Synthesis and Characterization of $Ln(OH)_3$ (Ln = La, Eu, Sm) Nanorods via a convenient hydrothermal approach

Bin Deng[1,a], Haiying Huang[1,b], and Ruijin Yu[2,c]

1.Department of Chemistry and Life Sciences, Xiangnan University, Chenzhou 423000, China;

2.College of Science, Northwest A&F University, Yangling 712100, China.

[a]dbhy88@sina.com, [b]xnxyhy@126.com, [c]ddhbyjs@126.com

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Abstract. In this paper, Rare earth (La, Eu, Sm) hydroxide nanorods have been prepared by facile hydrothermal treatment of the corresponding bulk oxide powders. The obtained samples were characterized in detail by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). $La(OH)_3$, $Eu(OH)_3$ and $Sm(OH)_3$ nanorods consist almost entirely of nanorods with the diameters of approximately 50 nm, and lengths ranging from 250 nm to 600 nm. This method does not need any surfactant or template, and provides an approach for large-scale and low-cost production.

Introduction

Much attention has been focused on one-dimensional (1D) nanostructures since the discovery of carbon nanotubes.[1] The unique physical and chemical properties of 1D nanorod and nanotube have been well documented and proposed for a wide range of applications.[2] Till date, many approaches have been developed for the synthesis of nanorods or nanowires, including chemical vapor deposition (CVD), laser ablation, chemical bath deposition, catalytic assisted method and so on.[3] Although these strategies provide effective methods to fabricate 1D nanostructure, complicated process, special apparatus, or rigid experimental conditions used in these methods severely restrict their large-scale application. Recently, significant efforts have been devoted to green synthetic scheme that takes into account the human and the environmental impact in the selection of reactants and the reaction conditions for material fabrication.[4] Many recent studies have demonstrated that wet chemical solution process is one of effective and versatile routes for the synthesis of 1D nanostructure in terms of low cost, high efficiency and good potential for high-quantity production.[5]

Rare earth compounds have been extensively utilized as luminescent devices, catalysts, high-performance magnets, and other functional materials based on the optical, chemical,and electronic characteristics resulting from their 4f shell of electrons.[6] Most of these useful functions depend strongly on the composition and structure, which are sensitive to the bonding states of rare earth atoms or ions.[7] Rare earth hydroxides of 1D nanostructure form would hold promise as highly functionalized materials as a result of both shape-specific and quantum size effects.[8] Very recently, the synthesis of 1D nanostructure of some rare earth compounds has also been reported, such as lanthanide hydroxide single-crystal nanowires through a facile solution-based hydrothermal synthetic pathway.[9,10] Herein, we report the synthesis of $Ln(OH)_3$ (Ln=La, Eu, Sm) nanorods by facile hydrothermal treatment of the corresponding bulk oxide powders without any surfactant or template.

Experimental Section

Preparation.All the reagents purchased from commercial market were of analytical grade and used without further purification. In a typical synthesis, commercial La_2O_3 powders (800 mg, purity: 99.99%) were transferred into a stainless Teflon-lined autoclave (40 ml) and then added 35 ml of distilled water. The autoclave was statically maintained at 165 °C for 48 h, After the reaction, the autoclave was cooled to room temperature naturally. The sample was separated by centrifugation,

washed by distilled water and absolute ethanol, then dried under vacuum at 60 °C for further characterization. $Eu(OH)_3$ and $Sm(OH)_3$ nanorods were prepared using Eu_2O_3 and Sm_2O_3 powders (800 mg, purity: 99.99%) as starting material, which was added to water under hydrothermal treatment at 165 °C for 48 h following the same method.

Characterization. The X-ray powder diffraction (XRD) patterns of all samples were performed on a Rigaku/Max-3A X-ray diffractometer with CuKα radiation (λ = 1.5418 Å), the operation voltage and current maintained at 40 kV and 40 mA, respectively. Scanning electron microscopic (SEM) images were obtained with a JEOL JSM-6330F operated at a beam energy of 10.00 kV. Transmission electron microscopic (TEM) images, high resolution transmission electron microscopic (HRTEM) images and the selected area electron diffraction (SAED) patterns were obtained on a JEOL-2010 microscope with an accelerating voltage of 200 kV. Sample grids were prepared by sonicating powdered samples in ethanol for 20 min and evaporating one drop of the suspension onto a carbon-coated, holey film supported on a copper grid for TEM measurements.

Results and Discussion

XRD pattern of the as-synthesized $La(OH)_3$ products is showi in Fig.1A. The XRD pattern indicates that the $La(OH)_3$ products were well-crystallized. All of the strong and sharp reflection peaks of the XRD pattern can be readily indexed to a pure hexagonal phase [space group: $P6_3/m(176)$] of $La(OH)_3$ with lattice constants a = 6.547 Å and c = 3.854 Å (JCPDS 83-2034). This XRD pattern indicates that $La(OH)_3$ products were obtained after hydrothermal treatment. The morphology and structure of the products were examined with SEM. As shown in Fig.1B, the as-made $La(OH)_3$ products consist a large quantity of nanorods with the diameters of 40-60 nm and lengths ranging between 400 nm and 600 nm. The results demonstrate that $La(OH)_3$ nanorods can be obtained by this simple method.

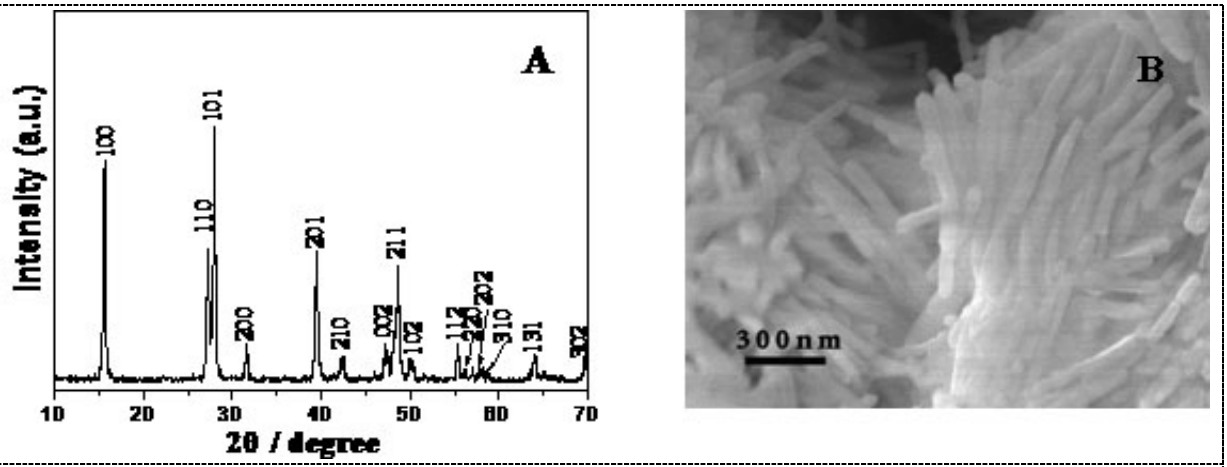

Fig. 1. (A) XRD pattern and (B) SEM image of the as-synthesized $La(OH)_3$ nanorods.

The morphology and structure of the products were further examined with TEM and HRTEM. Fig.2A shows TEM image of $La(OH)_3$ nanorod with diameter of 50 nm and length of 480 nm. Selected-area electron diffraction (SAED) pattern (Fig.2B) taken from a single $La(OH)_3$ nanorod reveals the single-crystalline nature of the sample, and can be indexed as the [010] zone axis of hexagonal $La(OH)_3$, which is consistent with the XRD results presented above. HRTEM image (Figure 2C) shows that the nanorod is structurally uniform with an interplanar spacing is about 0.316 nm, which corresponds to the (101) plane of hexagonal $La(OH)_3$.

Fig.3A shows typical XRD patterns for the $Eu(OH)_3$ products. All of the reflections could be readily indexed to a pure hexagonal phase (space group P63/m (no.176)) of $Eu(OH)_3$ with lattice constants a = 6.352 Å and c = 3.653 Å (JCPDS 83-2305). No peak characteristic of any impurity was observed. Similar XRD pattern has also been obtained from $Sm(OH)_3$, which exhibited hexagonal crystal structures.

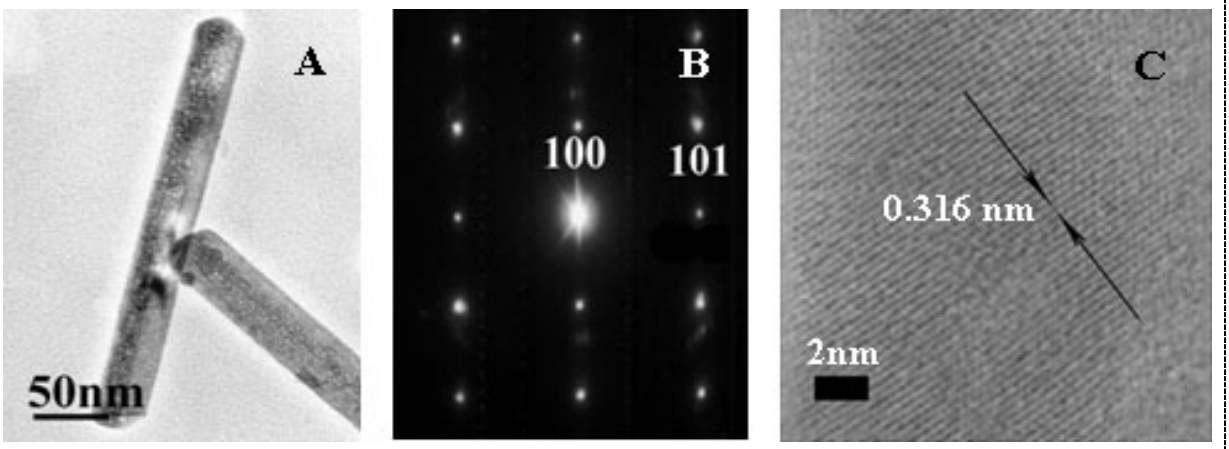

Fig.2. (A) TEM image of $La(OH)_3$ nanorods; (B) Electron diffraction pattern taken from a single $La(OH)_3$ nanorod; (C) HRTEM image taken from a single $La(OH)_3$ nanorod.

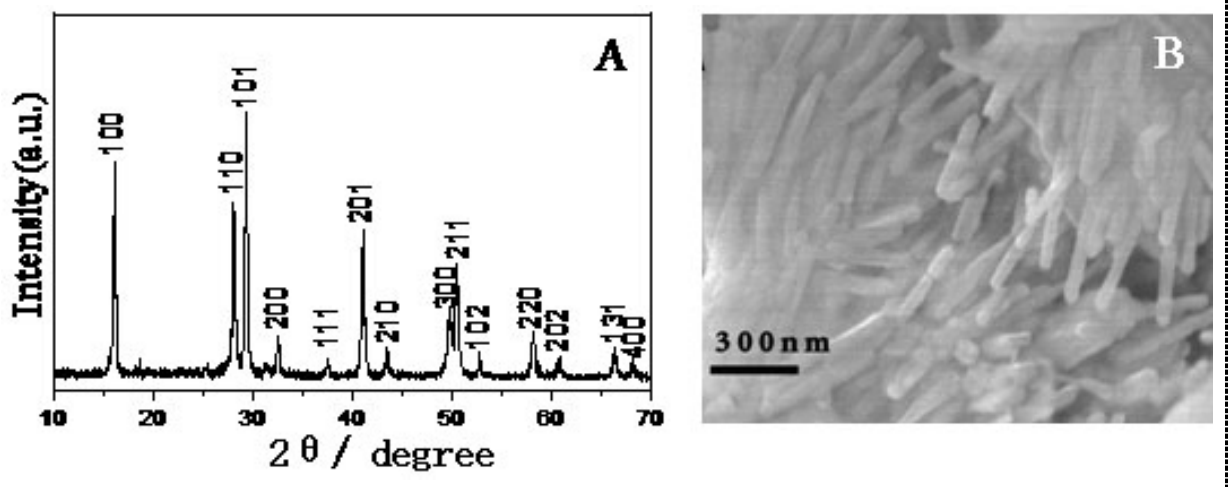

Fig. 3. (A) XRD pattern and (B) SEM image of the as-synthesized $Eu(OH)_3$ nanorods.

The morphology and structure of the as-synthesized $Eu(OH)_3$ products were examined with SEM. Fig.4A shows SEM image of $Eu(OH)_3$ nanorods with a typical size of approximately 50 nm in diameter and 250-400 nm in length. The excellent crystallinity of the $Eu(OH)_3$ nanorods is also reflected in the coupling among the as-grown $Eu(OH)_3$ nanorods. As elucidated in Fig.4A and in Fig.4B, a small number of detached nanorods underwent a multiplying growth via a "cementing mechanism" (a larger crystal was grown from direct combination of small crystals; also called "oriented attachment")[11,12] under the same processing conditions. The similar shape of coupling nanorods was also observed in the $La(OH)_3$ and $Sm(OH)_3$ products. The SAED pattern insetted upper left in Fig.4B and taken from a T-shape $Eu(OH)_3$ nanorods reveals the single-crystalline nature of the sample. A typical SEM image of $Sm(OH)_3$ nanorods is shown in Fig.4C with diameters of approximately 50 nm and lengths of 250-600 nm.

It is interesting to observe that under controlled experimental conditions, the oher light rare earth hydroxides nanostructures, such as $Nd(OH)_3$, $Ce(OH)_4$, $Pr(OH)_3$, $Pm(OH)_3$, could be prepared with high aspect ratios and uniform morphologies of nanorods, whereas heavier lanthanide hydroxides ($Dy(OH)_3$, $Tb(OH)_3$, $Ho(OH)_3$, and $Tm(OH)_3$) etc., usually have high aspect ratios and uniform morphologies of nanotube when prepared under the same conditions. Since this synthetic method has no catalyst to serve as the energetically favorable site for the absorption of reactant molecules, and has no template to guide the directional growth of 1D nanostructure. Thus, it is reasonable to imagine that there would be many anisotropic seeds of rare earth hydroxides in solution following hydrothermal process and Highly anisotropic nanostructures (tubes, wires and rods) could be directly nucleated and grown starting from these anisotropic seeds in solution without the use of any physical templates. The driving force for the anisotropic growth of 1D nanostructure of rare earth hydroxides derives from their 4f electrons and the inherent crystal structure of rare earth hydroxides. Although the exact mechanism for the formation of these 1D nanostructures is still unclear, we believe the growth of 1D nanostructure is governed by a solid-liquid-solid process (SLS),[11] in which temperature and pressure also play a crucial role.

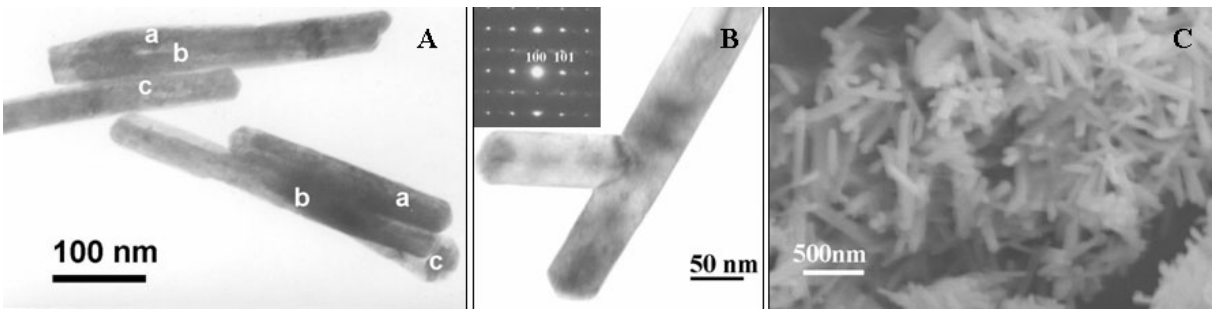

Fig.4. (A) TEM image of three $Eu(OH)_3$ nanorods attached with their side wall planes; (B) TEM image of a T-model $Eu(OH)_3$ nanorods of two $Eu(OH)_3$ nanorods via a cross attachment process; SAED pattern insetted upper left and taken from a T-model $Eu(OH)_3$ nanorods; (C) SEM image of $Sm(OH)_3$ nanorods.

Conclusions

In summary, $Ln(OH)_3$(Ln=La, Eu, Sm) nanorods have been successfully synthesized via a simple solution-based hydrothermal synthetic pathway.The aspect ratio of the products can be easily controlled by adjusting the aging time and pressure of reaction system. This method doesnot need any surfactant or template, and provides an approach for large-scale and low-cost production. This work may open a new approach for the green chemical synthesis of shape-controlled nanomaterials in mild reaction conditions. The as-synthesized $Ln(OH)_3$ nanorods are expected to be used in catalysis, gas, sensors, and other fields in the future.

Acknowledgments

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