



Effect of pH on the Controlled Synthesis of Dysprosium Hydroxide with Morphological Evolution *via* Hydrothermal Processing

J. JUNYANG*, N. YARU, D. MINGYE, L. CHUNHUA and X. ZHONGZI

State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, Jiangsu Province, P.R. China

*Corresponding author: Fax: +86 25 58139081; Tel: +86 25 58139092; E-mail: chhlu001@gmail.com

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A simple hydrothermal method to fabricate dysprosium hydroxide nanomaterial with fully tunable morphologies without any catalysts or templates was presented. Analytical method such as XRD, FESEM, TEM, EDS were employed to characterize the morphology and microstructure of the as-synthesized products. The results reveal that the pH value changed by adjusting ammonia concentration of the solution and dysprosium hydroxide materials with the fibers-sheets-fibers morphology evolution could be obtained. The pH variation is found to play a key role in the morphology evolution. Furthermore, a possible growth mechanism of morphological evolution of the as-prepared dysprosium hydroxide was briefly discussed. Photoluminescence measurement shows that the products have two emission peaks around 490 and 575 nm, which should come from the electron transition from $4F^{9/2}$ to $6H^{15/2}$ levels and $4F^{9/2}$ to $6H^{13/2}$ levels, respectively.

Keywords: Hydrothermal, Controlled synthesis, Morphological evolution, pH.

INTRODUCTION

The morphology plays an important role in determining the property of nanomaterials. Most of the properties are highly sensitive to the morphology¹⁻³. Control of morphologies are currently a key job in developing functional materials and much effort has been done for promoting the properties of materials^{4,5}. Among the various functional materials, including nano-particles/quantum dots^{6,7}, nanotubes/nanorods/nanobelts^{8,9} and nanosheets^{10,11}, have been explored. Rare earth nanomaterials have been the subject of intense interest due to their potential wide-ranging application. Rare earth hydroxides are versatile as intermediates by employing morphology-maintained evolution, for various rare earth anisotropic nanostructures, such as oxides, oxyfluorides and oxysulfides^{12,13}, which can be used as high-performance luminescent devices¹⁴, magnets¹⁵, catalysts¹⁶ and other functional materials¹⁷. Most of these properties are highly sensitive to the morphology. Recently, well defined rare earth nanomaterials^{18,19}, with various morphologies such as nanoparticles, nanowires, nanorods, nanobelts, nanofibers and nanosheets have been fabricated. However, earlier works focused on stabilizing specific morphology rather than providing a strategy to freely direct the morphology²⁰. And only emphasized the importance of pH variation during the growth process of nanostructure *via* hydrothermal process^{21,22}, but the exact role and how to obtain

rare earth functional materials with tunable morphology is still a challenge.

Here, we report the controllable synthesis of dysprosium hydroxide materials with the fibers-sheets-fibers morphology evolution which was achieved simply by using ammonia to adjust the pH value of the initial solution through a facile hydrothermal method without using any catalyst or template for the first time. We also proposed a possible reaction mechanism and photoluminescence (PL) properties of products were also discussed.

EXPERIMENTAL

All the reagents used in this experiments were of analytical pure and purchased from Shanghai Chemical Reagent Company.

Synthesis: In a typical synthesis process, the appropriate amount of Dy_2O_3 was dissolved in diluted nitric acid to obtain the $Dy(NO_3)_3$ (0.025 M) solution. Then, the ammonia solution (25 wt. %) was slowly added to adjust pH value in a range from 9 to 12 at room temperature. A white precipitate of colloidal $Dy(OH)_3$ appeared immediately. The as-obtained precipitate was then transferred into a Teflon-lined stainless steel autoclave of 60 mL capacity. Finally, the autoclave was sealed and followed by hydrothermal treatment at different pH values and temperature of 120-240 °C for different time (12 h, 24 h). After that, it was cooled down to room temperature naturally. The as-

prepared products were separated by centrifugation, washed with deionized water and ethanol for three times, dried in a vacuum oven at 60 °C for 4 h.

The crystal structure was characterized by X-ray diffraction analysis (XRD, ARL X'TRA, American Thermo Elemental Company) employing $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm), with a scanning rate of $10^\circ/\text{min}$ in the 2θ range from 5° to 80° . The size and morphology of the products were measured by field emission scanning electric microscope (FESEM, Hitachi S-4800) and transmission electric microscope (TEM, JEOL JEM-2010) operated at 200 kv. The chemical composition was determined by energy dispersive spectrometry (EDS, Noran-VANTAGE).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of these dysprosium hydroxide as-products at various pH values is shown in Fig. 1. All the diffraction peaks of these products can be perfectly indexed to the hexagonal phase of $\text{Dy}(\text{OH})_3$ with lattice constants $a = 6.529$ Å, $c = 3.858$ Å, consistent with the values of standard card JCPDS No. 83-2039. No other crystalline phases are detected. It was worth pointing out that there was a large difference from each other in the relative intensities, indicating the possibility of different preferential growth orientations under different pH conditions²⁰.

Direct evidence of the morphology of the products were given by FESEM and TEM images. Fig. 2 shows the FESEM and TEM images at different pH values in the presence of ammonia. Fiber-like products obtained at pH value 9.72, as shown in Fig. 2a. With the increasing of ammonia, in the case when the pH value was 9.86, most of the obtained products were in fiber-like morphology, but products with sheet-like morphology can be seemed (Fig. 2b). Further increasing the amount of ammonia, the pH value was 10.16, the as-products turned from 1D fibers into 2D sheets (Fig. 2c). When the pH value at 10.30, the as-synthesized products exhibit a mixed morphologies of fibers and sheets (Fig. 2d). When the pH value

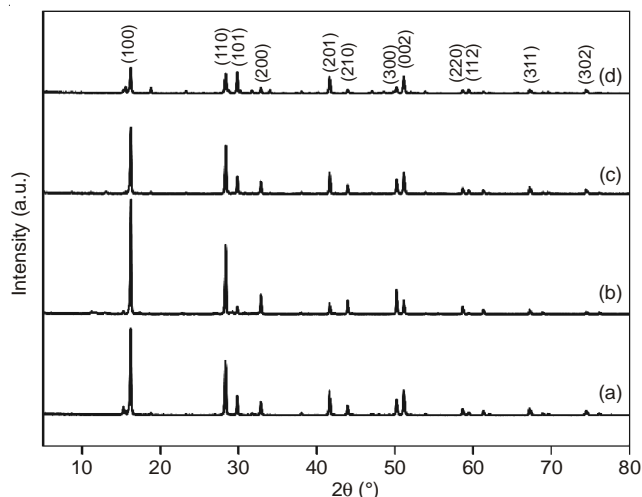


Fig. 1. XRD patterns of as-prepared $\text{Dy}(\text{OH})_3$ at different pH values: (a) 9.72, (b) 10.16, (c) 10.30, (d) 10.84

was increased to 10.84 (Fig. 2e), the obtained products were fiber morphology again. The sheets only existed in a narrow range of pH values. Fig. 2f shows a typical TEM images of the as-synthesized products prepared by using ammonia as the alkaline source by the hydrothermal method. These sheets are roughly square in shape with lengths ranging from 200 to 400 nm and the thickness of nanosquares are about 20-30 nm.

The energy dispersive spectrometry (EDS) analysis was employed to determine the composition of the nanosquares. As shown in Fig. 3, the EDS clearly identify that the nanosquares are composed of O and Dy, with the molar ratio of about 3 (O/Dy). Taking into the consideration of H, they should therefore be attributed to $\text{Dy}(\text{OH})_3$.

The morphology of dysprosium hydroxide was greatly influenced by the pH values, while the size was affected by reaction time as well as temperature. The addition of ammonia played an important role. The ammonia could not only serve as a buffer to control pH values, but also serve as a capping agent to mediate the synthesis²³. In the process, the ammonia

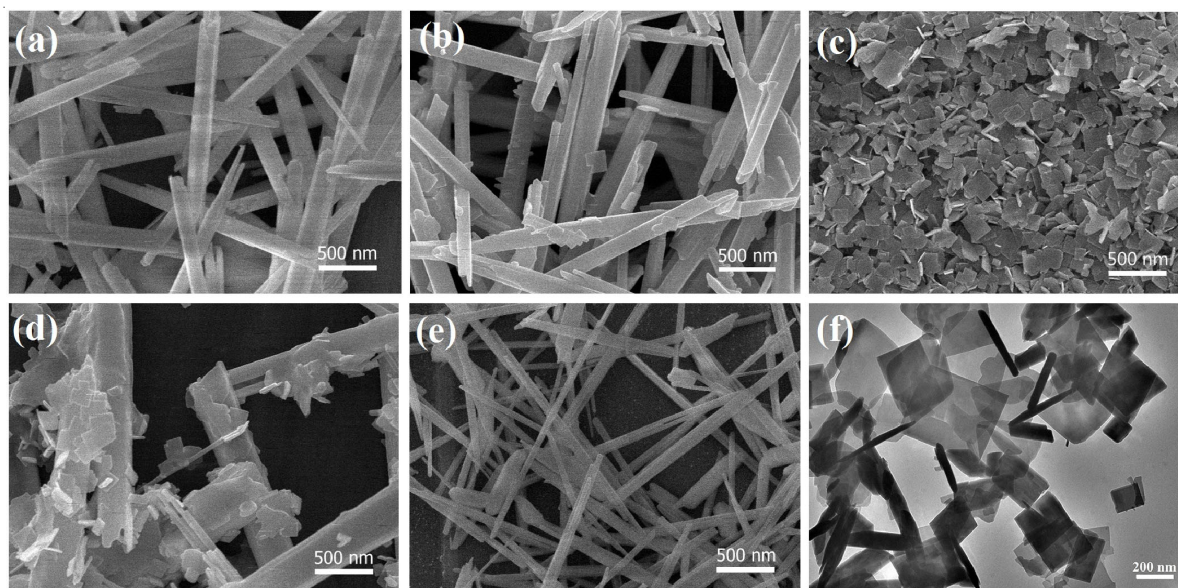


Fig. 2. FESEM (a, b, c, d, e) and TEM (f) images of the as-prepared products

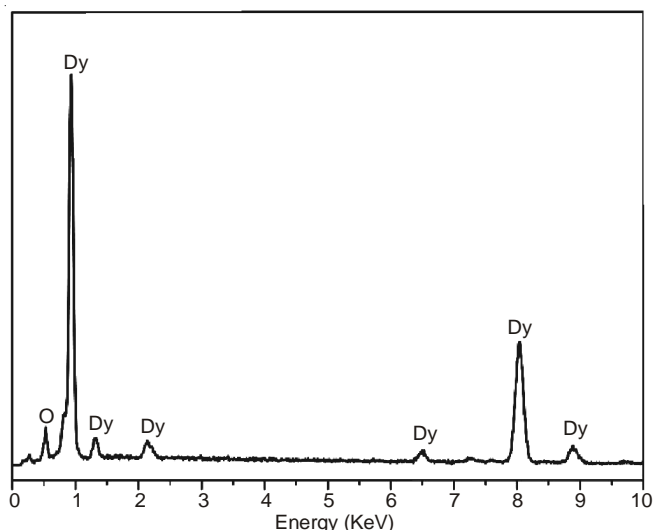


Fig. 3. EDS pattern of as-synthesized products

was gradually dissociated in the solution to release OH^- and NH_4^+ , which could selectively be absorbed on specific crystal facets of the initial $\text{Dy}(\text{OH})_3$ crystals and change the growth rates of different facets to affect the morphology significantly. Reaction time effects the rate of release OH^- , because ammonia should be gradually dissociated in the solution. With the time increased, a higher OH^- concentration in solution, a higher NH_4^+ concentration also in solution, high-quality sheets are obtained.

The photoluminescence (PL) spectrum of as-synthesized $\text{Dy}(\text{OH})_3$ nanosheets and $\text{Dy}(\text{OH})_3$ nanorods at room temperature is shown in Fig. 4. The excitation wavelength is 300 nm. It is found that there are two emission peaks centred at 483 and 575 nm of the $\text{Dy}(\text{OH})_3$ nanosheets, respectively. The 483 nm emission peak may correspond to the electron transition from $^4\text{F}_{9/2}$ to $^6\text{H}_{15/2}$ levels and the 575 nm emission peak should be produced by the electron transition from $^4\text{F}_{9/2}$ to $^6\text{H}_{13/2}$ levels^{24,25}. It seems, the emission peaks of the $\text{Dy}(\text{OH})_3$ nanorods have a red shift than the $\text{Dy}(\text{OH})_3$ nanosheets. These experimental results imply that there exists a relationship between the product morphology and its optical properties²⁶.

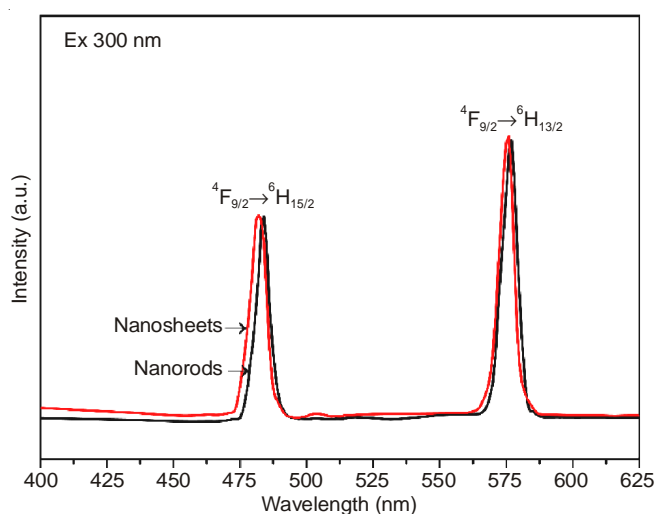


Fig. 4. Photoluminescence spectrum (excitation at 300 nm) of $\text{Dy}(\text{OH})_3$ nanosheets and nanorods at room temperature

Conclusion

In summary, the as-obtained products of the $\text{Dy}(\text{OH})_3$ with different morphology have been successfully synthesized by a facile hydrothermal method without any catalysts or templates. Influence of the pH value has been investigated. The XRD, FESEM, TEM, EDS were used to characterize the products and the photoluminescence properties of different morphologies were discussed.

The morphology of dysprosium hydroxide was greatly influenced by pH value. The ammonia was found to play a key role in morphology evolution and the sheet-like crystal could only be obtained by careful control of pH values. A possible growth mechanism of morphological evolution of the as prepared dysprosium hydroxide was also proposed.

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