Research Article

Hydrothermal Synthesis of $\text{Ln}(\text{OH})_3$ Nanorods and the Conversion to Ln_2O_3 ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) Nanorods via Annealing Process

Yanhua Zhu, Xiang Zhai, and Lingling Wang

School of Physics and Microelectronics, Hunan University, Changsha 410082, China

Correspondence should be addressed to Lingling Wang; llwang@hnu.edu.cn

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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 $\text{Ln}(\text{OH})_3$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) nanorods by a hydrothermal method with the assistance of *n*-butylamine as an alkaline resource. The porous Ln_2O_3 nanorods were produced through annealing the corresponding $\text{Ln}(\text{OH})_3$ nanorods. XRD and TEM techniques were employed to characterize the products. The annealing process and the optical properties of as-synthesized Ln_2O_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 $\text{Ln}(\text{OH})_3$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) nanorods. Moreover, the porous Ln_2O_3 nanorods with the same shape have been obtained through annealing the $\text{Ln}(\text{OH})_3$ 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 $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) 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

FIGURE 1: XRD patterns of the as-synthesized $\text{Ln}(\text{OH})_3$: (a) $\text{Eu}(\text{OH})_3$, (b) $\text{Nd}(\text{OH})_3$, and (c) $\text{Dy}(\text{OH})_3$.

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 Ln_2O_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 $\text{Cu K}\alpha$ 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 $\text{Eu}(\text{OH})_3$, $\text{Nd}(\text{OH})_3$, and $\text{Dy}(\text{OH})_3$ nanorods, respectively. The diffraction patterns of the as-prepared three products can be indexed to the pure hexagonal phase (space group $\text{P6}_3/\text{m}$), which are consistent with the values in the standard cards (JCPDS no. 85-2203 for $\text{Eu}(\text{OH})_3$, 17-0781 for $\text{Nd}(\text{OH})_3$, and 19-0430 for $\text{Dy}(\text{OH})_3$). The narrow sharp peaks suggest that the $\text{Ln}(\text{OH})_3$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) samples are highly crystalline. No other peaks are observed, indicating high purity of the as-prepared

samples. Interestingly, we found that as Ln atom increases, the diffraction patterns shift to small angles. This is attributed to the fact that crystal lattice of $\text{Ln}(\text{OH})_3$ is increased as the atomic number is increased.

The morphology and structure of as-synthesized $\text{Ln}(\text{OH})_3$ nanorods were characterized by transmission electron microscope (TEM), as shown in Figure 2. Figures 2(a) and 2(b) show the low- and high-magnification TEM images of $\text{Eu}(\text{OH})_3$ nanorods, respectively. In Figure 2(a), one can find that the length of $\text{Eu}(\text{OH})_3$ 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 $\text{Nd}(\text{OH})_3$ and $\text{Dy}(\text{OH})_3$ nanorods, respectively. The length of $\text{Nd}(\text{OH})_3$ nanorods is about 120 nm, and their diameter ranges from 20 to 30 nm, as shown in Figure 2(c). For $\text{Dy}(\text{OH})_3$ 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 $\text{Nd}(\text{OH})_3$ and $\text{Dy}(\text{OH})_3$ nanorods (Figures 2(d) and 2(f)) display that 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 $\text{Ln}(\text{OH})_3$ nanorods can be explained by the 1D growth habit and assistance of *n*-butylamine [25].

3.2. Conversion of $\text{Ln}(\text{OH})_3$ to Ln_2O_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 $\sim 13.9\%$ (for $\text{Eu}(\text{OH})_3$), $\sim 14.1\%$ (for $\text{Nd}(\text{OH})_3$), and $\sim 13.3\%$ (for $\text{Dy}(\text{OH})_3$), which are corresponding to the theoretical values (13.3% for $\text{Eu}(\text{OH})_3$, 13.9% for $\text{Nd}(\text{OH})_3$ and 12.7% for $\text{Dy}(\text{OH})_3$, 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 Ln_2O_3 nanostructures. Moreover, TGA curves also exhibit a multiple dehydration process during the

FIGURE 2: TEM images of the as-synthesized $\text{Ln}(\text{OH})_3$: ((a) and (b)) $\text{Eu}(\text{OH})_3$, ((c) and (d)) $\text{Nd}(\text{OH})_3$, and ((e) and (f)) $\text{Dy}(\text{OH})_3$.

decomposition, which can generally be described by the two equations [26]:

Figure 4 shows the XRD patterns of the as-decomposed products of the $\text{Ln}(\text{OH})_3$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) nanorods obtained after 2 h treatment at 700°C . The XRD peaks of $\text{Ln}(\text{OH})_3$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) completely disappeared and only the

peaks of Ln_2O_3 ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) 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 Eu_2O_3 , 12-0393 for Nd_2O_3 , and 10-0059 for Dy_2O_3). After complete decomposition at 700°C , the well-faceted $\text{Ln}(\text{OH})_3$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) nanorods were fully transformed into nanoporous Ln_2O_3 ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) nanorods with no significant changes in the overall morphology, as shown in Figures 5(a)–5(f). The detailed structures of the as-synthesized Ln_2O_3 ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$)

FIGURE 3: TGA curves of decomposition processes: (a) $\text{Eu}(\text{OH})_3$, (b) $\text{Nd}(\text{OH})_3$, and (c) $\text{Dy}(\text{OH})_3$.

FIGURE 4: XRD patterns of the as-synthesized Ln_2O_3 : (a) Eu_2O_3 , (b) Nd_2O_3 , and (c) Dy_2O_3 .

FIGURE 5: TEM images of the as-synthesized Ln_2O_3 : ((a) and (b)) Eu_2O_3 , ((c) and (d)) Nd_2O_3 , and ((e) and (f)) Dy_2O_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 Eu_2O_3 nanorods (the insets of Figure 5(b)). In addition, the pores on the Ln_2O_3 ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) 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 Eu_2O_3 nanorods that were selected as a representative to study the optical property of the as-synthesized Ln_2O_3 nanorods. One can find from the figure that the Eu_2O_3 nanorods exhibit a strong emission peak around 618 nm, which is caused by the forced electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) [28]. This indicates that the pure cubic

phase Eu_2O_3 has been produced, which is consistent with the XRD result.

4. Conclusion

In summary, we have successfully synthesized the $\text{Ln}(\text{OH})_3$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Dy}$) nanorods via a facile hydrothermal route assisted by n-butylamine and obtained the corresponding porous Ln_2O_3 nanorods through annealing the $\text{Ln}(\text{OH})_3$ nanorods. The XRD and TEM techniques have been employed to characterize the hydroxide and oxide nanorods. Moreover, the possible formation mechanism of $\text{Ln}(\text{OH})_3$

FIGURE 6: Luminescence spectrum (excitation at 254 nm) of as-synthesized Eu_2O_3 nanorods at room temperature.

nanorods has been proposed. The as-synthesized $\text{Ln}(\text{OH})_3$ and Ln_2O_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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