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LETTER

Synthesis and characterization of ultralong lanthanum hydroxide nanorods via solvothermal method

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Nanoscale materials are of great interest due to their unique optical, electrical, and magnetic properties compared with bulk materials [1–6]. These properties are strongly dependent on the size and the shape of the particle, and therefore it is very important to be able to finely control the morphology of the nanomaterials. In recent years, the synthesis of one-dimensional nanomaterials such as nanowires, nanorods, or nanofibers has became the focus of research work because the morphological anisotropy results in many very complex physical properties and self-assembly behaviors compared with those of spherical nanoparticles [7–9].

Lanthanum hydroxide ($La(OH)_3$) has been used in many fields, such as ceramic, superconductive materials, hydrogen storage materials, electrode materials, etc., especially catalyst and sorbent materials [10, 11]. For all these applications, the particle size, the agglomerated state, the porosity, and the specific surface area are of major importance. Generally, these features are strongly dependent on the preparation process and the used thermal treatment method. The study of one-dimensional $La(OH)_3$ has also been of growing interest owing to the promising application in nanoscale optoelectronic devices. Ma et al. [12] synthesized poly-crystalline $La(OH)_3$ nanorods via a hydrothermal method and Deng et al. [13] also obtained $La(OH)_3$ nanorods under the similar conditions. Herein, we report a simple solvothermal route to the synthesis of $La(OH)_3$ nanorods, whose crystal growth habit is different from that via the hydrothermal method reported by Ma et al. [12]. From this synthesis method, the single crystalline $La(OH)_3$ nanorods can be synthesized with longer length and larger diameter.

In a typical synthesis, 2 g of lanthanum nitrate ($La(NO_3)_3$) was dissolved into 40 ml of distilled water to form a clear solution. Then 20 ml of absolute ethanol and 20 ml of ethylene glycol monomethyl ether ($HO(CH_2)OCH_3$) were added into the solution. After that, 5 g of NaOH was added into the above-mentioned solution to form white slurry. At last, the white slurry was stirred for 10 min and transferred into a 100 ml Teflon-lined autoclave for a solvotherml process at 240 °C for 24 h. After the solvotherml process, the gained white precipitation was filtrated, washed with distilled water, and then dried in oven at 110 °C for 12 h. The as-obtained product was denominated as A. In addition, one sample prepared with 1 g of ($La(NO_3)_3$) in initial reactant was denominated as B and another sample prepared using pure water without ethylene glycol monomethyl ether and absolute ethanol as solvent with 1 g of ($La(NO_3)_3$) in initial reactant was denominated as C (Table 1).

The phase purity of the as-prepared products was evidenced using D/max2500 X-ray diffractometer (XRD) with monochromatized CuKα radiation ($\lambda = 1.5406$ Å). The diffraction peaks of the samples in Fig. 1 can be indexed to the hexagonal $La(OH)_3$, whose calculated cell constants were numerically close to the reported values of the bulk materials in the standard card ($a = 6.529$ Å and $c = 3.859$ Å, JCPDS File No. 36-1481). No other phase was detected in the final products. From the XRD patterns, it is observed that the peaks of the sample C were consistent with that in the standard card; the strongest peak is

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Table 1 Processing conditions and the notations of the samples

No	Solvents (ml)			$La(NO_3)_3$ (g)	Diameter (nm)	Length (μm)
	Water	Ethanol	$HO(CH_2)OCH_3$			
A	40	20	20	2	>100	~10
B	40	20	20	1	50–80	1 ~ 5
C	80	–	–	1	20–30	0.2 ~ 1

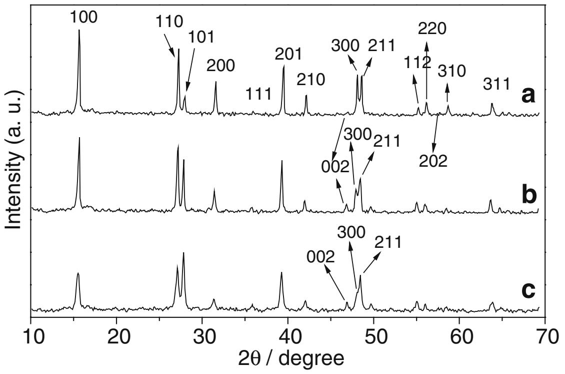


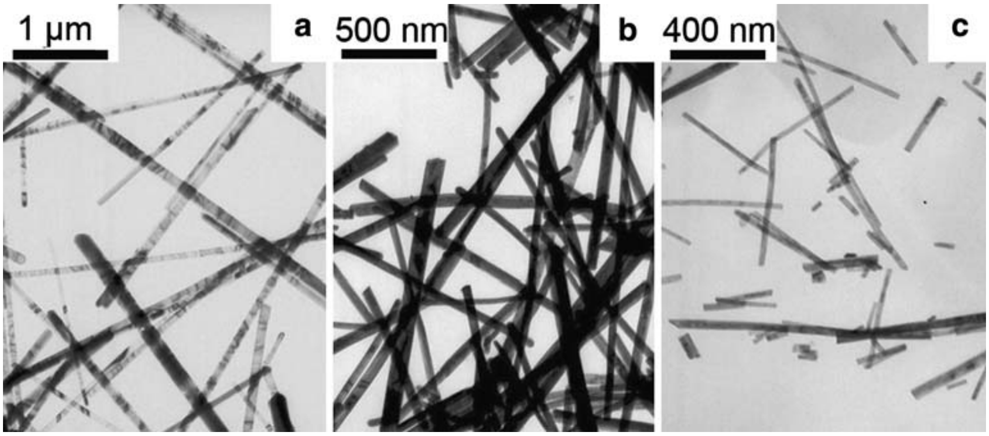
Fig. 1 Power X-ray diffractogram of the samples A, B and C with hexagonal crystallographic assignments

[101] and the [300] appears as the shoulder peak of [211]. But, for the sample B, [100] becomes the strongest peak and the splitting of [300] and [211] peak appeared to form an obvious double peak. With increasing the amount of initial reactant $La(NO_3)_3$, the peak intensity continued to increase but the peak of [101] weaken (see Fig. 1a, b).

The morphology of the as-synthesized $La(OH)_3$ samples was observed using transmission electron microscopy (TEM, Hitachi-600-2, 75 kV). The typical TEM images of the sample A, B and C are shown in Fig. 2. It can be seen that the as-synthesized samples are totally composed of uniform nanorods. The length and diameter of the as-synthesized nanorods varies with the reaction conditions. The lengths and diameter of the samples A and B prepared using a mixed solvent were larger than that of the sample C prepared using pure water. Increasing the amount of initial reactant $La(NO_3)_3$ will also result in larger length and diameter. For most nanorods from sample C, the length is several hundred nanometers, and the diameter is 20–30 nm, as shown in Fig. 2c; for sample B, the length several microns and diameter 50–80 nm; for sample A, the length is tens of microns and the diameter is more than 100 nm.

Figure 3 shows high-resolution TEM (HRTEM, JEOL-JEM-2010, 200 kV) images and the selected area electron diffraction (SAED) patterns of the sample B and C, respectively. HRTEM was employed to demonstrate the crystalline structure and the growth direction of the nanorods. It reveals that an individual $La(OH)_3$ nanorod has a uniform diameter, as shown in Fig. 3(B1) and (C1). For the sample B, the lattice fringe spacing of 0.327 nm is consistent with the interplanar spacing of the [110] planes, and the growth direction of the nanorod makes an angle of about 30° with the [110] lattice planes (see Fig. 3B2). But, for the sample C, the lattice fringe spacing is also 0.327 nm consistent with the interplanar spacing between the [110] lattice, and the growth direction of the nanorod makes an angle of about 60° with the [110] lattice planes (see Fig. 3C2). The HRTEM results suggest that the change of the strongest peak in XRD pattern is due to the preferential growth of nanorod along different zone axis. The $La(OH)_3$ nanorods prepared in the mixed solvents grow nearly in the [100] direction, but the $La(OH)_3$ nanorods prepared in pure water grow in the [101] direction. The HRTEM images taken from different regions of the two single nanorods exhibit similar results, indicating that the entire nanorods are of single crystalline nature. The corresponding SAED patterns also prove that the nanorods are single crystalline (see Fig. 3B3, C3). The HRTEM results of the sample A (not shown here) are similar to that of the sample B. The chemical composition of the as-prepared nanorods was analyzed by

Fig. 2 The TEM images of the samples A, B and C



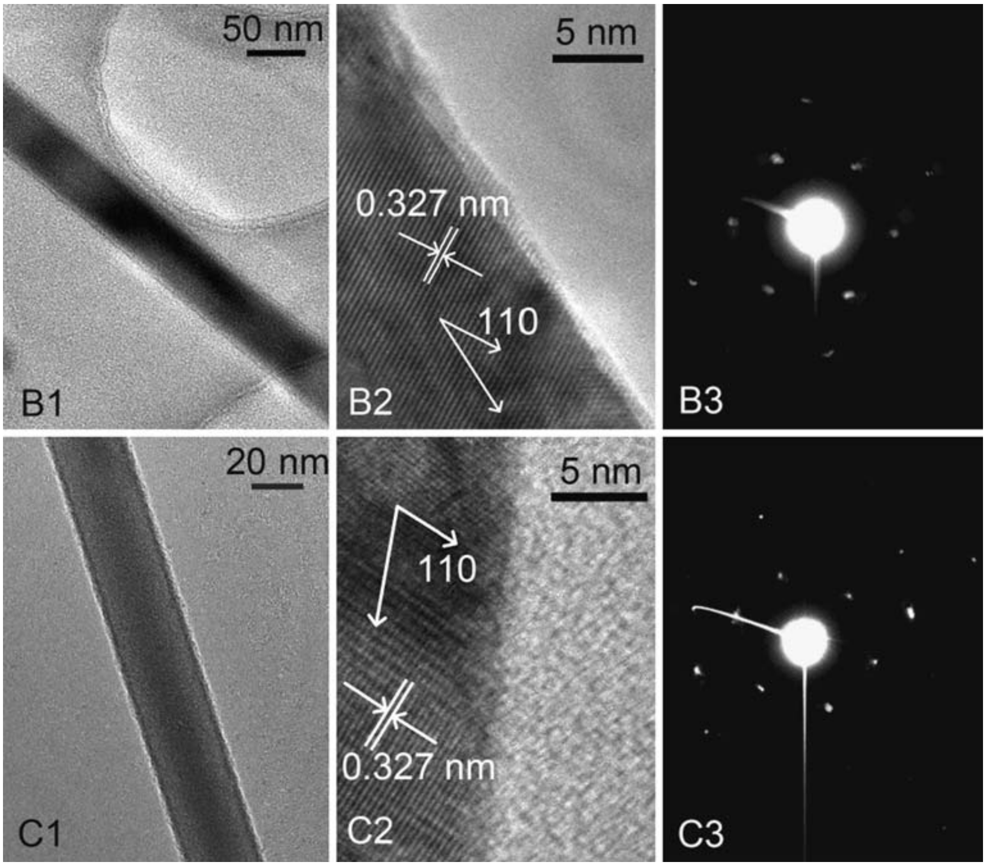


Fig. 3 The HRTEM images and SAED patterns of the samples B and C

energy-dispersive X-ray spectroscopy (EDS). The results indicate that La and O elements of the sample A and B are of an approximate molar ratio of 1:3, but La/O molar ratio of the sample C is about 1:2. The reason will be investigated in our next work.

The obtained La(OH)$_3$ nanorods are of hexagonal crystal structure, which is characteristic of highly anisotropic growth. Consequently, the habit of anisotropic growth is the inherent reason for the formation of La(OH)$_3$ nanorods. In our experimental, the resultant La(OH)$_3$ nanorods prepared using pure water as solvent at 240 °C are single crystalline nature, which is not fully consistent with that by Ma et al. [12]. At the same time, La(OH)$_3$ nanorods prepared using the mixed solvent have different crystal growth character comparing with that using pure water as solvent. The growth rate of different planes is dependent on its plane energy. In all the planes of La(OH)$_3$, the (101) plane has the lowest plane energy, i.e., the high growth rate, which results in the formation of nanorod morphology in hydrothermal process. However, the reaction system used in our experimental provides an environment that changes the plane energies, i.e., adjusts the plane growth rate and alters the crystal growth direction, which results in different XRD and HRTEM results.

It was concluded that perfect La(OH)$_3$ nanorods could be obtained via a simple solvothermal method. According to the SAED and HRTEM patterns, La(OH)$_3$ nanorods are single crystalline. Using the solvothermal methods, single crystalline La(OH)$_3$ nanorods could attained with longer length and larger diameter than that using hydrothermal method. A formation mechanism of the rodlike crystals is tentatively suggested. It is our hope that this simple aqueous solution synthetic route can be applied as a general method for the preparation of other hydroxides with 1D nanostructures.

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References

1. Ngomsik AF, Bee A, Draye M, Cote G, Cabuil V (2005) Comptes Rendus Chimie 8:963
2. Cheng Y, Zheng YH, Wang YS, Bao F, Qin Y (2005) J Solid State Chem 178:2394
3. Kim JH, Kim EK, Lee CH, Song MS, Kim YH, Kim J (2005) Phys E: Low-dimensional Syst Nanostr 26:432
4. Tamir S, Berger S (2000) Mater Sci Eng B 69–70:479
5. Kitazawa N, Watanabe Y (2005) Surf Coat Tech 198:9

6. Zhang P, Gao L (2003) Langmuir 19:208
7. Chen CL, Lou ZS, Chen QW (2005) Chem Lett 34:430
8. Wang DB, Yu DB, Shao MW, Yu WC, Qian YT (2002) Chem Lett 31:1056
9. Cordente N, Respaud M, Senocq F, Casanove MJ, Amiens C, Chaudret B (2001) Nano Lett 1:565
10. Zhu JL, Zhou YH, Yang HX (1997) J Power Sources 69:169
11. Rosynek MP, Magnuson DT (1977) J Catal 46:402
12. Ma XY, Zhang H, Ji YJ, Xu J, Yang DR (2004) Mater Lett 58:1180
13. Deng Y, Wu JB, Liu J, Wei GD, Nan CW (2003) J Phys Chem Solids 64:607