Research Article

Hydrothermal Synthesis of Ln(OH)$_3$ Nanorods and the Conversion to Ln$_2$O$_3$ (Ln = Eu, Nd, Dy) Nanorods via Annealing Process

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One-dimensional rare earth oxides and hydroxides are of importance in many applications due to their rich physicochemical properties. In this work, we synthesized Ln(OH)$_3$ (Ln = Eu, Nd, Dy) nanorods by a hydrothermal method with the assistance of n-butylamine as an alkaline resource. The porous Ln$_2$O$_3$ nanorods were produced through annealing the corresponding Ln(OH)$_3$ nanorods. XRD and TEM techniques were employed to characterize the products. The annealing process and the optical properties of as-synthesized Ln$_2$O$_3$ are also investigated by TG and PL test. We expected that these nanomaterials could find potential applications in the future.

1. Introduction

Over the past decades, one-dimensional (1D) nanostructures, such as nanowires, nanorods, nanotubes, and nanoribbons, have attained increasing attention due to unique properties in mesoscopic physics and applications for nanoscale devices [1–6]. In particular, the corresponding porous nanomaterials are of interest in a broad range of applications, relying on the incorporation of specific guests into pores of different sizes and on the transport of such guests through the pores [7–9]. Moreover, chemical composition also plays an important role in determining physicochemical properties of the materials and interfacial interactions [10–13]. Therefore, it is meaningful to synthesize the 1D mesoporous nanostructures with varied chemical components and investigate the relations between chemical components and properties.

Rare earth compounds have been extensively investigated in many fields including high performance magnets, luminescent devices, catalysts, and other technical applications based on the electronic, optical, and chemical characteristics arising from their 4f electrons [14–20]. So much effort has focused on the synthesis of rare earth oxides [20–22]. Hydrothermal method is proved to be an effective route to synthesize materials with various nanostructures [23, 24]. Therefore, it is meaningful to develop an alternative hydrothermal method for preparing rare earth compounds.

In this work, we developed a facile hydrothermal method for synthesizing Ln(OH)$_3$ (Ln = Eu, Nd, Dy) nanorods. Moreover, the porous Ln$_2$O$_3$ nanorods with the same shape have been obtained through annealing the Ln(OH)$_3$ nanorods. Various techniques were employed to characterize the products, and the results showed that the hydroxide and oxide nanorods displayed the same shape and high crystallinity. It is expected that these nanomaterials could find potential applications in the future.

2. Experimental Section

2.1. Chemicals. All of the chemicals were purchased without further purification.

2.2. Synthesis. In a typical synthesis, 0.5 mmol of Ln(NO$_3$)$_3$·6H$_2$O (Ln = Eu, Nd, Dy) was dissolved in 12 mL of distilled water, and then 3 mL of n-butylamine was added under constant stirring. Subsequently, the resulting solution was transferred into a 20 mL Teflon-lined autoclave. The autoclave was sealed, heated, and maintained at 180°C for 16 h. After
the autoclaves were completed, the resulting product was centrifuged, followed by washing with distilled water and ethanol several times. The as-synthesized precursor nanorods were finally dried in a vacuum oven at 60°C for 4 h and used for further characterization. Porous \( \text{Ln}_2\text{O}_3 \) (\( \text{Ln} = \text{Eu}, \text{Nd}, \text{Dy} \)) nanorods were obtained by calcining the as-prepared precursor nanowires at 700°C for 2 h.

2.3. Characterization. The X-ray diffraction (XRD) patterns of the products were recorded with a Rigaku D/Max Diffraction System, using a Cu K\( \alpha \) source (\( \lambda = 0.15406 \text{nm} \)). The high-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV. The specimen of HR-TEM measurement was prepared via spreading a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air. The thermogravimetric analysis (TGA) was investigated on continuous measurement of weight on a thermobalance as sample temperature is increased. The room temperature photoluminescence (PL) spectra of samples were recorded on a Hitachi F-4500 FL spectrophotometer with a Xe lamp as the excitation light source.

3. Results and Discussion

3.1. Characterizations of Structure and Morphology. The purity and crystallinity of as-prepared samples were examined by XRD technique (Figure 1). Figures 1(a)–1(c) show the XRD patterns of the as-prepared \( \text{Eu(OH)}_3 \), \( \text{Nd(OH)}_3 \), and \( \text{Dy(OH)}_3 \) nanorods, respectively. The length of \( \text{Eu(OH)}_3 \), \( \text{Nd(OH)}_3 \), and \( \text{Dy(OH)}_3 \) nanorods ranges from 60 to 150 nm, and their diameter is about 15 nm. In Figure 2(b), one can find that not all the surface of the nanorods is well crystalline. Figures 2(c) and 2(e) show the TEM images of \( \text{Nd(OH)}_3 \) and \( \text{Dy(OH)}_3 \) nanorods, respectively. The length of \( \text{Nd(OH)}_3 \) nanorods is about 120 nm, and their diameter ranges from 20 to 30 nm, as shown in Figure 2(c). For \( \text{Dy(OH)}_3 \) nanorods, they have not a uniform length ranging from 200 nm to several micrometers, and diameter is about 20 nm. Similarly, the high-magnification TEM images of \( \text{Nd(OH)}_3 \) and \( \text{Dy(OH)}_3 \) nanorods display their surface is not well crystalline. However, there are clear crystalline lattices for some places of their surfaces, as shown in the inset of Figures 2(b), 2(d), and 2(f). The growth of \( \text{Ln(OH)}_3 \) nanorods can be explained by the 1D growth habit and assistance of n-butylamine [25].

3.2. Conversion of \( \text{Ln(OH)}_3 \) to \( \text{Ln}_2\text{O}_3 \) (\( \text{Ln} = \text{Eu}, \text{Nd}, \text{Dy} \)). The decomposition process was studied by TGA test. As shown in Figure 3, the TGA results indicate the experimental mass losses of ∼13.9% (for \( \text{Eu(OH)}_3 \)), ∼14.1% (for \( \text{Nd(OH)}_3 \)), and ∼13.3% (for \( \text{Dy(OH)}_3 \)), which are corresponding to the theoretical values (13.3% for \( \text{Eu(OH)}_3 \), 13.9% for \( \text{Nd(OH)}_3 \), and 12.7% for \( \text{Dy(OH)}_3 \), resp.). The good agreement with theoretical values implies that the as-prepared precursor nanorods have been completely decomposed during the calcination process, which lays an excellent foundation for the crystallization of the \( \text{Ln}_2\text{O}_3 \) nanostructures. Moreover, TGA curves also exhibit a multiple dehydration process during the
decomposition, which can generally be described by the two equations [26]:

\[
\begin{align*}
\text{Ln(OH)}_3 & \rightarrow \text{LnOOH} + \text{H}_2\text{O} \\
2\text{LnOOH} & \rightarrow \text{Ln}_2\text{O}_3 + \text{H}_2\text{O}
\end{align*}
\]

Figure 4 shows the XRD patterns of the as-decomposed products of the Ln(OH)₃ (Ln = Eu, Nd, Dy) nanorods obtained after 2h treatment at 700°C. The XRD peaks of Ln(OH)₃ (Ln = Eu, Nd, Dy) completely disappeared and only the peaks of Ln₂O₃ (Ln = Eu, Nd, Dy) were observed. All of the peaks in this pattern can be indexed as the pure cubic phase, which are consistent with the values in the standard cards (JCPDS no. 86-2476 for Eu₂O₃, 12-0393 for Nd₂O₃, and 10-0059 for Dy₂O₃). After complete decomposition at 700°C, the well-faceted Ln(OH)₃ (Ln = Eu, Nd, Dy) nanorods were fully transformed into nanoporous Ln₂O₃ (Ln = Eu, Nd, Dy) nanorods with no significant changes in the overall morphology, as shown in Figures 5(a)–5(f). The detailed structures of the as-synthesized Ln₂O₃ (Ln = Eu, Nd, Dy)
Figure 3: TGA curves of decomposition processes: (a) Eu(OH)$_3$, (b) Nd(OH)$_3$, and (c) Dy(OH)$_3$.

Figure 4: XRD patterns of the as-synthesized Ln$_2$O$_3$: (a) Eu$_2$O$_3$, (b) Nd$_2$O$_3$, and (c) Dy$_2$O$_3$. 
samples were further investigated by TEM (Figures 5(b), 5(d), and 5(f)). One could see that there exist some defects on the surface of Eu₂O₃ nanorods (the insets of Figure 5(b)). In addition, the pores on the Ln₂O₃ (Ln = Eu, Nd, Dy) nanorods could also be clearly detected, as shown in Figures 5(b), 5(d), and 5(f). The formation of porous structures is originated from the release of water molecular [27].

Figure 6 shows the PL spectrum of Eu₂O₃ nanorods that were selected as a representative to study the optical property of the as-synthesized Ln₂O₃ nanorods. One can find from the figure that the Eu₂O₃ nanorods exhibit a strong emission peak around 618 nm, which is caused by the forced electric dipole transition (⁵D₀→⁷F₂) [28]. This indicates that the pure cubic phase Eu₂O₃ has been produced, which is consistent with the XRD result.

4. Conclusion

In summary, we have successfully synthesized the Ln(OH)₃ (Ln = Eu, Nd, Dy) nanorods via a facile hydrothermal route assisted by n-butylamine and obtained the corresponding porous Ln₂O₃ nanorods through annealing the Ln(OH)₃ nanorods. The XRD and TEM techniques have been employed to characterize the hydroxide and oxide nanorods. Moreover, the possible formation mechanism of Ln(OH)₃...
nanorods has been proposed. The as-synthesized Ln(OH)$_3$ and Ln$_2$O$_3$ nanorods are expected to be used in catalysis, gas sensors, and other fields in the future.

**Conflict of Interests**

The authors would like to declare that they do not have any commercial or associative interests that represents a conflict of interest in connection with the submitted paper.

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