Hydrothermal synthesis of spindle-like architectures of terbium hydroxide

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The spindle-like architectures consisting of Tb(OH)₃ nanowires were successfully prepared from Tb₂O₃ powder by hydrothermal treatments in acetic acid solutions without adding other surfactants. The products were characterized by XRD, FE-SEM and FT-IR. The influence of the concentration of acetic acid, reaction temperature and reaction time on the crystalline phases and morphologies of the products was investigated. The concentration of acetic acid plays a key role in determining the morphology of the Tb(OH)₃ products. The effect of acetic acid on the morphologies of the products was systematically discussed.

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1. Introduction

Rare-earth elements form a group in the periodic table, consisting of 17 metallic elements with chemical similarities, including the scandium and yttrium plus 15 lanthanides. The rare-earth compounds have been extensively used in various fields owing to their excellent optic, magnetic, electric, and catalytic properties resulting from their unique 4f electronic structures.¹⁾ However, the properties of the functional materials strongly depend on the compositions, crystalline phases, morphology and dimensionality of the as-prepared products.²⁾ Recently, many kinds of rare-earth compounds with different dimensions, including oxides, hydroxides, phosphates, borates and fluorides have been prepared to generate unexpected properties.^{3)–6)} Among them, the nanowire is an important material as a result of quantum confinement effects, which exhibit significant physical and chemical properties differing from the bulk materials. Nowadays, nano-scale particles of terbium oxides are one of the important functional rare earth materials among the family of the rare earth compounds. Terbium oxides have been widely used in high performance luminescent devices, magnets, catalysts, and other functional materials.^{7)–9)} According to the previous report,¹⁰⁾ rare earth oxides can be directly formed through dehydration of the corresponding hydroxides, and the oxides can retain the morphology of the hydroxides. Therefore, preparation of rare-earth hydroxides with various morphologies is of great importance.

Hydrothermal method is an excellent way to synthesize functional materials with excellent properties, due to its low cost, environmental friendship, and easy control in terms of purity and morphology of the final products.^{11)–15)} Generally, the hydrothermal process of controlled construction of architectures needs the aid of surfactants or template reagents. Yang and Li et al.¹⁶⁾ synthesized Ln³⁺-doped lutetium oxide precursor with flowerlike microarchitectures by a hydrothermal process with the assistance of ethylene glycol; Wang and Bai et al.¹⁷⁾ used oleylamine as a

surfactant to synthesize layered lanthanide (Pr, Nd, Sm, Eu and Gd) hydroxide nanowires; Tang and Shen et al.⁷⁾ used sodium dodecyl benzenesulfonate (SDBS) as template reagent to synthesize terbium hydroxide nanotubes. There are many surfactants frequently used, such as polyvinylpyrrolidone (PVP),²⁾ cetyltrimethyl ammonium bromide (CTAB),⁹⁾ and ethylenediamine.¹⁸⁾

It's worth noting that the rare earth hydroxides are usually obtained by the above-mentioned method through two steps, which consist of the dissolution of oxides and precipitation of precursor colloids by adding a basic solution as precipitators before hydrothermal treatment. Thus, the surfactants or template reagents directly reach out to hydroxide precursors. In the present study, we exploited a one-step hydrothermal route using terbium oxide as a raw material by adjusting the concentration of acetate acid without adding any surfactants to prepare the spindle-like architectures of terbium hydroxide. The influence of the concentration of acetic acid, reaction temperature and reaction time on the crystalline phase and morphologies of products was systematically investigated. In addition, a possible formation mechanism for the morphological evolution of these microstructures was discussed.

2. Experimental

2.1 Preparation of Tb(OH)₃

All chemicals with analytical grade were purchased from Wako Pure Chemical Industries, Ltd., Japan, and used without further treatment. A detailed description of the preparation process is as follows:

15 mL of acetic acid (CH₃COOH) solution with different concentrations (0.001–0.2 mol/L) and 0.45 g of Tb₂O₃ were placed in a 25 mL Teflon-lined autoclave. The autoclave was sealed, heated in an electric oven to 200°C at a heating rate of 5°C/min, and maintained at 200°C for 6 h with rotation for agitation. The autoclave was then cooled to room temperature via air quenching. The precipitate was collected using a centrifuge, washed with distilled water, and dried at room temperature. In order to investigate the formation mechanism, the reaction temperature and reaction time were systematically changed. In addition,

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sodium hydroxide and the other type of solutions were used as a solvent instead of acetic acid solution.

2.2 Characterization

Powder X-ray diffractions (XRD) were performed using a Rigaku RTP-300RC diffractometer operating at 40 kV and 20 mA with Cu K α radiation (λ ; 0.15418 nm). The patterns were collected in the range of 5 to 70° with a 0.02° step and scanning speed of 4°/min. The micrographs by field emission scanning electron microscopy (FE-SEM) were obtained using a JEOL JSM-6500F electron microscope operating at 15 kV. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu FTIR-8200PC spectrophotometer at room temperature.

3. Result and discussion

3.1 Influence of acetic acid concentration

Figure 1 shows the XRD patterns of the as-prepared samples in CH₃COOH solutions with different concentrations. It is easy to find that the XRD patterns can be indexed to be a pure hexagonal phase of Tb(OH)₃, in agreement with the reported data (JCPDS 83-2038) when the concentration of CH₃COOH was lower than 0.15 M [Figs. 1(a)–1(e)]. With the increase in concentration of CH₃COOH, the intensity of main diffraction peak (100) was gradually reduced, meanwhile the full width at half maximum (FWHM) was increased. This result indicates that the crystallinity of the products was gradually decreased. It is important to note that the relative intensity ratio of (110) and (101) diffraction was changed with the increase in concentration of CH₃COOH, suggesting that the preferential growth along *c*-axis occurred with the increase in concentration of CH₃COOH. When the concentration was further increased to 0.2 M [Fig. 1(f)], an unknown phase was formed. The peak located at $2\theta = 6.76^\circ$ suggests an inter-layer d-spacing of 1.306 nm, and the peaks with relatively low intensity at $2\theta = 13.56^\circ$ and 20.36° can be assigned to its second-order and third-order reflection, respectively. Therefore, the above d values of the XRD patterns show that a compound with the layered structure was formed in 0.2 M CH₃COOH solution.

In order to characterize the unknown phase, the infrared spectra were measured. Figure S1 (Supplementary file) shows the FT-IR spectra of the as-prepared samples. The Tb(OH)₃ products [Figs. S1(a)–S1(e)] had the same absorption at 3610 and 670

Fig. 1. XRD patterns of the products prepared in CH₃COOH solutions with different concentrations of (a) 0.001 M, (b) 0.01 M, (c) 0.03 M, (d) 0.067 M, (e) 0.15 M, and (f) 0.2 M.

cm⁻¹. In accordance to the literature,⁸⁾ these two bands can be associated with O–H stretching vibration of Tb(OH)₃ and with Tb–O–H bending vibration. The FT-IR spectra of the unknown phase [Fig. S1(f)] show that the occurrence of a broad 3380 cm⁻¹ band may be attributed to residual absorbed water in the sample, the bands at 2924 and 2853 cm⁻¹ correspond to –CH₃ stretching and –CH₃ against stretching vibration, respectively.¹⁹⁾ The bands located between 1568 and 1443 cm⁻¹ are typical for asymmetric stretching vibrations and symmetric stretching vibrations of carboxylate groups COO⁻, respectively. On the basis of the IR spectra, the sample (f) might contain acetate hydrate.

The SEM images of the several typical samples with distinct morphologies are presented in **Fig. 2**. Tb(OH)₃ could be obtained at the concentration between 0.001 and 0.15 M [Figs. 2(a)–2(e)]. At low CH₃COOH concentration of 0.001 M [Fig. 2(a)], the obtained product was composed of granular aggregates and it is difficult to distinguish each particle. By the increase in concentration to 0.01 M [Fig. 2(b)], the morphology was changed to micro-cylinders with diameter of 1.5 μm and length up to 5 μm. It is easy to find that these micro-rods were composed of bundles of nanowires. The diameter of these nanowires ranges from 50 to 100 nm. As CH₃COOH concentration was further increased to 0.03 M [Fig. 2(c)], the spindle-like structures with diameter less than 2 μm and length longer than 10 μm were obtained. In 0.067 M CH₃COOH solution, the diameter of the spindles was decreased but the length was increased [Fig. 4(c)]. When CH₃COOH concentration was 0.1 M [Fig. 2(d)], Tb(OH)₃ crystallized into homogeneous spindles in shape. The diameter of the spindles was 1 μm and the length was 13 μm. When the concentration was increased further, the bundles of nanowires predominantly split into the nanowires with a wide scale of size, ranging in length between 2 and 10 μm [Fig. 2(e)]. When the concentration was 0.2 M, the morphology of the product

Fig. 2. SEM images of the products prepared in CH₃COOH solution with different concentration of: (a) 0.001 M, (b) 0.01 M, (c) 0.03 M, (d) 0.1 M, (e) 0.15 M, (f) 0.2 M.

Fig. 3. XRD patterns of the products prepared in 0.067 M CH_3COOH solution at different temperature of (a) 100°C, (b) 160°C, (c) 200°C, (d) 220°C for 6 h.

changed dramatically. The product consisted of plate-like crystals [Fig. 2(f)]. This result is in agreement with the XRD pattern of the product which suggested the product had a layered structure.

3.2 Effect of reaction temperature

Tb_2O_3 was hydrothermally treated in 0.067 M CH_3COOH solution at different temperatures from 100 to 220°C for 6 h. **Figure 3** shows the XRD patterns of the as-prepared samples. A small amount of $\text{Tb}(\text{OH})_3$ was formed at 100°C and a large amount of the unreacted raw material Tb_2O_3 remained [Fig. 3(a)]. With the increase in reaction temperature to 160°C [Fig. 3(b)], the diffractions of the raw material Tb_2O_3 disappeared and the product was the pure phase of $\text{Tb}(\text{OH})_3$. When the temperature was increased further [Figs. 3(c) and 3(d)], the crystallinity of $\text{Tb}(\text{OH})_3$ was significantly increased.

Figure 4 shows typical SEM images of the $\text{Tb}(\text{OH})_3$ samples as-prepared at different temperatures. The product obtained at 100°C consisted of two kinds of particles, spindles and particles with an indefinite form [Fig. 4(a)]. The former must be $\text{Tb}(\text{OH})_3$ and the latter could be the unreacted Tb_2O_3 . When the reaction temperature was 160°C, bundles composed of $\text{Tb}(\text{OH})_3$ nanowires with length of about 13 μm were obtained [Fig. 4(b)]. With the increase in reaction temperature to 200°C, the width of spindle-like bundles was gradually decreased, as shown in Fig. 4(c). The size of the spindles obtained at 220°C was decreased to 0.5 μm in diameter and 3–5 μm in length [Fig. 4(d)]. The spindles were composed of nanowires and the diameter of a nanowire was increased by increasing reaction temperature [the insets of Figs. 4(b) and 4(d)]. In addition, it is clearly found that the growth direction of $\text{Tb}(\text{OH})_3$ nanowires prepared at 160°C is non-uniform, as observed in the inset of Fig. 4(b). Those nanowires grew along the various directions, gathered at an angle into a bundle. However, the $\text{Tb}(\text{OH})_3$ nanowires obtained at 220°C grew in the same direction [inset of Fig. 4(d)]. The growth directions of those nanowires are uniformly along the c axis. Combining with the results of XRD, the crystallinity of $\text{Tb}(\text{OH})_3$ prepared at 160°C is obviously lower than 220°C. We speculated that the $\text{Tb}(\text{OH})_3$ nanowires prepared at 160°C might not be the single crystals.

3.3 Effect of reaction time

In order to understand the formation mechanism, the reaction time was changed from 0 to 24 h, while the CH_3COOH concentration and reaction temperature were fixed to 0.067 M and

Fig. 4. SEM images of the products prepared in 0.067 M CH_3COOH solution at different temperature of (a) 100°C, (b) 160°C, (c) 200°C (d) 220°C for 6 h.

200°C, respectively. Figure S2 shows the XRD patterns of the samples obtained by the reaction for 0 h (just when the oven reached 200°C at a heating ramp of 5°C/min), 0.5, 2, 6 and 24 h. The characteristic peaks of hexagonal $\text{Tb}(\text{OH})_3$ began to appear in the XRD patterns of the sample obtained just after the oven reached 200°C [Fig. S2(a)]. Most of the diffraction peaks were proved to be the raw material Tb_2O_3 . The single phase of $\text{Tb}(\text{OH})_3$ could be obtained by the hydrothermal reaction for 30 min, and with the increase in reaction time, the intensity of main diffraction peak (100) gradually increase [Figs. S2(b)–S2(d)]. This result suggests that the crystallinity was increased with the increase in reaction time.

Figure 5 shows SEM images of the samples received after the hydrothermal reaction at 200°C for different reaction time. When the oven reached 200°C, the product was composed of small spindles and infinite shaped particles [Fig. 5(a)]. The spindles must be $\text{Tb}(\text{OH})_3$ and the other particles must be the unreacted Tb_2O_3 . With the increase in reaction time to 0.5 h [Fig. 5(b)], the spindles with diameter of 1.5 μm and length longer than 5 μm were obtained. It is easy to find that these spindles are bundles of nanowires. As the reaction time was further increased to 6 h [Fig. 4(c)], the diameter of the spindle-like structures was slightly decreased and the length was increased. Finally, by the long reaction time of 24 h, the tips of the spindle-like bundles began to split lightly into nanowires [Fig. 5(c)].

3.4 Formation mechanism of spindle-like architectures of terbium hydroxide

The results described above suggest that CH_3COOH plays a key role in determining the morphology of the spindle-like architectures. The morphology of growing crystals is determined by the relative growth rate of different crystal faces. $\text{Tb}(\text{OH})_3$ has the hexagonal structure, so that crystals of $\text{Tb}(\text{OH})_3$ are expected to grow in hexagonal prisms with large prismatic planes or hexagonal plates with large basal planes. In CH_3COOH solutions, $\text{Tb}(\text{OH})_3$ crystals grew in the c axis direction to form nanowires. It is considered that CH_3COO^- ions adsorb on prismatic planes and inhibit the growth of prismatic planes. As a consequence, $\text{Tb}(\text{OH})_3$ crystals grow in the c axis direction.

To get a further understanding of the effect of CH_3COOH , 0.067 M of sodium hydroxide (NaOH), sodium acetate

Fig. 5. SEM images of the products prepared in 0.067M CH_3COOH at 200°C for different time: (a) 0 h, (b) 0.5 h, (c) 24 h.

Fig. 6. SEM images of the products synthesized from 0.45g of Tb_2O_3 in (a) 0.067 M NaOH solution, (b) 0.067 M CH_3COONa , (c) 0.067 M $\text{CH}_3\text{COONH}_4$.

(CH_3COONa) and ammonium acetate ($\text{CH}_3\text{COONH}_4$) solutions were used as a solvent to compare with 0.067 M CH_3COOH solution. The pH values of 0.067 M of NaOH , CH_3COONa , $\text{CH}_3\text{COONH}_4$ and CH_3COOH solutions were 12.8, 8.65, 7.12 and 3.28, respectively. The pure phase of $\text{Tb}(\text{OH})_3$ was obtained in all kinds of solutions, as shown in Fig. S3. However, the relative intensity ratio of (110) and (101) diffraction were different from each other. This result suggests that the degree of orientation of $\text{Tb}(\text{OH})_3$ crystals is different, depending on the solvents. The intensity of (101) peak against that of (110) peak was increased in the following order: NaOH , CH_3COONa , $\text{CH}_3\text{COONH}_4$, and CH_3COOH , which is the same order of alkalinity of the solutions.

Figure 6 shows SEM images of the products obtained in different solvents. As shown in Fig. 6(a), the product obtained in NaOH was composed of nanoparticle aggregates. The products composed of rods and nanoparticles were obtained in CH_3COONa [Fig. 6(b)], while bundles of $\text{Tb}(\text{OH})_3$ nanowires were formed in $\text{CH}_3\text{COONH}_4$ [Fig. 6(c)]. The morphologies of the products obtained in the solutions including the same amount of CH_3COO^- ions were different from each other, depending on their pH value. The length and width of the bundles obtained in 0.067 M $\text{CH}_3\text{COONH}_4$ were larger and the tips of the bundles lightly split into nanowires, compared with those obtained in 0.067 M CH_3COOH [Fig. 4(c)]. It is concluded that the adsorption of CH_3COO^- ions occurred in neutral and acidic solutions but not in basic solutions.

A proposed formation process seems to be responsible for the observed development of morphologies of $\text{Tb}(\text{OH})_3$ synthesized in various solutions. The key elements of this mechanism involve the pH value and the concentration of acetate ions of the initial solution. In a basic solution of NaOH , nanoparticles are formed because the uniform adsorption of OH^- ions on the crystal surfaces may not cause the oriented growth of the hydroxide crystals. In dilute CH_3COOH solutions, $\text{Tb}(\text{OH})_3$ crystals grow promiscuously into nanoparticles without the orientation growth. With the increase in the concentration of CH_3COOH , $\text{Tb}(\text{OH})_3$ crystals grow directionally along the c axis to form nanowires by

inhibition of the growth of prismatic planes due to the adsorption of CH_3COO^- ions. These nanowires were aggregated together to form bundles of nanowires and spindle-like architectures in order to reduce the surface energy. With the further increase in the concentration of CH_3COOH solutions, the excess CH_3COO^- ions adsorb on the surface of nanowires, blocking the formation the spindle-like architectures.

As described above, the transformation of Tb_2O_3 to $\text{Tb}(\text{OH})_3$ in 0.067 M CH_3COOH solution is very fast. At the initial stage of the reaction, short nanowires of $\text{Tb}(\text{OH})_3$ might be formed and these nanowires tend to align side by side and fuse together spontaneously by the oriented attachment to form the small spindle-like particles as observed in Fig. 5(a). These spindles grow larger by the reaction up to 0.5 h at 200°C [Fig. 5(b)]. At this moment, the starting oxide has been completely exhausted. These spindles are composed of the nanowires, but the orientation of nanowires along the c axis is not complete and some defects exist between nanowires. When the reaction time is increased, the width of the spindles is decreased and the tips of the bundles split into nanowires by the dissolution and recrystallization process, which results in increase in the crystallinity (Fig. S2). At high temperature, the transformation of Tb_2O_3 to $\text{Tb}(\text{OH})_3$ is further accelerated, which results in formation of a large number of small $\text{Tb}(\text{OH})_3$ spindles composed of high crystalline nanowires with orientation along the c axis.

Figure 7 shows the XRD patterns of the product obtained by calcination at 800°C for 2 h from $\text{Tb}(\text{OH})_3$ prepared in 0.067 M CH_3COOH at 200°C for 6 h. It is shown that the pure phase of Tb_4O_7 was obtained after calcination of $\text{Tb}(\text{OH})_3$ at 800°C . As shown in inset of Fig. 7, the Tb_4O_7 particles were spindle-like in shape. The morphology of the Tb_4O_7 particles retained that of the $\text{Tb}(\text{OH})_3$ particles, even after the transformation to the oxide. However, a slight decrease of the particle size was observed due to the higher density of the oxide. Thus, the $\text{Tb}(\text{OH})_3$ spindles can be converted into Tb_4O_7 without morphological deformation by calcination. This is an important basis for the preparation of rare earth oxides with various morphologies from hydroxides prepared by adjustment of hydrothermal reactions.

Fig. 7. XRD patterns and SEM image of the product obtained by calcination at 800°C for 2 h from $\text{Tb}(\text{OH})_3$ prepared in 0.067M CH_3COOH at 200°C for 6 h.

4. Conclusion

The spindle-like architectures consisting of $\text{Tb}(\text{OH})_3$ nanowires were successfully produced from Tb_2O_3 by hydrothermal treatments in acetic acid solutions. The concentration of acetic acid, reaction temperature, reaction time and types of solvents strongly affected the morphology and size of the products. The morphology of the $\text{Tb}(\text{OH})_3$ products were changed from granular aggregates, micro-cylinders composed of nanowires, spindles composed of nanowires and to separated wires with the increase in concentration of CH_3COOH . The CH_3COO^- ions adsorbed on prismatic planes of $\text{Tb}(\text{OH})_3$ crystals with the hexagonal crystal structure and inhibited the growth of prismatic planes, which resulted in the oriented growth of $\text{Tb}(\text{OH})_3$ in the c axis direction. The crystallinity of the $\text{Tb}(\text{OH})_3$ products was increased by enhancing reaction temperature and reaction time. The method utilized in this study to fabricate $\text{Tb}(\text{OH})_3$ crystals is a general

one-step hydrothermal route and could be extended to synthesize the other rare earth hydroxides with tunable morphologies by simply adjusting the concentration of acetic acid.

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