Chemical Engineering Journal 214 (2013) 386–393

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

PVP-assisted assembly of lanthanum carbonate hydroxide with hierarchical architectures and their luminescence properties

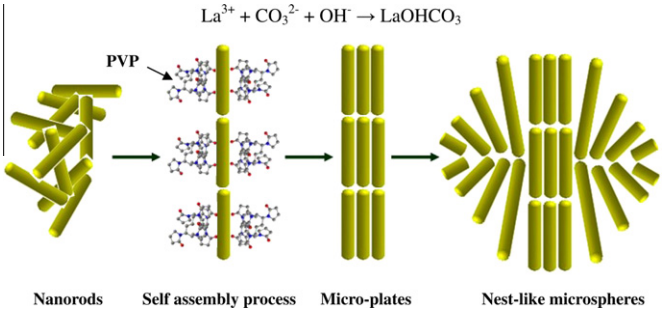
Gang Wang [a], Hui Wang [b,*], Jintao Bai [a,*], Zhaoyu Ren [a], Jinbo Bai [c]

[a] National Key Laboratory of Photoelectric Technology and Functional Materials (Culture Base), National Photoelectric Technology and Functional Materials & Application International Cooperation Base, Institute of Photonics & Photon-Technology, Northwest University, Xi'an 710069, PR China
[b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry (Ministry of Education), College of Chemistry & Materials Science, Northwest University, Xi'an 710069, PR China
[c] Laboratory MSS/MAT, CNRS UMR 8579, Ecole Centrale Paris, 92295 Chatenay Malabry, France

HIGHLIGHTS

- Hierarchical $LaOHCO_3$ was synthesized by a simple PVP-assisted hydrothermal route.
- The $LaOHCO_3$ was assembled by numerous nanorods with uniform size.
- The morphology of $LaOHCO_3$ can be adjusted by changing the reaction time.
- The optical property of $LaOHCO_3$ with different morphology was studied.
- The luminescence property of $LaOHCO_3$ was size- and shape-dependent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 July 2012
Received in revised form 21 October 2012
Accepted 22 October 2012
Available online 30 October 2012

Keywords:
$LaOHCO_3$ microspheres
Polyvinylpyrrolidone
Hierarchical structure
Luminescence property

ABSTRACT

In the presence of polyvinylpyrrolidone (PVP), three-dimensional (3D) hierarchical nest-like architecture of lanthanum carbonate hydroxide ($LaOHCO_3$) with uniform size is successfully synthesized by a facile hydrothermal process using $La(NO_3)_3$ as the starting material. The result indicates that $LaOHCO_3$ microspheres are constructed layer-by-layer from a large number of two-dimensional plates, which are composed of numerous nanorods with a length of ~50 nm. The formation mechanism is discussed on the basis of the result of a time-dependent experiment. It is demonstrated that PVP played an important role in the formation of the hierarchical structure. The room temperature photoluminescence properties of the $LaOHCO_3$ with different morphologies and size are investigated, showing that the nest-like $LaOHCO_3$ exhibits a relative stronger luminescence intensity at 420 nm than the synthesized rod- and apple-like $LaOHCO_3$ samples.

1. Introduction

Rare-earth compounds have received significant attention in the area of electronics, photonics and magnetics due to their extraordinary crystal type, shape, size and composition [1]. Nowadays, much attention has been focused on the synthesis of lanthanide compounds. And there have been many reports for the synthesis of lanthanide oxides (La_2O_3) [2–5], lanthanide hydroxide ($La(OH)_3$) [6–9], and lanthanide carbonate ($La_2(CO_3)_3$)

* Corresponding authors. Address: National Key Laboratory of Photoelectric Technology and Functional Materials (Culture Base), National Photoelectric Technology and Functional Materials & Application International Cooperation Base, Institute of Photonics & Photon-Technology, Northwest University, Xi'an 710069, PR China (H. Wang). Tel.: +86 29 8836 3115; fax: +86 29 8830 3798.
E-mail addresses: huiwang@nwu.edu.cn (H. Wang), jintaobai@sina.cn (J. Bai).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.10.033

[10]. Although lanthanide compounds with various morphologies and compositions have been synthesized, there are few papers reported the controlled synthesis of $LaOHCO_3$ microcrystals. Up to now, only sporadic successful examples of the rational design of $LaOHCO_3$ were reported [11,12]. Considering the fact that the size- and shape-controlled synthesis of $LaOHCO_3$ was hardly realized, developing a facile method to produce the barely studied $LaOHCO_3$ is absolutely necessary.

Recently, two strategies have been used for producing nano- or micro-structured materials with controlled morphology. One is the use of hard templates, which will physically confine the size and shape of the growing particles [13–15]. The other is the use of surfactants, which will control the materials' dimension and growth direction during the reaction process [16–19]. Until now, various types of surfactants have been used to produce well structured materials thanks to their efficient self-assembly property. These surfactants included cetyltrimethyl ammonium bromide (CTAB) [20,21], dodecyl benzene sulfonic acid sodium salt (SDBS) [22,23], hexamethylenetetramine (HMT) [24], and PVP [25–27]. Among them, PVP is a common non-ionic surfactant and often used for producing materials with hierarchical architecture. Plenty of hierarchical inorganic compounds now have been prepared by PVP-assisted reaction [26,28,29]. And it is worth noting that the hierarchical structure not only provided a large surface area but also presented extra functions (e.g. improved photocatalytic [30], electrocatalysis [31], or electrochemical performance [32]) to the products when compared with other morphological structures. Considering the benefit obtained from the novel structure, it can be speculated that once the hierarchical $LaOHCO_3$ was synthesized, some properties such as photoluminescence (PL) property might be generated or improved [11]. Moreover, due to its analogy-graphite layer structure, the $LaOHCO_3$ may served as an efficient matrix for the support of other rare earth compounds and thus have potential application in optics, catalysis, intercalation chemistry, etc. [33].

In this article, we report the direct growth, by the PVP-assisted hydrothermal method, of $LaOHCO_3$ with controlled size and specific hierarchical microarchitecture, which is different from the reported $LaOHCO_3$ products [11,12]. The morpholoty, structure, and composition of the as-prepared samples were characterized by X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetric analysis (TG/DSC), X-ray photoelectron spectrum (XPS), fourier transform infrared (FTIR) spectra, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Based on the above characterization and a time-dependent experiment, the formation process of the 3D hierarchical nest-like $LaOHCO_3$ microstructures are proposed. Additionally, the PL property of the $LaOHCO_3$ was investigated and compared with other $LaOHCO_3$ samples.

2. Experimental section

2.1. Materials

The chemicals used in this study were all of analytical pure grade and no further purification was performed prior to use. Lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$), polyvinylpyrrolidone (PVP, molecular weight = 10,000 g/mol), and ammonia ($NH_3{\cdot}H_2O$) were all purchased from Shanghai Chemical Reagent Ltd. Co. of China. Carbon dioxide (CO_2) of 99.99% purity was obtained from Xi'an Weiguang Gas Co., Ltd. of China. Deionized water was used as a solvent.

2.2. Synthesis

In a typical synthesis, 0.13 g $La(NO_3)_3{\cdot}6H_2O$, 1 g PVP (1 g) and 1 ml $NH_3{\cdot}H_2O$ were added to deionized water (30 ml) with vigorous stirring for 10 min at 25 °C. Then carbon dioxide was introduced into the solution for 5 min with a flow rate of 5 ml min^{-1}. The resulting solution was transferred into a 40 ml Teflon-lined autoclave. The autoclave was sealed and maintained at 180 °C for 24 h, then air-cooled to room temperature. The products were filtered and washed several times, first with distilled water and then ethanol, and finally dried in a vacuum oven at 80 °C for 10 h. Finally, white powders were obtained and collected to characterize.

2.3. Characterization

XRD patterns were recorded by a Rigaku D-max C III X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm) at a scanning rate of 0.02° s^{-1} in the 2θ range from 15° to 70°. TG/DSC were performed using 5 mg of sample and a NETZSCH STA 449C thermal analysis instrument over the temperature range of 30–1000 °C at the heating rate of 10 °C min^{-1}. The experiment was carried out at a constant flow of Ar. XPS measurement was performed on an PHI-5400 electron spectrometer with nonmonochromatized Mg Kα X-ray as the excitation source. FTIR spectroscopic measurements were made with an IR spectrophotometer (Brucker-Tensor 27, Germany) having a diffuse reflectance ranging from 600 to 4000 cm^{-1} range at a resolution of 4 cm^{-1}. The KBr pellet technique with about 5% of samples was used to facilitate the FTIR characterization. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM6700 F field-emission scanning electron microscopy. Samples for SEM observation were prepared by dispersing the powders in ethanol and immersing them in an ultrasonic bath for 5 min, few drops of the resulting suspension were placed onto a SEM specimen mount, dried in an Ar atmosphere and gold coated. Transmission electron microscopy (TEM), high-magnification TEM (HMTEM), high-resolution TEM (HRTEM) image and selected area electron diffraction (SAED) were obtained on a JEOL JEM-3010 instrument with an accelerating voltage of 200 kV. Samples for TEM analysis were prepared by dispersing the powders in ethanol and immersing them in an ultrasonic bath for 5 min, few drops of the resulting suspension were placed onto a Formvar coated copper grid. All fluorescence measurements were carried out at room temperature on a Hitachi F-4500 spectrofluorimeter (instrument resolution: 10 nm) using an excitation wavelength of 365 nm. The excitation and emission wavelength bandpasses were both set at 5.0 nm, and the analysis range was 300–1000 nm.

3. Results and discussion

Fig. 1 gives the XRD patterns of samples obtained at different reaction times of 1, 24 and 48 h. The diffraction peaks of each sample could be mainly indexed to the hexagonal phase of $LaOHCO_3$ (cell constants a = 1.261 nm and c = 1.002 nm, JCPDS No. 26-0815) with trace of $La_2O_2CO_3$ phase is found in the products [9]. A similar XRD pattern was reported by Li et al. [12]. The result indicates that $LaOHCO_3$ crystals can be easily obtained under the current synthetic condition. Additionally, it is worth noting that the sample obtained after 48 h of reaction shows diffraction peaks with much higher intensities compared to those with shorter reaction times. Similar result can be found in the previous study on the formation of TiO_2, which indicates that the sample formed with longer reaction time will have a better crystallized structure [34]. According to the starting materials used and the XRD result obtained, detailed chemical reactions involved in the formation of the sample can be formulated as follows [11]:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (1)$$