low temperature according to cooperation interactions of ion-pairs charges and organic Van der Waals forces. After hydrothermal treatment at 180°C for 24 h, the surfactant reorganized the changing interface charge density, so more $\text{Sn}(\text{OH})_4^{2-}$ was absorbed by CTAB. The inorganic surfactant composites $\text{CTAB}^+-\text{Sn}(\text{OH})_4^{2-}-\text{Na}^+-\text{Sn}(\text{OH})_4^{2-}-\text{CTAB}^+$ were formed as shown in Figure 5(d). Finally, when the inorganic surfactant composites were introduced to Ba^{2+} aqueous solution, the Ba^{2+} replaced the Na^+ of these composites assisted by ultrasonic treatment. Accompanying the formation of $\text{BaSn}(\text{OH})_6$, strong stress appeared in the crystal. To release the stress and lower the total energy, the original plates split to nanorods. So the possible function of the surfactant CTAB in the present process is to be a template for the formation of 1D nanostructures.

For a complete view of the formation process of the $\text{BaSn}(\text{OH})_6$ nanorods array and their growth mechanism, a detailed time-dependent morphology evolution study during the ultrasonic process was conducted (Figures 6(a)–6(d)). Most of the product obtained after 5 min treatment exhibited micrometer sheets, and the rodlike structure could

(a)

(b)

FIGURE 2: SEM images of the products: (a) $\text{Na}_2\text{Sn}(\text{OH})_6$ and (b) $\text{BaSn}(\text{OH})_6$.

FIGURE 3: TEM and SAED images of the $\text{BaSn}(\text{OH})_6$ nanorods.

be seen on the big sheets (Figure 6(a)). Prolonging the reaction time to 10 min, more and more nanorods were formed as shown in Figure 6(b). For reaction times of 20 min, the product consisted predominantly of nanorods that were adherent to each other (Figure 6(c)). The ion-exchange reaction was complete at 30 min, and the nanorods were separate due to the partial dissolution of the CTAB (Figure 6(d)).

(a)

(b)

FIGURE 4: SEM images of the products in the presence of (a) PEG and (b) PVP.

In order to investigate the thermal stability and its phase transformation, we thermally treated $\text{BaSn}(\text{OH})_6$ at 450°C . The phase of the product was studied by XRD measurement as shown in Figure 7. All of the reflections could be indexed to the BaSnO_3 phase with the cubic structure BaSnO_3 (JCPDS 74-1300). The morphology of the final product BaSnO_3 was investigated with SEM. As shown in Figure 8, the rod shape retained after heat treatment at 450°C , but their feature of unidirection was lost and the size of rod was increased from average 100 nm to about 400 nm due to the recrystallization of nanorods. To get further information of the nanorods, Brunauer-Emmett-Teller (BET) N_2 adsorption-desorption analysis was performed. Figure 9 displays the adsorption-desorption isotherm, from which the BET surface area could be calculated as $22.09\text{ m}^2\text{g}^{-1}$. The value is larger than that of the nanoparticles previously reported in the literature [12], which means that the 1D BaSnO_3 nanorods we prepared may have a potential application in gas sensors or catalysts.

4. Conclusions

It has been found that a two-step technique can be used to synthesize nanocrystalline stannates. Well-defined $\text{BaSn}(\text{OH})_6$ nanorods have been successfully prepared using this novel method in high yields. The formation of the plates-formed precursor $\text{Na}_2\text{Sn}(\text{OH})_6$ plays a very important role in the final morphology of sample. The $\text{BaSn}(\text{OH})_6$ nanorods array were formed due to the split of $\text{Na}_2\text{Sn}(\text{OH})_6$ during

FIGURE 5: Schematic representation of different periods in the CTAB-assisted hydrothermal preparation of $\text{Na}_2\text{Sn}(\text{OH})_6$.

FIGURE 6: SEM images of the $\text{BaSn}(\text{OH})_6$ obtained after an ion-exchange time of (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min.

FIGURE 7: XRD pattern of BaSnO₃. FIGURE 8: SEM image of the BaSnO₃. FIGURE 9: N₂ adsorption isotherm of BaSnO₃ nanorods.

the ion-exchange treatment. BaSnO₃ has been obtained by thermally treating BaSn(OH)₆ nanorods at 450°C, for 5 h under an inert gas protecting condition. The rod shape of BaSn(OH)₆ was sustained after thermal decomposition to BaSnO₃.

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