OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 7, No. 7-8, July - August 2013, p. 505 - 508

Electrospinning: a versatile method for preparation of $La(OH)_3$ mesoporous nanotubes and chain-shaped nanofibers

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A promising technique for the preparation of $La(OH)_3$ mesoporous nanotubes and chain-shaped nanofibers, which are obtained by calcination of electrospun polyvinyl pyrrolidone (PVP)/ lanthanum nitrate composite nanofibers (CNFs) at different temperatures, is presented. The prepared samples are characterized by thermogravimetry and differential thermal analysis, X-ray diffractometry, scanning electron microscopy and Fourier transform infrared spectrometry. The CNFs are amorphous and the surface is smooth with a diameter of 1-3 µm. Mesoporous $La(OH)_3$ nanotubes, formed by the nanoparticles, are obtained at 600 ºC, while chain-shaped $La(OH)_3$ nanofibers are obtained at 800 ºC. The $La(OH)_3$ nanotubes/nanofibers have a diameter of 500-800 nm and are hexagonal with space group $P6_3/m$. A process for the formation of the $La(OH)_3$-containing nanotubes and nanofibers is proposed.

(Received August 7, 2012; accepted July 11, 2013)

Keywords: Lanthanum hydroxide, Mesoporous Nanotubes, Chain-shaped Nanofibers, Electrospinning

1. Introduction

Over the past decades, the fabrication and properties of 1D nanomaterials, such as nanowires, nanorods, nanowhiskers and nanofibers, have been paid much attention due to their importance for potential technological applications [1-5]. These materials are expected to play a key role as functional components in the preparation of nanoscaled electronic and optoelectronic devices. In order to obtain these materials, various preparation methods have been developed including arc discharge, laser ablation, template, precursor thermal decomposition and hydrothermal methods [6-8]. The electrospinning technique is widely applied to prepare polymeric nanofibers [9]. Recently, there has been a substantial growth of research exploring the technology of electrospinning to fabricate nanofibers with low dimensionality and high aspect ratio [10-14]. Lanthanum hydroxide has attracted much attention due to its applications in catalysis, adsorption and phosphor matrix [15,16]. However, only few methods for the preparation of $La(OH)_3$ nanomaterials have been reported [17-19]. To the best of our knowledge, there are no reports on the preparation of $La(OH)_3$ hollow-centered or chain-shaped nanofibers by electrospinning. Herein, we report the fabrication of $La(OH)_3$-containing mesoporous nanotubes and chain-shaped nanofibers by the calcination of electrospun CNFs.

2. Experimental

Polyvinyl pyrrolidone (PVP, Mr = 10 000) was purchased from Tianjin Kermel Chemical Reagents Development Center. $La(NO_3)_3·6H_2O$, was obtained from Tianjin Guangfu Institute of Fine Chemicals. All chemicals were analytically pure and used as received without further purification.

$PVP/La(NO_3)_3$ composite sol was prepared by dissolving PVP (9.07 g) and $La(NO_3)_3·6H_2O$ (2.68 g) in distilled water (8.40 g). The mixture (sol) was stirred for 10-h and left without stirring for 2-h.

The electrospinning apparatus consists of three major components: a DC high voltage power supply (0-30 kV), a spinneret (plastic syringe with a stainless steel needle, 1mm in inner diameter) and a collector (grounded aluminum foil). The $PVP/La(NO_3)_3$ composite sol was introduced into the spinneret. A copper wire, connected to a DC high-voltage generator anode, was placed in the sol. The distance between the needle tip and the collector was fixed at 20 cm. Electrospinning experiments were performed when the ambient temperature was greater than 18 °C and relative air humidity was 50-60 %. A voltage of 20 kV was applied to the sol and the CNF was collected on the aluminum foil. The CNFs were dried initially at 70 ºC for 12-h under vacuum and then calcined at 300 ºC, 600 ºC and 800 ºC in air for 10-h at a heating rate of 2 ºC/min, respectively. $La(OH)_3$ nanofibers were obtained above 600 ºC.

X-ray diffractometry (XRD) analysis was performed with a Holland Philips Analytical PW1710 BASED X-ray diffractometer using $CuK_{\alpha1}$ radiation (λ = 1.5406 Å). The morphology and size of the fibers were observed with a Hitachi S-4200 SEM. Thermogravimetric and differential thermal (TG-DTA) analysis was carried out with a PE SDT-2960 thermal analyzer in air. Fourier transform infrared (FTIR) spectra of the samples were recorded on BRUKER Vertex 70 Fourier transform infrared spectrometer. Specimens were prepared by mixing the sample (0.2 mg) with KBr (200 mg) and pressing the mixture into pellets.

3. Results and discussion

3.1 XRD analysis

The XRD patterns of the CNF composite fiber and the sample calcined at 300 ºC (Fig. 1) indicate an amorphous structure. The $La(OH)_3$ mesoporous nanotubes and chain-shaped nanofibers obtained at 600-800 ºC are hexagonal in structure with space group $P6_3/m$ (PDF 36-1481). Because the carbon generated by carbonization of PVP gives a reducing environment and the oven is well-sealed, the lanthanum salt is converted to $La(OH)_3$ at 800 °C.

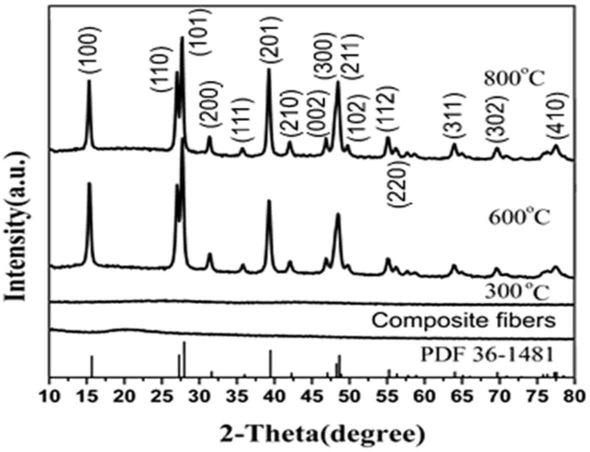

Fig. 1. XRD patterns of CNF samples.

3.2 SEM analysis

The nanofibers fabricated at different calcination temperatures were investigated by SEM (Fig. 2). Figs. 2a-d are SEM images of CNF (a) and the samples calcined at 300 ºC (b), 600 ºC (c) and 800 ºC (d), respectively. The morphology and size of these fibers vary strongly with an increase of calcination temperatures. All the CNFs possess a smooth surface with a diameter of 1-3 µm. The surface morphology of the fibers became coarse with an increase in calcination temperature. Mesoporous nanotubes are formed above 300 ºC. $La(OH)_3$ mesoporous nanotubes, which are constructed by the nanoparticles, are obtained at 600 ºC; $La(OH)_3$ chain-shaped nanofibers are observed at 800 ºC. The diameter of the $La(OH)_3$ nanotubes/nanofibers range from 500-800 nm and are smaller than the composite-fiber CNFs owing to oxidative decomposition of PVP and NO_3^-.

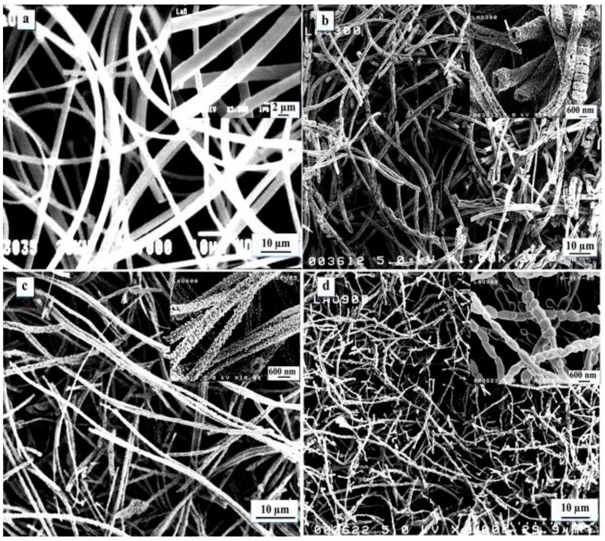

Fig. 2. SEM images of (a) $PVP/La(NO_3)_3$ composite fibers and the fibers obtained at (b) 300 ºC, (c) 600 ºC and (d) 800 ºC (insets: higher magnification).

3.3 TG-DTA analysis

The TG and DTA curves of the CNF without thermal treatment are given in Fig. 3. Three stages of weight loss are observed. The first weight loss step (7 %) occurs from 25-140 ºC and is accompanied by a small endothermic peak near 60 ºC. This weight loss is likely a result of evolution of absorbed and/or residual water on the CNF surface and is more than the theoretical weight loss (5.1 %) from $La(NO_3)_3 \cdot 6H_2O$. It is assumed that the residual water (1.9 %) is adsorbed onto the CNF. The second weight loss (38 %) occurs from 140-375 ºC and is accompanied by a broad exothermic (~328 ºC), which may be a result to the decomposition of nitrate and the PVP side-chain. The last weight loss (44 %) occurs from 375-490 ºC. A sharp exothermic peak is located at 484 ºC and is probably a result of oxidation-combustion of the

PVP main chain [20]. The total weight loss is 89 % (theoretical for residual $La(OH)_3$, 88.7 %). No weight loss occurs above 490 ºC.

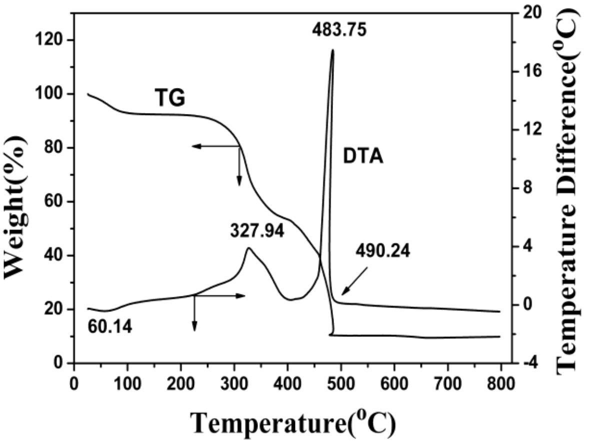

Fig. 3. TG-DTA curves of PVP/La(NO_3)$_3$ composite fibers.

3.4 FTIR spectra analysis

The FTIR spectra of PVP, CNF and $La(OH)_3$-contining nanofibers are given in Fig. 4. The spectra of PVP (Fig. 4a) and CNF (Fig. 4b) are identical. The intensity of the CNF bands is less than for pure PVP. This resulted from the lower content of PVP in the CNFs. All absorption peaks at 3441 cm^{-1}, 2955 cm^{-1}, 1665 cm^{-1}, 1424 cm^{-1}, and 1289 cm^{-1} are attributed to the stretching vibrations of hydroxyl group (ν_{O-H}), C-H bond (ν_{C-H}), carbonyl group ($\nu_{C=O}$), C-H bond (ν_{C-H}), and C-N bond or C-O bond (ν_{C-N} or ν_{C-O}), respectively, of the PVP molecule [21,22]. All the PVP peaks disappear and a new absorption peak appears at 640 cm^{-1} (Fig. 4c). This new absorption peak is ascribed to the bending vibration of La-O-H [23] indicating that $La(OH)_3$ was formed.

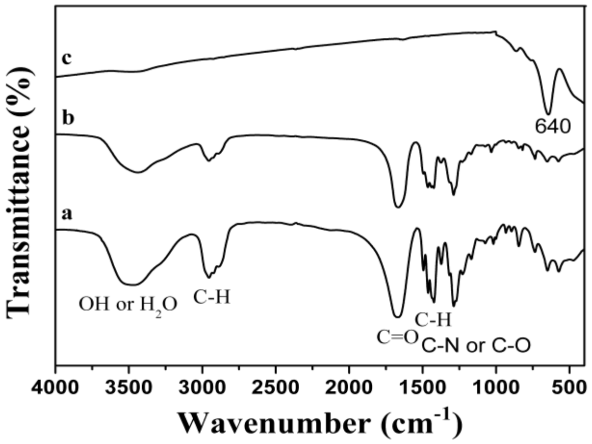

Fig. 4. FTIR spectra of (a) PVP, (b) PVP/La(NO_3)$_3$ composite fibers, (c) $La(OH)_3$–containing nanofibers.

3.5 Formation mechanism

The proposed process for the formation of the $La(OH)_3$ mesoporous nanotubes and chain-shaped nanofibers is summarized in Fig. 5. Thus, $La(NO_3)_2 \cdot 6H_2O$ and PVP are mixed with distilled water to form a viscous sol with PVP acting as a template for the formation of $La(OH)_3$ nanotubes and nanofibers. The La^{3+} and NO_3^- are then mixed with or absorbed onto PVP to form CNFs by electrospinning. During the calcination of the CNFs, solvent water- containing La^{3+} and NO_3^- ions in the composite fibers are transferred to the fiber surface and evaporate. Then the La^{3+} and NO_3^- ions are transported to the CNF surface by water, and at the same time, the La^{3+} is hydrolyzed to $La(OH)_3$. With increasing calcination temperature, the PVP and NO_3^- oxidatively decompose rapidly under air. $La(OH)_3$ coalesced to $La(OH)_3$ nanoparticles. These nanoparticles mutually interconnected to generate the $La(OH)_3$-containing mesoporous nanotubes. At 800 ºC, the $La(OH)_3$ nanoparticles merge and grow to form a solid chain-shaped structure. This fabrication process could serve as a method for the synthesis of mesoporous nanotubes and/or chain-shaped nanofiber materials.

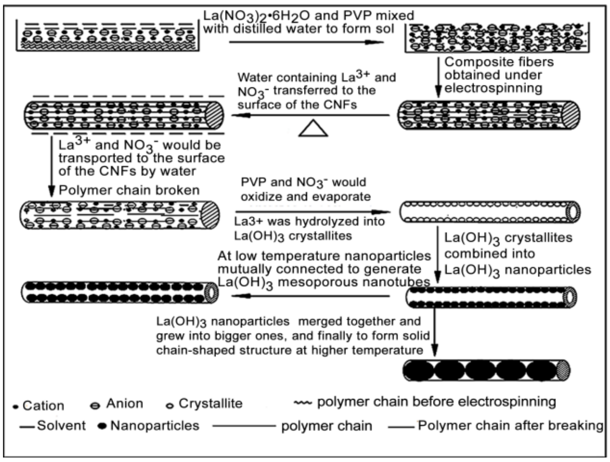

Fig. 5. Proposed fabrication for the formation of the $La(OH)_3$ mesoporous nanotubes and chain-shaped nanofibers.

4. Conclusions

In summary, a simple and effective technique is proposed for the preparation of nanotubes and chain-shaped $La(OH)_3$ nanofibers by calcination of electrospun CNFs. XRD analysis reveals that the CNFs are amorphous and the resultant $La(OH)_3$ nanofibers are hexagonal with space group $P6_3/m$ on calcination from 600 ºC – 800 ºC. This method could serve as a method for the synthesis of hollow-centered or chain-shaped nanostructure materials.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (50972020, 51072026) and Ph.D. Programs Foundation of the Ministry of Education of China (20102216110002, 20112216120003).

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