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Synthesis of $LaMnO_3$ Nanofibers via Electrospinning

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Abstract

Polyvinyl alcohol(PVA)/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers were fabricated by electrospinning, and polycrystalline $LaMnO_3$ nanofibers were prepared by calcination of the PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers at 600ºC 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/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers are amorphous in structure, and pure phase $LaMnO_3$ nanofibers are orthorhombic with space group Pbnm. The surface of as-prepared composite nanofibers is smooth, and the diameter is about 150nm. The diameter of $LaMnO_3$ nanofibers is smaller than that of the relevant composite fibers. The surface of the $LaMnO_3$ nanofibers becomes coarse with the increase of calcination temperatures. The diameter of $LaMnO_3$ nanofibers is ca. 100nm, and the length is greater than 100μm. The mass of the sample remains constant when the temperature is above 450ºC, and the total mass loss percentage is 94.6%. Possible formation mechanism of $LaMnO_3$ nanofibers is preliminarily proposed.

Keywords: $LaMnO_3$, 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 sol with suitable inorganic precursor and proper polymer, and achieving the right rheology for electrospinning process; (2) Electrospinning of the sol 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. $LaMnO_3$ has attracted much interest recently due to their specific electrical and catalytic properties (Dong, 1994, Weng, 2001, Yang, 2003 & Deng, 2006). A few methods on the preparation of $LaMnO_3$ nanocrystalline materials were reported (Maglia, 2008, Krupicka, 2002, Zhu, 2002 & Jeffrey, 2004). In this paper, $LaMnO_3$ nanofibers were fabricated by calcination of the electrospun fibers of PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite, and some new results were obtained.

2. Experimental

2.1 Chemicals

Polyvinyl alcohol (PVA)(Mr=80000) was bought from the Third Chemical Reagents Factory of Tianjin, and manganese acetate tetrahydrate[$Mn(CH_3COO)_2·4H_2O$] were purchased from Tianjin Kermel Chemical Reagents Development Center. Lanthanum nitrate hexahydrate[$La(NO_3)_3·6H_2O$] 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 Preparation of PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite sol

PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite solution was prepared by dissolving an amount of PVA powders, $La(NO_3)_3·6H_2O$ and $Mn(CH_3COO)_2·4H_2O$ in distilled water, and stirring for 5h, then remaining motionlessly for 2h. Thus, a viscous sol of PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite containing 9%(wt%) PVA, 3% (wt%) metallic salts, 88%(wt%) H_2O, and the molar ratio 1:1 of La^{3+} to Mn^{2+} was obtained for electrospinning processing.

2.3 Synthesis of PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers and $LaMnO_3$ nanofibers

The setup used for electrospinning was indicated in Figure 1. The above composite sol of PVA, $La(NO_3)_3$, $Mn(CH_3COO)_2$ 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 15º. 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 18ºC 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 PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers. The prepared composite nanofibers were dried initially at 70ºC for 12h under vacuum, and then calcined at a heating rate of 2ºC/min and remained for 10h at 300ºC, 600ºC and 900ºC, respectively. Thus, $LaMnO_3$ nanofibers were obtained when calcination temperature was 600ºC.

2.4 Characterization methods

XRD analysis was performed with a Y-2000 X-ray diffractometer made by Dandong Aolong Radiative Instrument Co. Ltd using Cu Kα radiation and Ni filter, the working current and voltage were 20mA and 40kV, respectively. Scans were made from 20° to 75° at the speed of 3°/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^oC/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 patterns

In order to investigate the lowest crystallizing temperature and the variety of phases, the PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] 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 PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite fibers were amorphous in structure, only a broad peak was located around 22º, it was the typical peak of the amorphous polymer, indicating that the composite fibers were amorphous in structure. The sample was partly crystallized at 300ºC. The polycrystalline $LaMnO_3$ nanofibers with single phase were synthesized when calcination temperature was in the range of 600-900ºC, the d(spacing between crystallographic plane)values and relative intensities of $LaMnO_3$ were consistent with those of JCPDS standard card(35-1353), and the crystal structure of the prepared $LaMnO_3$ was orthorhombic system with space group Pbnm.

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 PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers was very smooth, and the diameter of the composite fibers was about 150nm. The diameter of the fibers was ca. 120nm at 300ºC. The surface morphology of $LaMnO_3$ nanofibers became coarse with the increase of calcination temperatures. The diameter of the synthesized $LaMnO_3$ nanofibers was ca. 100nm at 600ºC, and their lengths were greater than 100μm. The diameters of $LaMnO_3$ nanofibers were smaller than those of the PVA/[$La(NO_3)_3$+ $Mn(CH_3COO)_2$] composite nanofibers owing to the decomposition and evaporation of PVA, NO_3^-, CH_3COO^-. The fibers were broken at 900ºC. Therefore, $LaMnO_3$ nanofibers with good morphology should be prepared at low calcination temperature.

3.3 TG-DTA analysis

TG and DTA curves of the PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite fibers were indicated in Figure 4. It was noted that there were mainly three stages of weight loss. The first weight loss step (7.6%) was in the range of 29ºC to 127ºC accompanied by a small endothermic peak near 71.08ºC 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 (50%) was noticed between 127ºC and 248ºC accompanied by an exothermic peak near 229ºC in the DTA curve due to the decomposition of the acetate, nitrate and side-chain of PVA. The last weight loss was 37% from 248ºC to 450ºC. In the DTA curve, a wide exothermic peak was located at 363.07ºC. This was likely to be the oxidation combustion of the PVA main chain. And above 450ºC, the TG and DTA curves were all stable, indicating that water, organic compounds, nitrate and acetate in the composite fibers were completely volatilized and inorganic compounds nanofibers could be obtained above 450ºC. The total weight loss rate was 94.6%. This result tallied with the XRD analysis.

3.4 FTIR spectra analysis

Pure PVA, PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers and $LaMnO_3$ nanofibers(obtained by calcination of the relevant composite nanofibers at 600ºC for 10h) were analyzed by FTIR, as shown in Figure 5. As seen from Figure 5, pure PVA(Figure 5a) and PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers(Figure 5b) had the identical spectra, but absorption peaks intensity of spectrum for PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers was lower than those of spectrum for pure PVA. This resulted from the lower content of PVA in the PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] 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($\nu_{O\text{-}H}$), C-H bond($\nu_{C\text{-}H}$), carbonyl group($\nu_{C=O}$), C-H bond($\nu_{C\text{-}H}$), C-C bond($\nu_{C\text{-}C}$), C-O bond($\nu_{C\text{-}O}$), and O-H bond($\nu_{O\text{-}H}$), respectively. It was seen from Figure 5c that all peaks of PVA disappeared, and at low wave number range, a new absorption peak at 614cm^{-1} appeared. The new absorption peak was ascribed to the vibration of metal-oxygen bond, indicating that $LaMnO_3$ was formed. The results of FTIR analysis were in good agreement with XRD results.

3.5 Possible formation mechanism of $LaMnO_3$ nanofibers

Possible formation mechanism of $LaMnO_3$ nanofibers was indicated in Figure 6. $La(NO_3)_3 \cdot 6H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and PVA were mixed with distilled water to form sol with certain viscosity. PVA acted as template during the formation processing of $LaMnO_3$ nanofibers. La^{3+}, Mn^{2+}, CH_3COO^- and NO_3^- were mixed with or absorbed onto PVA molecules to fabricate PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite fibers under electrospinning. During calcination treatment of the composite fibers, solvent water would remove to the surface of the PVP/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite fibers and eventually evaporated from the composite fibers. With the increasing in calcination temperature, PVA molecular chains were broken, PVA, CH_3COO^-, and NO_3^- would oxidize and volatilize gradually, La^{3+} and Mn^{2+} were oxidized into $LaMnO_3$ crystallites in air, and many crystallites were sintered to form small $LaMnO_3$ nanoparticles, these small nanoparticles were combined into big particles, and these particles were mutually connected to generate $LaMnO_3$ nanofibers.

4. Conclusions

4.1 PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite nanofibers were fabricated by electrospinning. Polycrystalline $LaMnO_3$ nanofibers were synthesized by calcining the relevant composite fibers at 600ºC.

4.2 TG-DTA analysis showed that the mass of the PVA/[$La(NO_3)_3$+$Mn(CH_3COO)_2$] composite fibers remained constant when the temperature was above 450ºC, and the total mass loss percentage was 94.6%.

4.3 XRD analysis revealed that the composite fibers were amorphous in structure. The crystal structure of $LaMnO_3$ nanofibres was orthorhombic system with space group Pbnm.

4.4 SEM images indicated that the surface of the prepared composite fibres was smooth, and the diameters of the composite nanofibres were about 150nm. The diameters of $LaMnO_3$ nanofibers were smaller than those of the composite nanofibers. The surface of the $LaMnO_3$ nanofibers became coarse with the increase of calcination temperatures. The diameter of $LaMnO_3$ nanofibers was ca. 100nm, and their lengths were greater than 100μm.

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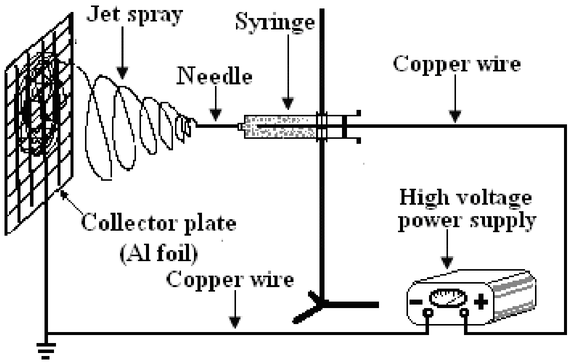

Figure 1. Schematic diagram of electrospinning setup

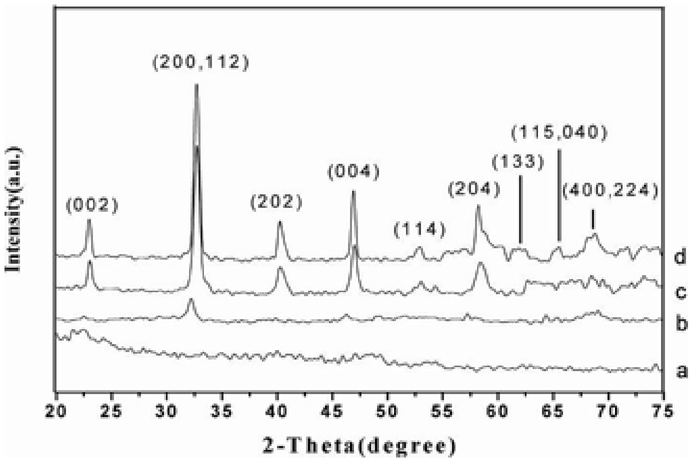

Figure 2. XRD patterns of samples

a. PVA/[La(NO_3)$_3$+Mn(CH_3COO)$_2$] composite fibers b. 300ºC c. 600ºC d. 900ºC

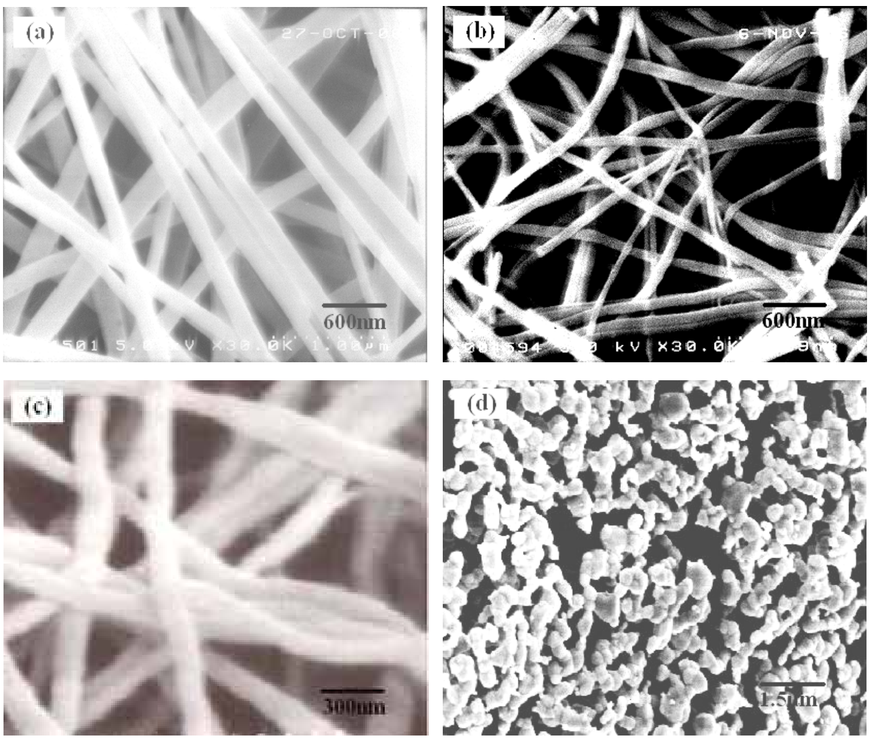

Figure 3. SEM images of the fibers obtained at different temperatures

(a) PVA/[La(NO_3)$_3$+Mn(CH_3COO)$_2$] composite fibers (b) 300ºC (c) 600ºC (d) 900ºC

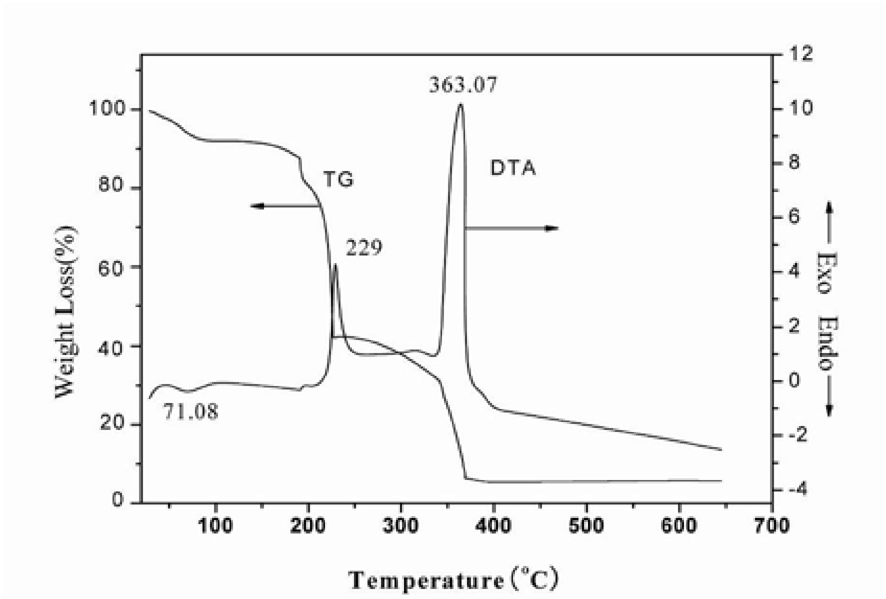

Figure 4. TG-DTA curves of PVA/[La(NO_3)$_3$+Mn(CH_3COO)$_2$] composite fibers

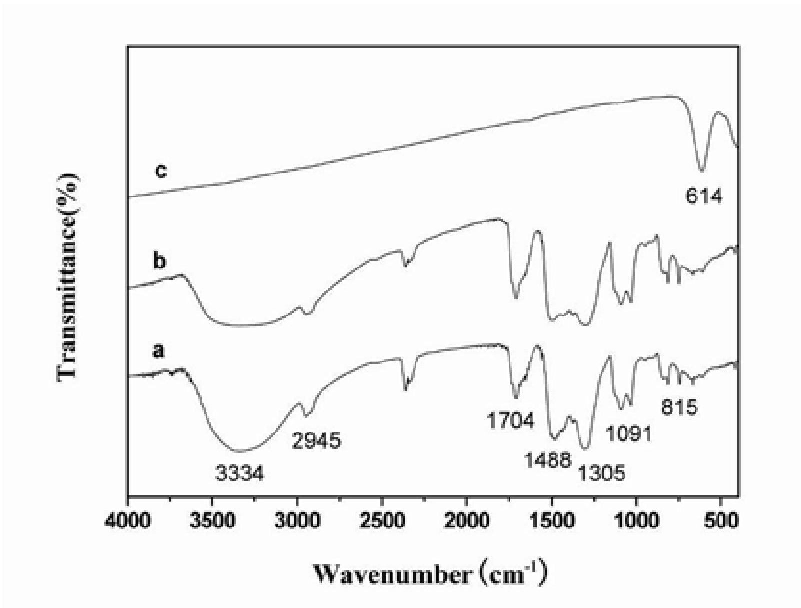

Figure 5. FTIR spectra of the samples

a. Pure PVA b. PVA/[La(NO_3)$_3$+Mn(CH_3COO)$_3$] composite fibers c. $LaMnO_3$ nanofibers

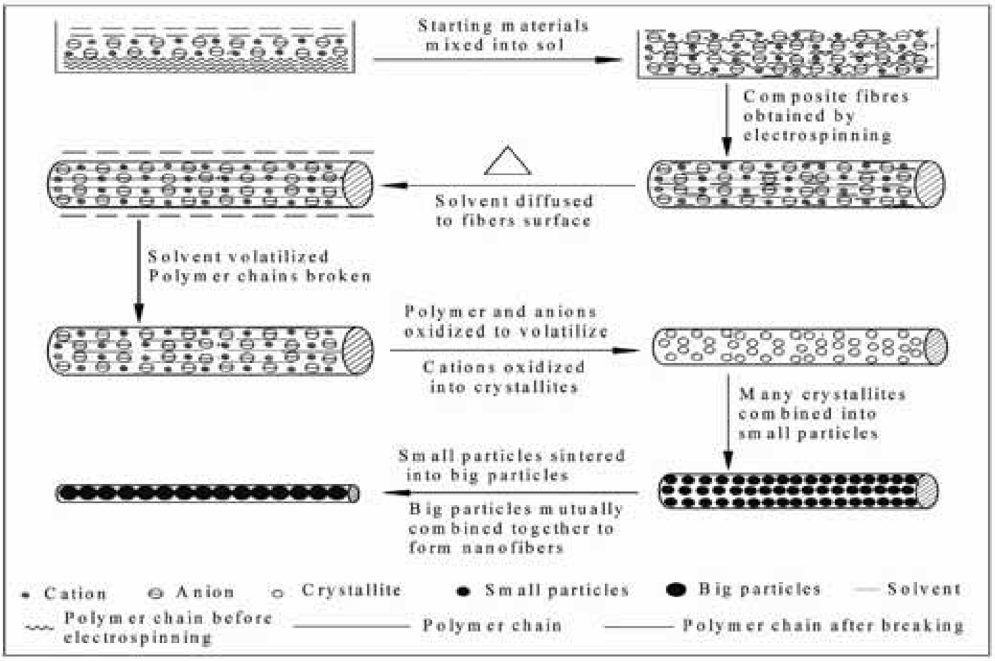

Figure 6. Illustrative diagram of possible formation mechanism of $LaMnO_3$ nanofibers