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Fabrication of $LaNiO_3$ Porous Hollow Nanofibers via an Electrospinning Technique

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Abstract

Polyvinyl Pyrrolidone(PVP)/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite nanofibers were fabricated via an electrospinning technique. SEM micrographs indicated that the surface of the prepared composite fibers was smooth, and the diameters of the nanofibers were in the range of 1-3μm. XRD analysis revealed that the composite nanofibers were amorphous in structure. $LaNiO_3$ nanofibers were fabricated by calcination of the PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers. The diameters of $LaNiO_3$ nanofibers were smaller than those of the relevant composite fibers. The surface of the $LaNiO_3$ nanofibers became coarse with the increase of calcination temperatures. $LaNiO_3$ porous hollow nanofibers formed by nanoparticles were acquired when firing temperature was 600-900ºC. SEM images indicated that the diameters of the synthesized $LaNiO_3$ nanofibers ranged from 500 to 800nm, and their lengths were greater than 100μm. XRD analysis revealed that $LaNiO_3$ nanofibers were trigonal in structure with space group $R\bar{3}m$. Possible formation mechanism for $LaNiO_3$ nanofibers was preliminarily proposed.

Keywords: $LaNiO_3$, Lanthanum, Nickel, Nanofibers, Electrospinning

1. Introduction

The science and technology of nanostructured materials is advancing at a rapid pace. Over the past decade, the preparation and functionalization of one-dimensional nanostructured materials has become one of the most highly energized research fields. 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. 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. Electrospinning technique is widely applied to prepare polymers nanofibers. Recently, some inorganic compounds nanofibers have been prepared by electrospinning technique using electrospun fibers of polymer/inorganic composite as the precursor. 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. $LaNiO_3$ has attracted much interest recently due to their specific electrical and catalytic properties. A few methods on the preparation of $LaNiO_3$ nanocrystalline materials were reported. However, to the best of our knowledge, there have been no reports on the preparation of $LaNiO_3$ nanofibers by electrospinning. In this paper, $LaNiO_3$ nanofibers were fabricated by calcination of the electrospun fibers of PVP/(lanthanum nitrate and nickel acetate) composite, and some new results were obtained.

2. Experimental section

2.1 Chemicals

Polyvinyl pyrrolidone(PVP)(Mr≈10000) and nickel acetate tetrahydrate[$Ni(CH_3COO)_2{\cdot}4H_2O$] were purchased from Tianjin Kermel Chemical Reagents Development Center. Lanthanum nitrate hexahydrate[$La(NO_3)_3{\cdot}6H_2O$] 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 PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite gel

PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite solution was prepared by dissolving 29.9700g of PVP powders, 5.6213g of $La(NO_3)_3 \cdot 6H_2O$ and 3.2306g of $Ni(CH_3COO)_2 \cdot 4H_2O$ in 26.33g of distilled water, and stirring for 10h, then remaining motionlessly for 2h. Thus, a viscous gel of PVP/[$La(NO_3)_3$+ $Ni(CH_3COO)_2$] composite containing 46%(wt%) PVP, 10%(wt%) metallic salts, 44%(wt%) H_2O, and the molar ratio 1:1 of La^{3+} to Ni^{2+} were obtained for electrospinning processing.

2.3 Fabrication of PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers and $LaNiO_3$ nanofibers

The setup used for electrospinning was indicated in Fig. 1. The above composite gel of PVP, $La(NO_3)_3$, $Ni(CH_3COO)_2$ and H_2O mixture was contained in a plastic syringe with a stainless steel needle on its top. A copper wire connected to a DC high-voltage generator was placed in the gel, and the gel was kept in the syringe by adjusting the angle between syringe and the fixing bar. A grounded aluminum foil served as counter electrode and collector plate. A voltage of 18 kV was applied to the composite gel and a sprayed dense web of fibers was collected on the aluminum foil. The collected fibers were PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers. The prepared composite fibers were dried initially at 70ºC for 12h under vacuum, and then calcined at a heating rate of 120ºC/h and remained for 10h at 300ºC, 600ºC and 900ºC, respectively. Thus, $LaNiO_3$ nanofibers were obtained when calcinations temperature is 600-900ºC.

2.4 Characterization methods

XRD analysis was performed with a Holland Philips Analytical PW1710 BASED X-ray diffractometer using Cu $K\alpha_1$ radiation, the working current and voltage were 30mA and 40kV, respectively. Scans were made from 10° to 80° at the speed of 3°/min, and step was 0.05°. The morphology and size of the fibers were observed with a S-4200 scanning electron microscope made by Japanese Hitachi company. 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 PVP/[($La(NO_3)_3$+$Ni(CH_3COO)_2$) composite fibers and samples obtained by calcining the composite fibers at different temperatures for 10h were characterized by XRD, as indicated in Fig. 2. The results showed that the PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers were amorphous in structure, only a broad peak was located around 20º, it was the typical peak of the amorphous polymer, indicating that the composite fibers were amorphous in structure. $LaNiO_3$ was not formed at 300ºC, and the sample was the mixture of metallic oxides. The polycrystalline $LaNiO_3$ 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 $LaNiO_3$ diffraction peaks were consistent with those of JCPDS standard card(34-1181), the crystal structure of the prepared $LaNiO_3$ was trigonal system in structure with space group is $R\bar{3}m$.

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 Fig. 3. As seen from Fig. 3, the morphology and size of the fibers varied strongly with the increase of calcination temperatures. The surface of the PVP/[$La(NO_3)_3$+ $Ni(CH_3COO)_2$] composite fibers was very smooth, and the diameter of the composite fibers was in the range of 1μm-3μm. The morphology and size of the fibers at 300ºC were almost the same as those of the composite fibers. The surface morphology of $LaNiO_3$ nanofibers became coarse with the increase of calcinations temperatures. $LaNiO_3$ porous hollow nanofibers formed by nanoparticles were acquired at 600ºC-900ºC. SEM analysis indicated that the diameters of the synthesized $LaNiO_3$ nanofibers were in the range of 500nm-800nm, and their lengths were greater than 100μm. The diameters of $LaNiO_3$ nanofibers were smaller than those of the PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers owing to the decomposition and evaporation of PVP, NO_3^- and CH_3COO^-.

3.3 FTIR spectra analysis

Pure PVP, PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers and $LaNiO_3$ nanofibers(obtained by calcination of the PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers at 900ºC for 10h) were analyzed by FTIR, as shown in Fig. 4. As seen from Fig.4, PVP(Fig.4a) and PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers(Fig.4b) had the identical spectra, but absorption peaks intensity of spectrum for PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers was lower than those of spectrum for pure PVP. This resulted from the lower content of PVP in the PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite

fibers. All absorption peaks were attributed to PVP at 3445cm^{-1}, 2955cm^{-1}, 1668cm^{-1}, 1424cm^{-1}, and 1289cm^{-1}, corresponding 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. It was seen from Fig. 4c that all peaks of PVP disappeared, and at low wave number range, new absorption peaks at 601, 563, 428cm^{-1} appeared. The new absorption peaks were ascribed to the vibration of metal-oxygen bonds, indicating that $LaNiO_3$ was formed. The results of FTIR analysis were in good agreement with XRD results.

3.4 Possible formation mechanism of $LaNiO_3$ porous hollow nanofibers

Possible formation mechanism of $LaNiO_3$ porous and hollow nanofibers was described as follows. $La(NO_3)_3{\cdot}6H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$ and PVP were mixed with distilled water to form gel with certain viscosity. PVP acted as template during the formation processing of $LaNiO_3$ nanofibers. La^{3+}, Ni^{2+}, NO_3^- and CH_3COO^- were mixed with or absorbed onto PVP molecules to fabricate PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers under electrospinning. During calcination treatment of the composite fibers, solvent water containing La^{3+}, Ni^{2+}, NO_3^- and CH_3COO^- ions in the composite fibers would remove to the surface of the PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers and eventually evaporated from the composite fibers. Thus, La^{3+}, Ni^{2+}, NO_3^- and CH_3COO^- ions would also remove to the surface of the composite fibers brought by removed water. With the increasing in calcination temperature, PVP, NO_3^- and CH_3COO^- would oxidize and volatilize rapidly, La^{3+} and Ni^{2+} were oxidized into $LaNiO_3$ crystallites, and many crystallites were combined to form small $LaNiO_3$ nanoparticles, and these nanoparticles were mutually connected to generate hollow-centered and porous $LaNiO_3$ nanofibers. It was found from experiments that the average molecular weight of PVP and PVP content in the starting mixed gel had important impact on the formation of $LaNiO_3$ porous hollow nanofibers. Further work is under way.

4. Conclusions

4.1 PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers were fabricated by electrospinning. Polycrystalline $LaNiO_3$ nanofibers were synthesized by calcining the relevant composite fibers at 600-900ºC.

4.2 XRD analysis revealed that the composite fibers were amorphous in structure. The crystal structure of $LaNiO_3$ nanofibres was trigonal system in structure with space group $R\bar{3}m$.

4.3 SEM micrographs indicated that the surface of the prepared composite fibres was smooth, and the diameters of the composite fibres were in the range of 1-3μm. The diameters of $LaNiO_3$ nanofibers were smaller than those of the composite fibers. The surface of the $LaNiO_3$ nanofibers became coarse with the increase of calcination temperatures. $LaNiO_3$ porous and hollow nanofibers formed by nanoparticles were acquired when calcining temperature was 600-900ºC. The diameters of $LaNiO_3$ nanofibers were in the range of 500nm-800nm, and their lengths were greater than 100μm.

References

Duan, X. F., Huang, Y., Agarwal, R., Lieber, C. M. (2003). Single-nanowire electrically driven lasers. *Nature*, 421, 241-245.

Hu, X. K., Qian, Y. T., Song, Z. T., et al. (2008). Comparative study on MoO_3 and H_xMoO_3 nanobelts: structure and electric transport. *J. Chem. Mater.,* 20(4), 1527-1533.

Huynh, W. U., Dittmer, J. J., Alivisatos, A. P. (2002). Hybrid nanorod-polymer solar cells. *Science*, 295, 2425-2427.

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354, 56-58.

Kar, S., Chaudhuri, S. (2006). Shape selective growth of CdS one-dimensional nano-structures by a thermal evaporation process. *J. Phys. Chem. B*, 110(10), 4542-4547.

Li, A. D., Ge, C. Z., Di, P. L., et al. (1997). Fabrication and Electrical properties of sol-gel derived $BaTiO_3$ films with metallic $LaNiO_3$ electrode. *Appl. Phys. Lett.*, 70(12), 1616-1618.

Li, D., Xia, Y. N. (2004). Direct Fabrication of Composite and Ceramic Hollow Nanofibers by Electrospinning. *Nano Lett.*, 4(5), 933-938.

Li, D., Xia, Y. N. (2004). Electrospinning of Nanofibers: Reinventing the Wheel? *Adv. Mater.*, 16(14), 1151-1170.

Liang, X. Y., Ma, Z., Bai, Z. C., et al. (2002). Properties and sonochemical preparation of nanostructured $LaNiO_3$. *Acta Physico-Chimica Sinica*, 18(6), 567-571.

Mohapatra, S. K., Misra, M., Mahajan, V. K., et al. (2008). Synthesis of Y-branched TiO_2 nanotubes. *Materials Letters*, 62, 1772-1774.

Morales, A. M., Lieber, C. M.(1998). A laser ablation method for the synthesis of crystalline semiconductor nanowires. *Science*, 279, 208-211.

Pan, Z. W., Dai, Z. R., Wang. E.L. (2001). Nanobelts of semiconducting oxides. *Science*, 291, 1947-1949.

Shao, C. L., Guan, H. Y., Liu, Y. C., et al. (2004). A novel method for making ZrO_2 nanofibres via an electrospinning technique. *J. Crystal Growth*, 267, 380-384.

Shi, W. S., Zheng, Y. F., Wang, N., et al. (2001). A general synthetic route to III-V compound semiconductor nanowires. *Adv. Mater.*, 13, 591-594.

Wang, Y. P., Zhu, J. W., Yang, X. J., et al. (2006). Preparation and characterization of $LaNiO_3$ nanocrystals. *Mater. Res. Bull.*, 41(8), 1565-1570.

Yang, Q. H., Fu, X. X. (2003). Analysis of photocatalytic oxidation activity of nano-$LaMO_3$(M=Cr Mn, Ni, Co) compounds. *J. Chin. Ceram. Soc.*, 31(3), 254-256.

Zhang, S. H., Dong, X. T., Xu, S. Z., et al. (2007). Preparation and characterization of TiO_2@SiO_2 submicron-scaled coaxial cables via a static electricity spinning technique. *Acta Chimica Sinica*, 65(23), 2675-2679.

Zhang, S. H., Dong, X. T., Xu, S. Z., et al. (2008). Preparation and characterization of TiO_2/SiO_2 composite hollow nanofibers via an electrospinning technique. *Acta Materiae Compositae Sinica*, 25(3), 138-143.

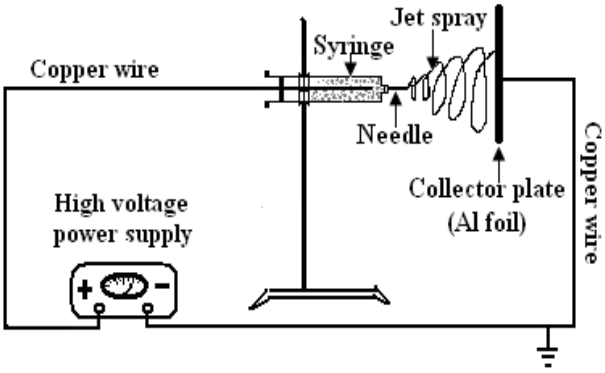

Figure 1. Schematic diagram of electrospinning setup

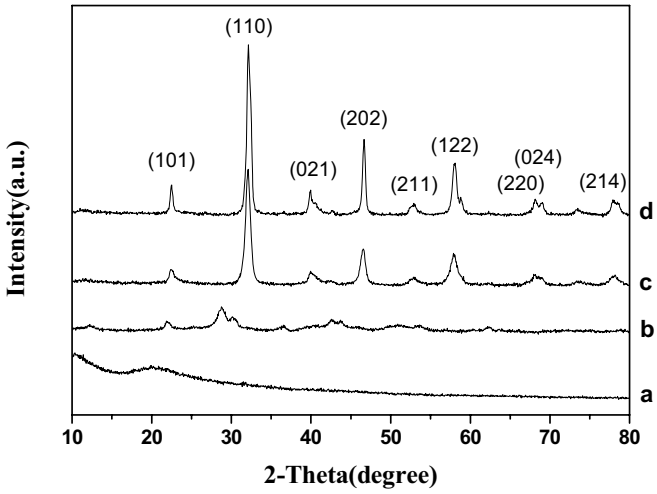

Figure 2. XRD patterns of samples

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

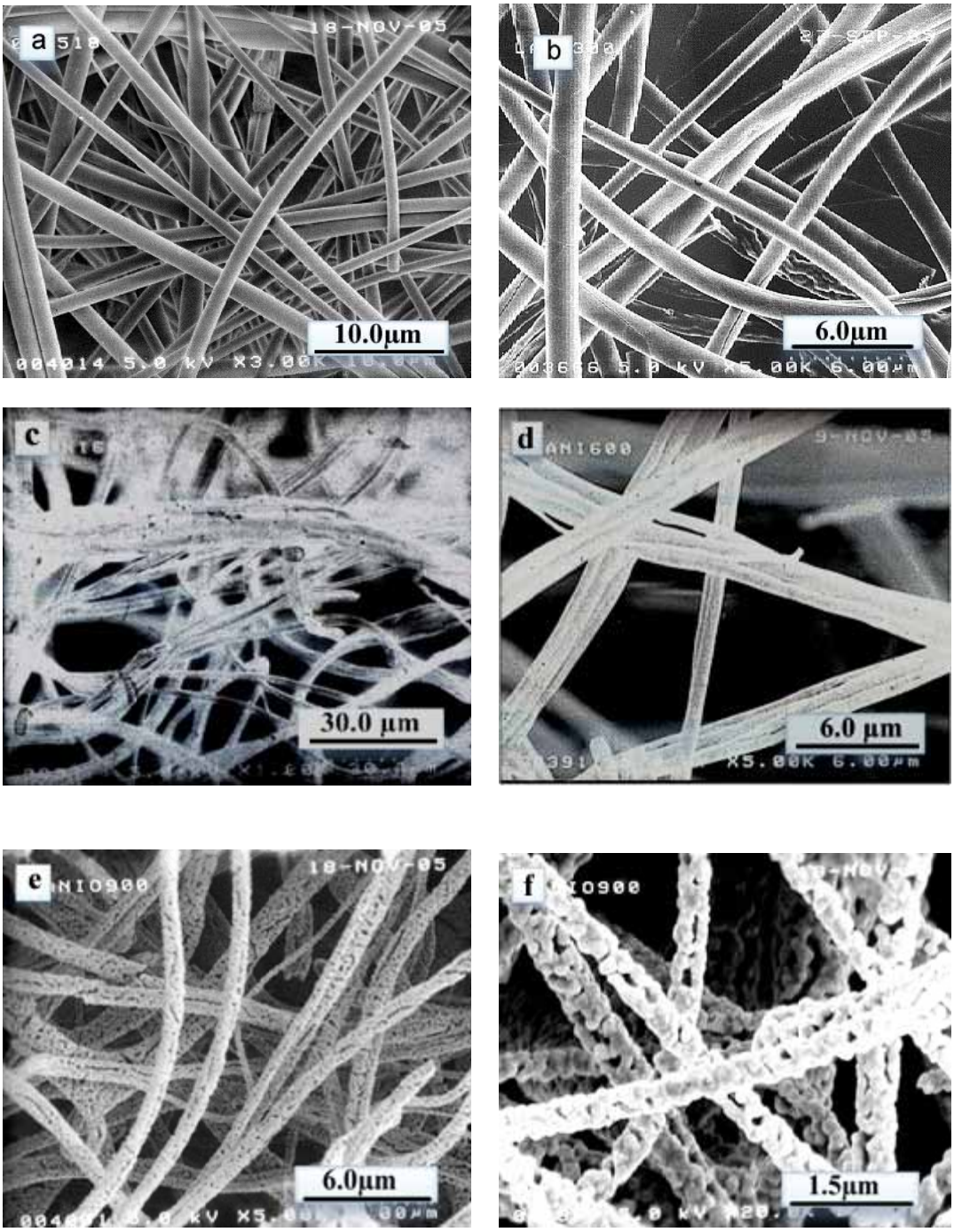

Figure 3. SEM micrographs of the fibers obtained at different temperatures

a. PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers b. 300ºC c. 600ºC(Low magnification)

d. 600ºC(High magnification) e. 900ºC(Low magnification) f. 900ºC(High magnification)

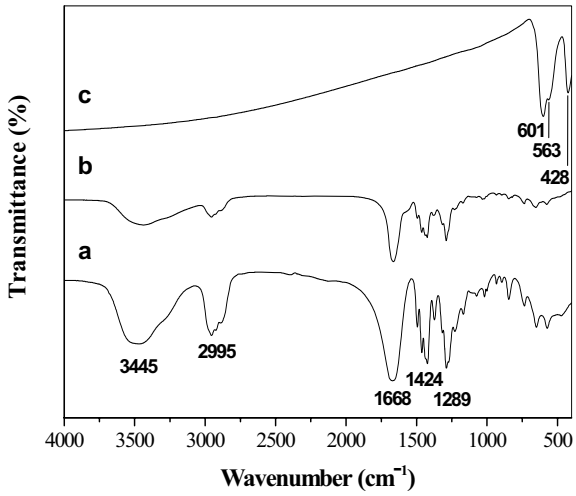

Figure 4. FTIR spectra of the samples

a: PVP b: PVP/[$La(NO_3)_3$+$Ni(CH_3COO)_2$] composite fibers c: $LaNiO_3$ nanofibers