

A simple microwave-assisted hydrothermal synthesis of lanthanum hydroxide nanowires with a high aspect ratio

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Uniform La(OH)₃ nanowires (NWs) with a high aspect ratio of more than 200 have been successfully synthesized by a simple microwave-assisted hydrothermal (MH) process. Comparing to a conventional hydrothermal (CH) one, the La(OH)₃ powders obtained are nanorods in shape with an aspect ratio below 100 and required higher temperature and longer time than the MH. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses revealed that MH-La(OH)₃ NWs were hexagonal structure with 5 μm long and 15-25 nm diameter. A formation mechanism of La(OH)₃ NWs was proposed and discussed in this research.

Key words: Lanthanum hydroxide, Nanowires, Microwave-hydrothermal method.

Introduction

In recent years, one-dimensional (1D) nanomaterials such as nanowires, nanobelts and nanorods have attracted considerable attention and great potential to address fundamental issue about dimensionality as well as their potential in the development of nanodevices including photonics, nanoelectronics and data storages because of their anisotropy of very complex physical properties and self-assemblies as compared to those of spherical nanoparticles [1, 2].

Lanthanum hydroxide (La(OH)₃) has been used in many fields such as ceramics, superconductive materials, electrode materials, hydrogen storage materials, optical coatings and next generation high dielectric constant gate dielectrics. Recently, research has been focused on two main features of La(OH)₃: its catalytic and sorbent properties. Concerning catalysis, La(OH)₃ as well as La₂O₃ is used as support for metals such as rhodium and platinum that are active for different conditions. In particular, 1D La(OH)₃ has been of growing interest owing to its promising application in nanoscale optoelectronic devices [1, 3, 4]. There are many reports on the synthesis of 1D nanomaterials using both physical and chemical methods. However, the first is more appropriate to prepare 1D hydroxide nanomaterials because it is easy to provide hydroxyl ions in the aqueous solution. The hydrothermal method is widely

used to prepare nanostructured materials due to the simplicity, high efficiency and low cost. To improve reaction kinetic enhancement, microwave radiation as a heating source is applied for the hydrothermal method. It has several advantages over the conventional: short reaction time, low synthetic temperature, small particle size, narrow size distribution and high purity [5-8].

Herein, we report a simple microwave-assisted hydrothermal (MH) method to synthesize the 1D La(OH)₃ nanowires in comparison with the product obtained by the conventional hydrothermal (CH) method. The MH method is more effective, more simple and consumes less energy than the CH one.

Experimental procedure

All chemicals were analytical grade and were used without further purification. In a typical synthesis, 0.01 mole La(NO₃)₃·6H₂O was dissolved in 50 ml deionized water with continuous stirring. After it was completely dissolved, the colorless lanthanum solution was transformed to a lanthanum gel by dropping of concentrated NH₄OH into the solution until achieving at the pH of 10. Then, it was transferred into a Teflon-lined autoclave of 100 ml capacity. The autoclave was filled with deionized water up to 80% of the total volume and heated by a 300 W microwave digestion by a Mars-5, CEM at 150 °C for 1 h with the heating rate of 5 °C.min⁻¹. At the conclusion of the process, the autoclave was left cool down to room temperature. The resulting product was filtered, washed with distilled water and absolute ethanol, and finally dried at 80 °C for 12 h. The La(OH)₃ sample by MH was compared to

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the $\text{La}(\text{OH})_3$ sample produced by the CH. For the CH method, white lanthanum gel was transferred into a Teflon-lined stainless steel autoclave and sealed. The autoclave was put in an electric oven as a heating source and heated at 160 °C and 200 °C for 1 h and 24 h. The resulting products were filtered, washed with distilled water and absolute ethanol, and finally dried at 80 °C for 12 h. The as-synthesized $\text{La}(\text{OH})_3$ samples were further characterized by X-ray diffractometer (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM) and transmission electron microscope (TEM).

Results and discussion

The XRD patterns of the samples synthesized by the MH and CH methods are shown in Fig. 1a. All diffraction

peaks of the as-synthesized $\text{La}(\text{OH})_3$ nanostructures can be indexed and specified as the hexagonal $\text{La}(\text{OH})_3$ structure which is in consistent with those of the JCPDS No. 36-1481 [9] ($a = b = 6.5286 \text{ \AA}$ and $c = 3.8588 \text{ \AA}$). The broadening of these diffraction peaks indicates that the size of crystal was very fine. In this research, the intensities of diffraction peaks of $\text{MH-La}(\text{OH})_3$ are stronger than those of the $\text{CH-La}(\text{OH})_3$, which indicates the $\text{La}(\text{OH})_3$ produced by the MH were of higher crystalline degree than that produced by the CH.

Fig. 1b shows FTIR spectra of the as-synthesized CH- and $\text{MH-La}(\text{OH})_3$ nanostructures in the wavelength range of 400–4000 cm^{-1} . The broad and sharp bands at 3000–3500 and 1640 cm^{-1} are assigned to O–H stretching and bending of residual absorbed water molecules on surfaces of the samples. Intense and

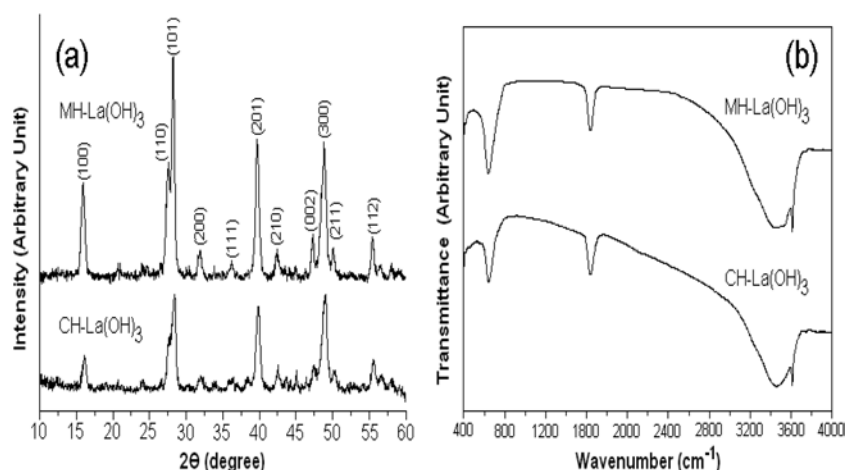


Fig. 1. (a) XRD patterns and (b) FTIR spectra of $\text{La}(\text{OH})_3$ nanostructures synthesized by CH at 200 °C for 24 h and MH at 150 °C for 1 h.

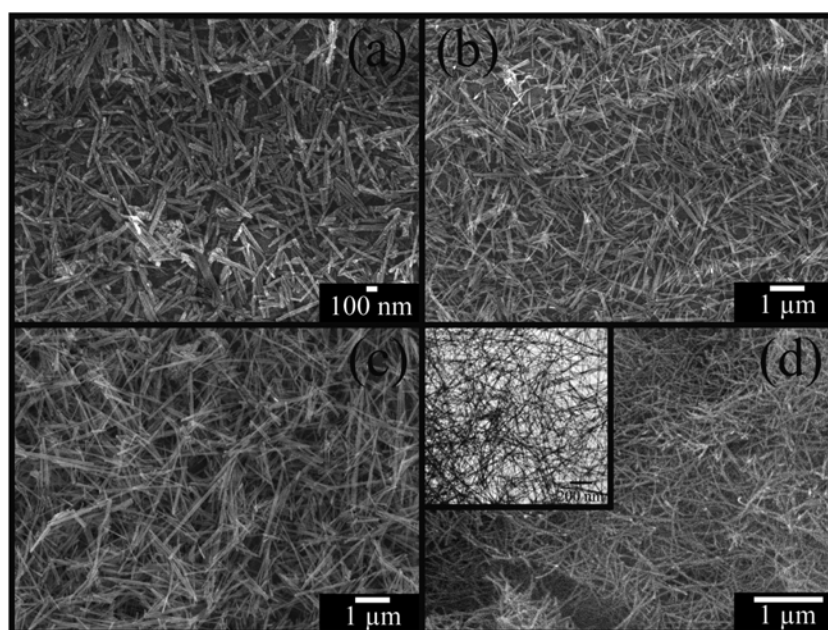


Fig. 2. SEM images of 1D $\text{La}(\text{OH})_3$ nanostructures synthesized by CH at (a) 160 °C for 1 h, (b) 160 °C for 24 h, (c) 200 °C for 24 h and (d) MH at 150 °C for 1 h. TEM image of $\text{MH-La}(\text{OH})_3$ NWs is inserted in Fig. 2d.

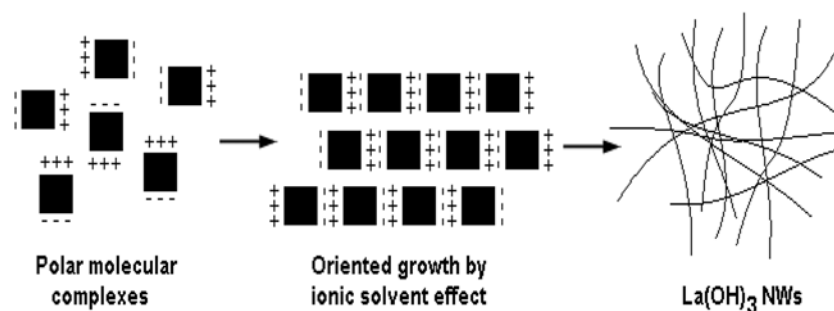


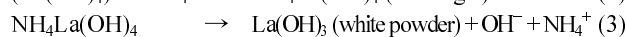
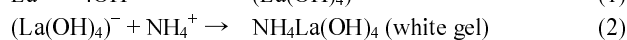
Fig. 3. Schematic representation of the proposed mechanism for the formation of 1D $\text{La}(\text{OH})_3$ nanostructures.

sharp bands at 3612 and 648 cm^{-1} belonged to the tension in the hydroxyl groups and bending vibration of the La-O-H modes of $\text{La}(\text{OH})_3$ samples [10-12].

The morphology of the as-synthesized $\text{La}(\text{OH})_3$ samples were observed through a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The typical SEM images of all samples are shown in Fig. 2. It can be seen that the as-synthesized samples are totally composed of uniform 1D $\text{La}(\text{OH})_3$ nanorods (NRs) for the CH method and $\text{La}(\text{OH})_3$ nanowires (NWs) for the MH method. For the CH method, different lengths and diameters of $\text{La}(\text{OH})_3$ NRs were controlled by the holding reaction time and reaction temperature. Alternately, the length and diameter of the as-synthesized $\text{La}(\text{OH})_3$ NRs of the CH method were increased with the increasing in the length of holding reaction time and reaction temperature. The short $\text{La}(\text{OH})_3$ NRs with length and diameter of $100\text{-}300$ and 20 nm were produced at 160°C for 1 h . The length and diameter of $\text{La}(\text{OH})_3$ NRs were increased to $1\text{-}2\text{ }\mu\text{m}$ and $30\text{-}35\text{ nm}$ for 160°C for 24 h , and to $2\text{-}4\text{ }\mu\text{m}$ and $40\text{-}60\text{ nm}$ for 200°C for 24 h under the CH processing. Comparing to the MH method at 150°C for 1 h , the $\text{La}(\text{OH})_3$ NWs were produced as shown in Fig. 2d. The length and diameter of $\text{La}(\text{OH})_3$ NWs were $5\text{ }\mu\text{m}$ and $15\text{-}25\text{ nm}$. From the XRD and EM results, the MH method is simple and can be used to synthesize high crystalline degree of 1D nanomaterials. The TEM image of $\text{La}(\text{OH})_3$ NWs synthesized by the MH method (inserted in Fig. 2d) shows that the product is uniform $\text{La}(\text{OH})_3$ NWs with no detection of any other morphological shapes in this research. In all the results, the MH method using microwave radiation as a heating source has an advantage over the CH one using an electric current as a heating source, because the MH is required shorter reaction time, and lower temperature to control uniformly morphological product.

The synthesis of 1D nanomaterials were influenced by many parameters such as surface energy, space group, surfactant, template, etc. In this research, formation mechanism of 1D $\text{La}(\text{OH})_3$ NWs synthesized by the MH method using $\text{La}(\text{NO}_3)_3$ solution with the pH of 10 adjusted by concentrated NH_4OH were

explained by the ionic solvent [13] as follows.



The ionic solvent dissociated in the solution to form free cations (NH_4^+) and anions (OH^-). This experiment has been conducted in highly concentrated alkaline condition, after dropping of concentrated NH_4OH into the solution until its pH was reached at 10 . The La^{3+} cations reacted with OH^- anions to form $(\text{La}(\text{OH})_4)^-$ species as shown in equation (1). In the solution of free NH_4^+ species, the electrostatic interaction between positive and negative ions was able to form $\text{NH}_4\text{La}(\text{OH})_4$ polar molecular complexes with white gel in equation (2). These polar molecular complexes might directionally attach each other (Fig. 3) to achieve equilibrium between attraction and repulsion forces, including the oriented attachment mechanism may originate from the inherent characteristics of the 1D hexagonal $\text{La}(\text{OH})_3$ nanostructures. The dissociation and diffusion rates of the molecules have strongly influenced by the processing temperature, which resulted in obtaining one dimensional structure at high temperature. Therefore, rising in the temperature under the MH condition activated the increasing in the two rates which were preferred for one dimensional growth species dissolved in the solution. For the optimal conditions under the MH method, NH_4^+ and OH^- ions were released from $\text{NH}_4\text{La}(\text{OH})_4$, and $\text{La}(\text{OH})_3$ molecules nucleated and grew in the lowest energy (101) plane at the highest growth rate as white powder shown in equation (3). Finally, $\text{La}(\text{OH})_3$ NWs were produced.

Conclusions

Hexagonal $\text{La}(\text{OH})_3$ NWs with the length and diameter of $5\text{ }\mu\text{m}$ and $15\text{-}25\text{ nm}$ were successful synthesized by a simple MH method. A formation mechanism of $\text{La}(\text{OH})_3$ NWs was proposed and discussed by an ionic solvent effect. The MH method required shorter reaction time and at lower temperature with controlled uniform product morphologies than the CH method.

Acknowledgements

The research was supported by the National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency, Thailand, and the Graduate School of Chiang Mai University.

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