



Fabrication and Characterization of LaCoO₃ Nanofibers via an Electrospinning Technique

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Abstract

Polyvinyl alcohol (PVA)/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers were prepared by combination of sol-gel method and electrospinning technique, and crystalline LaCoO₃ nanofibers were fabricated by calcination of the PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers at 600°C for 10h. The samples were characterized by using thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffraction spectrometry (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectrometry (FTIR). The results show that PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers are amorphous in structure, and pure phase LaCoO₃ nanofibers are trigonal in structure with space group *R*3*m*. The surface of as-prepared composite nanofibers is smooth, and the diameter is about 200nm. The diameter of LaCoO₃ nanofibers is smaller than that of the relevant composite fibers. The surface of the LaCoO₃ nanofibers becomes coarse with the increase of calcination temperatures. The diameter of LaCoO₃ nanofibers is ca. 80nm, and the length is greater than 100μm. The mass of the sample remains constant when the temperature is above 500°C, and the total mass loss percentage is 83%. Possible formation mechanism of LaCoO₃ nanofibers is preliminarily proposed.

Keywords: LaCoO₃, Nanofibers, Electrospinning

1. Introduction

The science and technology of nanostructured materials is advancing at a rapid pace (Yang, 2009, Gao, 2009, Mohapatra, 2008 & Zhang, 2007). Over the past decade, the preparation and functionalization of one-dimensional nanostructured materials has become one of the most highly energized research fields (Hu, 2008 & Kar, 2006). One-dimensional nanostructured materials, such as nanowires, nanorods, nanowhiskers and nanofibers, have stimulated great interest due to their importance in basic scientific research and potential technological applications (Huynh, 2002 & Duan, 2003). They are expected to play an important role as both interconnects and functional components in the fabrication of nanoscale 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 other methods (Iijima, 1991, Morales, 1998, Shi, 2001 & Pan, 2001). Electrospinning technique is widely applied to prepare polymers nanofibers (Li, 2004, 1151-1170). Recently, some inorganic compounds nanofibers have been prepared by electrospinning technique using electrospun fibers of polymer/inorganic composite as the precursor (Li, 2004, Zhang, 2008 & Shao, 2004). This processing involved the following three steps: (1) Preparation of a gel with suitable inorganic precursor and proper polymer, and achieving the right rheology for electrospinning process; (2) Electrospinning of the gel to obtain fibers of polymer/inorganic precursors composite; (3) Calcinations of the composite fibers to obtain final oxide fibers. It is important; however, to control all of the above three steps in order to obtain high quality fibers with the desired final properties. LaCoO₃ has attracted much interest recently due to their specific electrical, and catalytic properties (Dong, 1994, Chen, 1997 & Yang, 2003). A few methods on the preparation

of LaCoO_3 nanocrystalline materials were reported (Armelaio, 2002, Cheng, 2008 & Xiong, 1997). However, to the best of our knowledge, there have been no reports on the preparation of LaCoO_3 nanofibers by electrospinning. In this paper, LaCoO_3 nanofibers were fabricated by calcination of the electrospun fibers of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite, and some new results were obtained.

2. Experimental section

2.1 Chemicals

Polyvinyl alcohol(PVA)($M_r=80000$) was bought from the Third Chemical Reagents Factory of Tianjin, and cobalt acetate tetrahydrate $[\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}]$ were purchased from Tianjin Kermel Chemical Reagents Development Center. Lanthanum nitrate hexahydrate $[\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}]$ was obtained from Tianjin Guangfu Institute of Fine Chemicals. All chemicals were analytically pure and directly used as received without further purification. Distilled water was used as solvent.

2.2 Fabrication of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite sol

$\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite solution was prepared by dissolving an amount of PVA powders, $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ in distilled water, and stirring for 5h, then remaining motionlessly for 2h. Thus, a viscous sol of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite containing 9%(wt%) PVA, 3% (wt%) metallic salts, 88%(wt%) H_2O , and the molar ratio 1:1 of La^{3+} to Co^{2+} was obtained for electrospinning processing.

2.3 Preparation of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite nanofibers and LaCoO_3 nanofibers

The setup used for electrospinning was indicated in Figure 1. The above composite sol of PVA, $\text{La}(\text{NO}_3)_3$, $\text{Co}(\text{CH}_3\text{COO})_2$ and H_2O mixture was contained in a plastic syringe with a stainless steel needle on its top, and the diameter of the needle was 1mm. A copper wire connected to a DC high-voltage power supply was placed in the sol, and the sol was kept in the syringe by adjusting the angle between syringe and horizon, and the angle was kept at 15° . A grounded aluminum foil served as counter electrode and collector plate. The distance between the needle tip and the collector was fixed to 15cm. Electrospinning experiments were performed when ambient temperature was greater than 18°C and relative air humidity was 50%-60%. A voltage of 20kV was applied to the composite sol and a sprayed dense web of fibers was collected on the aluminum foil. The collected fibers were $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite nanofibers. The prepared composite nanofibers were dried initially at 70°C for 12h under vacuum, and then calcined at a heating rate of $2^\circ\text{C}/\text{min}$ and remained for 10h at 300°C , 600°C and 900°C , respectively. Thus, LaCoO_3 nanofibers were obtained when calcination temperature was 600°C .

2.4 Characterization methods

XRD analysis was performed with a Y-2000 X-ray diffractometer made by Dandong Aolong Radiative Instrument Co. Ltd using $\text{Cu K}\alpha$ radiation and Ni filter, the working current and voltage were 20mA and 40kV, respectively. Scans were made from 20° to 100° at the speed of $3^\circ/\text{min}$, and step was 0.02° . The morphology and size of the fibers were observed with a S-4200 scanning electron microscope made by Japanese Hitachi company. TG-DTA analysis was carried out with a SDT-2960 thermal analyzer made by American TA instrument company at a temperature-rising rate of $10^\circ\text{C}/\text{min}$ under stable air conditions. FTIR spectra of the samples were recorded on BRUKER Vertex 70 Fourier transform infrared spectrophotometer made by Germany Bruker company, and the specimen for the measurement was prepared by mixing the sample with KBr powders and then the mixture was pressed into pellets, the spectrum was acquired in a wave number range from 4000cm^{-1} to 400cm^{-1} with a resolution of 4cm^{-1} .

3. Results and discussion

3.1 XRD results

In order to investigate the lowest crystallizing temperature and the variety of phases, the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite fibers and samples obtained by calcining the composite fibers at different temperatures for 10h were characterized by XRD, as indicated in Figure 2. The results showed that the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite fibers were amorphous in structure, only a broad peak was located around 22° , it was the typical peak of the amorphous polymer, indicating that the composite fibers were amorphous in structure. The sample was partly crystallized at 300°C . The polycrystalline LaCoO_3 nanofibers with single phase were synthesized when calcination temperature was in the range of $600\text{-}900^\circ\text{C}$, the d (spacing between crystallographic plane) values and relative intensities of LaCoO_3 were consistent with those of JCPDS standard card(48-0123), and the crystal structure of the prepared LaCoO_3 was trigonal system with space group $R\bar{3}m$.

3.2 SEM images

In order to study the morphology and size of the as-synthesized fibers, the prepared fibers were investigated by SEM, as shown in Figure 3. As seen from Figure 3, the morphology and size of the fibers varied strongly with the increase of calcination temperatures. The surface of the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Co}(\text{CH}_3\text{COO})_2]$ composite nanofibers was very smooth,

and the diameter of the composite fibers was about 200nm. The diameter of the fibers was ca. 150nm at 300°C. The surface morphology of LaCoO₃ nanofibers became coarse with the increase of calcination temperatures. The diameter of the synthesized LaCoO₃ nanofibers was ca. 80nm at 600°C, and their lengths were greater than 100μm. The diameters of LaCoO₃ nanofibers were smaller than those of the PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers owing to the decomposition and evaporation of PVA, NO₃⁻, CH₃COO⁻. The fibers were broken at 900°C. Therefore, LaCoO₃ nanofibers with good morphology should be prepared at low calcination temperature.

3.3 TG-DTA analysis

TG and DTA curves of the PVP/[La(NO₃)₃+Co(CH₃COO)₂] composite fibers were indicated in Figure 4. It was noted that there were mainly three stages of weight loss. The first weight loss step (6%) was in the range of 32°C to 135°C accompanied by a small endothermic peak near 76.04°C in the DTA curve caused by the loss of the surface absorbed water or the residual water molecules in the composite fibers. The second weight loss step (31%) was noticed between 135°C and 306°C accompanied by an exothermic peak near 247.43°C in the DTA curve due to the decomposition of the acetate, nitrate and side-chain of PVA. The last weight loss was 46% from 306°C to 495°C. In the DTA curve, a wide exothermic peak was located at 472.06°C. This was likely to be the oxidation combustion of the PVA main chain. And above 500°C, the TG and DTA curves were all stable, indicating that water, organic compounds, nitrate and acetate in the composite fibers were completely volatilized and pure LaCoO₃ nanofibers could be obtained after 500°C. The total weight loss rate was 83%. This result tallied with the XRD analysis.

3.3 FTIR spectra analysis

Pure PVA, PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers and LaCoO₃ nanofibers (obtained by calcination of the relevant composite nanofibers at 600°C for 10h) were analyzed by FTIR, as shown in Figure 5. As seen from Figure 5, PVA (Figure 5a) and PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers (Figure 5b) had the identical spectra, but absorption peaks intensity of spectrum for PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers was lower than those of spectrum for pure PVA. This resulted from the lower content of PVA in the PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers. All absorption peaks were attributed to PVA at 3334cm⁻¹, 2945cm⁻¹, 1704cm⁻¹, 1488cm⁻¹, 1305cm⁻¹, 1091cm⁻¹, 815cm⁻¹ corresponding to the stretching vibrations of hydroxyl group (ν_{O-H}), C-H bond (ν_{C-H}), carbonyl group (ν_{C=O}), C-H bond (ν_{C-H}), C-C bond (ν_{C-C}), C-O bond (ν_{C-O}), and O-H bond (ν_{O-H}) respectively. It was seen from Figure 5c that all peaks of PVA disappeared, and at low wave number range, new absorption peaks at 601cm⁻¹, 558cm⁻¹ and 426cm⁻¹ appeared. The new absorption peaks were ascribed to the vibration of metal-oxygen bond, indicating that LaCoO₃ was formed. The results of FTIR analysis were in good agreement with XRD results.

3.4 Possible formation mechanism of LaCoO₃ nanofibers

Possible formation mechanism of LaCoO₃ nanofibers was demonstrated in Figure 6. La(NO₃)₃·6H₂O, Co(CH₃COO)₂·4H₂O and PVA were mixed with distilled water to form sol with certain viscosity. PVA acted as template during the formation processing of LaCoO₃ nanofibers. La³⁺, Co²⁺, CH₃COO⁻ and NO₃⁻ were mixed with or absorbed onto PVA molecules to fabricate PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite fibers under electrospinning. During calcination treatment of the composite fibers, solvent water would remove to the surface of the PVP/[La(NO₃)₃+Co(CH₃COO)₂] composite fibers and eventually evaporated from the composite fibers. With the increasing in calcination temperature, PVA molecular chains were broken, PVA, CH₃COO⁻, and NO₃⁻ would oxidize and volatilize gradually, La³⁺ and Co²⁺ were oxidized into LaCoO₃ crystallites in air, and many crystallites were sintered to form small LaCoO₃ nanoparticles, these small nanoparticles were combined into big particles, and these particles were mutually connected to generate LaCoO₃ nanofibers.

4. Conclusions

4.1

PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite nanofibers were fabricated by electrospinning. Polycrystalline LaCoO₃ nanofibers were synthesized by calcining the relevant composite fibers at 600°C.

4.2

TG-DTA analysis showed that the mass of the PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite fibers remained constant when the temperature was above 500°C, and the total mass loss percentage was 83%.

4.3

XRD analysis revealed that the composite fibers were amorphous in structure. The crystal structure of LaCoO₃ nanofibers was trigonal system with space group $R\bar{3}m$.

4.4

SEM images indicated that the surface of the prepared composite fibres was smooth, and the diameter of the composite nanofibers were about 200nm. The diameters of LaCoO₃ nanofibers were smaller than those of the composite

nanofibers. The surface of the LaCoO₃ nanofibers became coarse with the increase of calcination temperatures. The diameter of LaCoO₃ nanofibers was ca. 80nm, and their lengths were greater than 100µm.

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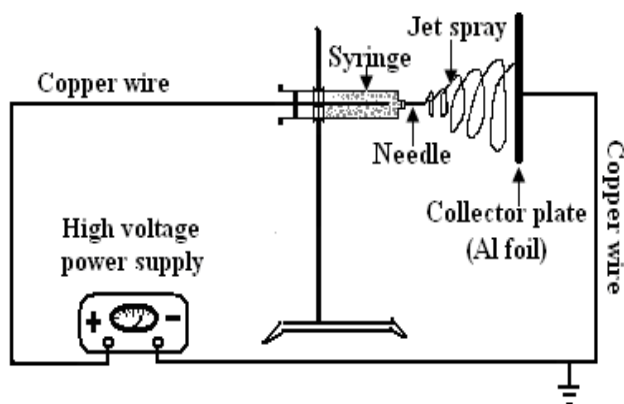


Figure 1. Schematic diagram of electrospinning setup

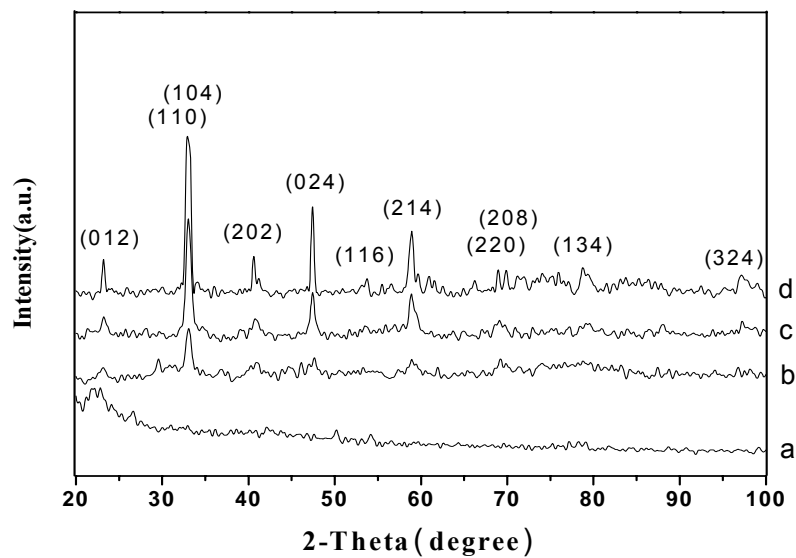


Figure 2. XRD patterns of samples

a. PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite fibers b. 300°C c. 600°C d. 900°C

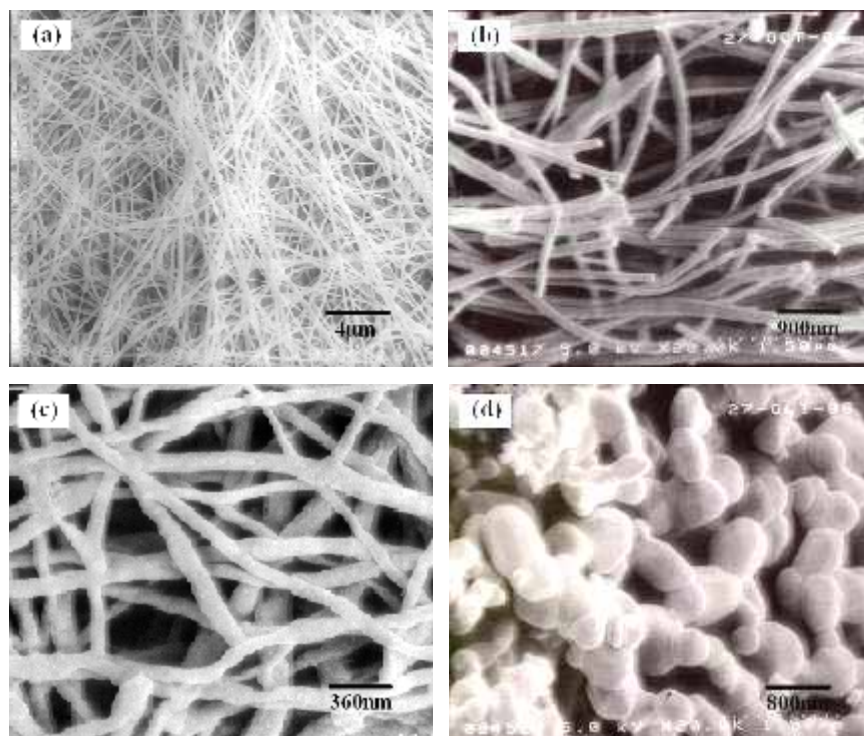


Figure 3. SEM micrographs of the fibers obtained at different temperatures
 (a) PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite fibers (b) 300°C (c) 600°C (d) 900°C

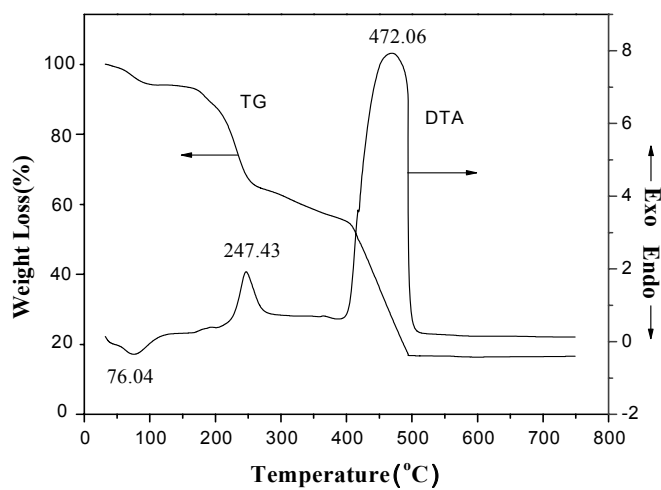


Figure 4. TG-DTA curves of PVA/[La(NO₃)₃+Co(CH₃COO)₂] composite fibers

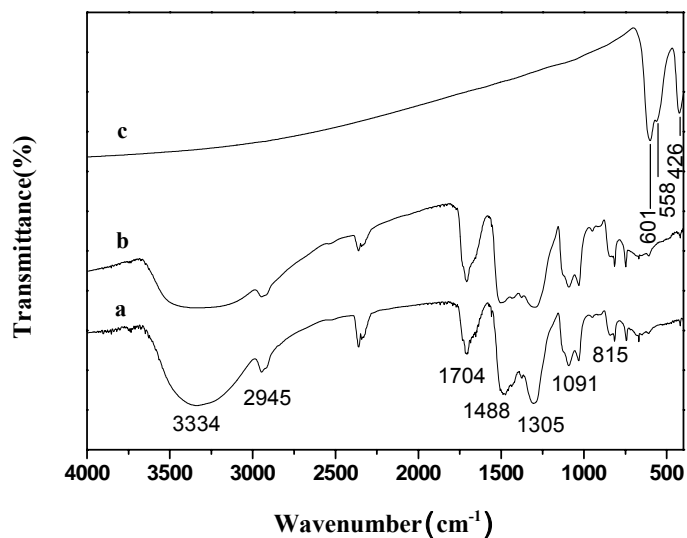
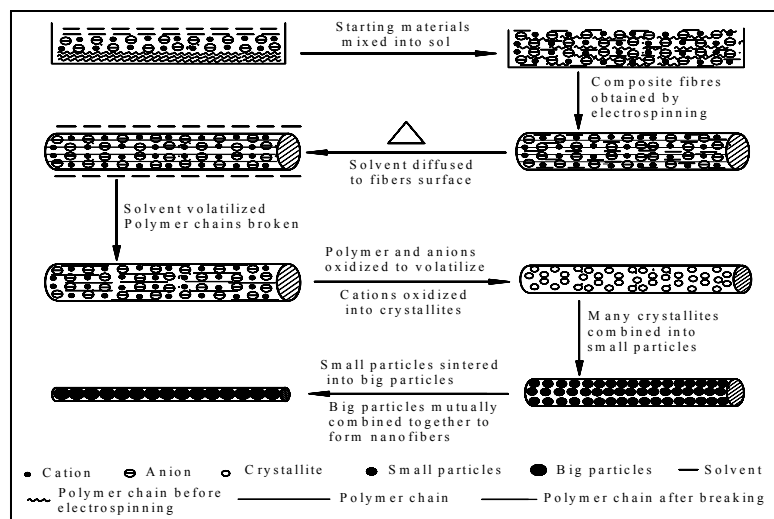


Figure 5. FTIR spectra of the samples

a. PVA b. PVA/[La(NO₃)₃+Co(CH₃COO)₃] composite fibers c. LaCoO₃ nanofibers

Figure 6. Illustrative diagram of possible formation mechanism of LaCoO₃ nanofibers