

# Preparation of $\text{Mn}_2\text{O}_3$ and $\text{Mn}_3\text{O}_4$ nanofibers via an electrospinning technique

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## Abstract

Thin PVA/manganese acetate composite fibers were prepared by using sol–gel processing and electrospinning technique. After calcinations of the above precursor fibers,  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  nanofibers with a diameter of 50–200 nm could be successfully obtained. The fibers were characterized by TG–DTA, Scanning electron microscopy, FT-IR, WAXD, respectively. The results showed that the crystalline phase and morphology of nanofibers were largely influenced by the calcination temperature.

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## 1. Introduction

In recent years, nanostructural materials have been actively studied due to both scientific interests and potential applications [1,2]. Among them, much attention has been focused on the research field of one-dimensional nanostructural materials, such as nanorods, nanowires, or nanofibers, because of their potential applications in nanodevices [3–5]. In order to obtain these materials, various preparation methods have been developed including arc discharge [6], laser ablation [7], template [8,9], precursor thermal decomposition [10], and other methods [11–13]. Recently, we found a new method to produce inorganic nanofibers by using electrospun fibers of polymer/inorganic composite as the precursor [14–16]. This processing involved the following steps: (1) Preparation of a sol with suitable inorganic precursor and polymer content, and achieving the right rheology for electrospinning. (2) Spinning of the solution to obtain fibers of polymer/inorganic composite. (3) Calcinations of the composite fibers to obtain final oxide fibers. It is important, however, to control all of the above three stages in order to obtain high-quality fibers with the desired final properties.

Furthermore, manganese oxides such as  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_3\text{O}_4$ , are widely used as electrode materials [17,18], catalysts for the decomposition of nitrogenoxides, selective reduction of nitrobenzene and so on [19–21], and also used for preparing soft magnetic materials such as manganese zinc ferrite, which is useful for magnetic cores in transformers for power supplies [22,23]. A few methods on the preparation of nanocrystalline powder and films of these materials were reported [24–26]. However, to our knowledge, there have been no reports on the preparation of the nanofibers of manganese oxides. In this paper, we obtained the electrospun fibers of PVA/manganese acetate composite by using sol–gel processing and electrospinning technique. Thus we received the nanofibers of  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  by calcinations of the precursor fibers under different temperatures. In this paper, we report the details.

## 2. Experimental

### 2.1. Materials

PVA was Mn 80,000, supplied by Shanxi Chemical Co. Ltd. Analytical pure manganese acetate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) was obtained from Aldrich. Distilled water was used as solvent.

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## 2.2. Preparation of PVA/manganese acetate composite gels

Aqueous PVA solution (about 10 wt%) was first prepared by dissolving PVA powder in distilled water and heating at 80°C with stirring for 2 h, then cooling to room temperature and stirring for 12 h. Then, 20.0 g aqueous PVA solution of 10 wt% was dropped slowly into the solution of manganese acetate (1.0 g  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and 2.0 g  $\text{H}_2\text{O}$ ), and the reaction proceeded in a water bath at 50°C for 5 h. Thus, a viscous gel of PVA/manganese acetate composite was obtained.

## 2.3. Preparation of nanofibers

The viscous solution of PVA/manganese acetate composites was contained in a plastic capillary. A copper pin connected to a high-voltage generator was placed in the solution, and the solution was kept in the capillary by adjusting the angle between capillary and the fixing bar. A grounded iron drum, sprayed with an aluminum foil, served as counter electrode. A voltage of 20 kV was applied to the solution and a dense web of fibers was collected on the aluminum foil. The fibers thus formed were dried initially 12 h at 70°C under vacuum, and then calcinated at 300–1000°C at a rate of 240°C h<sup>-1</sup> and remained for 10 h at the required temperature.

## 2.4. Characterization

TG and DTA were performed on a NETZSCH STA 449C thermo-analyzer in an air atmosphere. For Scanning electron microscopy (SEM) investigation, a Hitach-600 was used. WAXD patterns of the samples were recorded by a Siemens D5005 diffractometer, scans were made from 4° to 70°(2θ) at the speed of 2° min<sup>-1</sup>, Ni-filtered  $\text{CuK}\alpha$  was used. IR spectra were obtained on Impact 410 FT-IR spectrometer with a resolution of 1 cm<sup>-1</sup>, KBr wafers were used, and the weight percentage of nanofibers in KBr was about 0.5%.

## 3. Results and discussion

### 3.1. TG–DTA

Fig. 1 showed the thermal behavior of the precursor fibers of PVA/manganese acetate composites, which showed that most of the organic belonged to PVA and  $\text{CH}_3\text{COO}$  group of manganese acetate and other volatiles ( $\text{H}_2\text{O}$ ,  $\text{CO}_x$ , etc.) were removed at temperature <600°C. As observed in the DTA curve, there were three endothermic peaks below 360°C (around 116°C, 263°C and 327°C) corresponded to the loss of absorbed

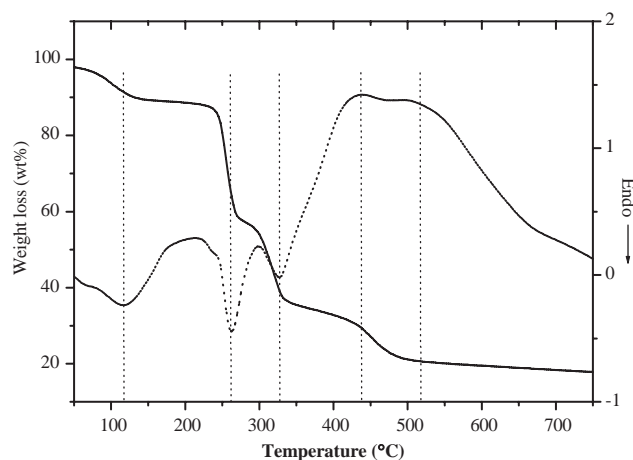


Fig. 1. TG–DTA curves of precursor fibers of PVA/manganese acetate composite.

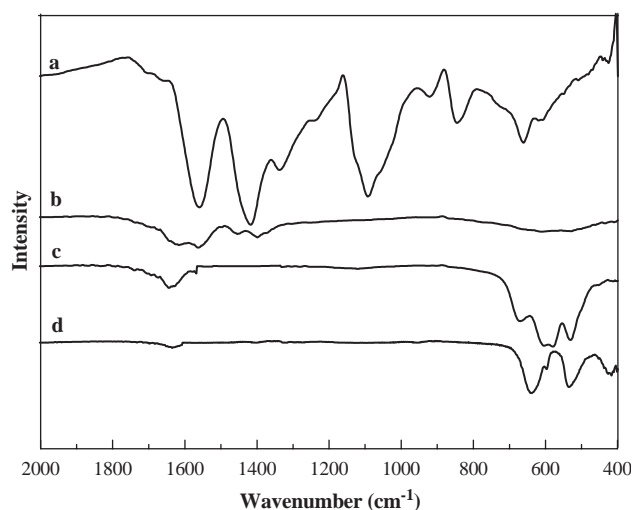


Fig. 2. FT-IR spectra of various fiber samples: (a) PVA/manganese acetate composite fibers; (b) calcinations at 300°C; (c) calcinations at 700°C; and (d) calcinations at 1000°C.

water, decomposition of manganese acetate, and the pyrolysis of PVA by a dehydration on the polymer side chain [27], which was in agreement with the weight loss of 65.5% in the TG curve. The broad exothermic peak at about 440°C and 517°C in the DTA curve was thought to be due to the decomposition of main chain of PVA [28]. There was only a weight loss of 16.3% from 360°C up to a temperature of 600°C, after which there was no change in weight loss, indicating the formation of pure inorganic oxide.

### 3.2. IR spectra

Fig. 2 displayed the FT-IR spectra for the PVA/manganese acetate composite fibers and for those calcined at different temperatures. As observed in Fig. 2(a) and (b), due to the decomposition of PVA and  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , the peaks at about 2938,

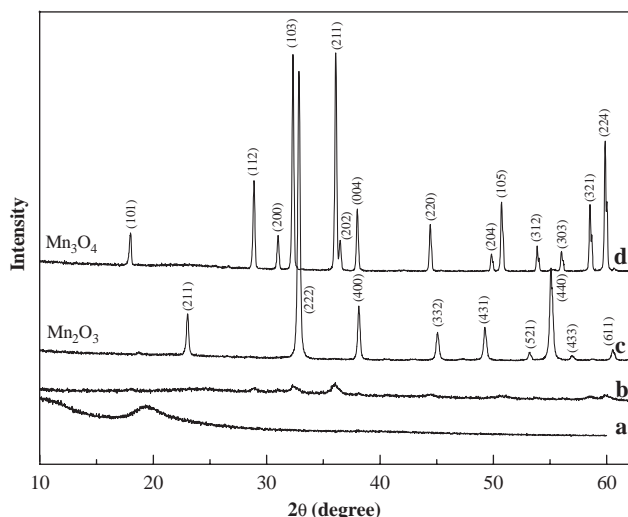


Fig. 3. WAXD results for various fiber samples: (a) PVA/manganese acetate composite fibers; (b) calcinations at 300°C; (c) calcinations at 700°C; and (d) calcinations at 1000°C.

1635, 1450, 1333, 1094, 920, 850, 674  $\text{cm}^{-1}$ , corresponding to  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C-C}}$ ,  $\nu_{\text{C-O}}$ ,  $\nu_{\text{O-H}}$ , respectively [29], weakened or disappeared after calcination at 300°C. All the peaks which belonged to organic groups of the polymer and manganese acetate disappeared at the calcination temperature of 700°C (Fig. 2(c)), and the new peaks around 530, 580, and 670  $\text{cm}^{-1}$  assigned to  $\nu_{\text{Mn-O}}$  of  $\text{Mn}_2\text{O}_3$  [30] appeared. When the calcination temperature reached 1000°C (Fig. 2(d)), the  $\text{Mn}_3\text{O}_4$  phase [31] appeared with the peaks of 417, 535, and 638  $\text{cm}^{-1}$ . Notably, there always existed one peak at 1636  $\text{cm}^{-1}$  in Fig. 2(a)–(d), which should be assigned to  $\text{H}_2\text{O}$  absorbed by the fibers samples or KBr. These results illustrated that the organic molecules could be removed completely from PVA/manganese acetate composite fibers when the calcination temperature was above 700°C, and the fibers obtained above this temperature were pure inorganic  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_3\text{O}_4$  species. The WAXD results in the next section also supported this suggestion.

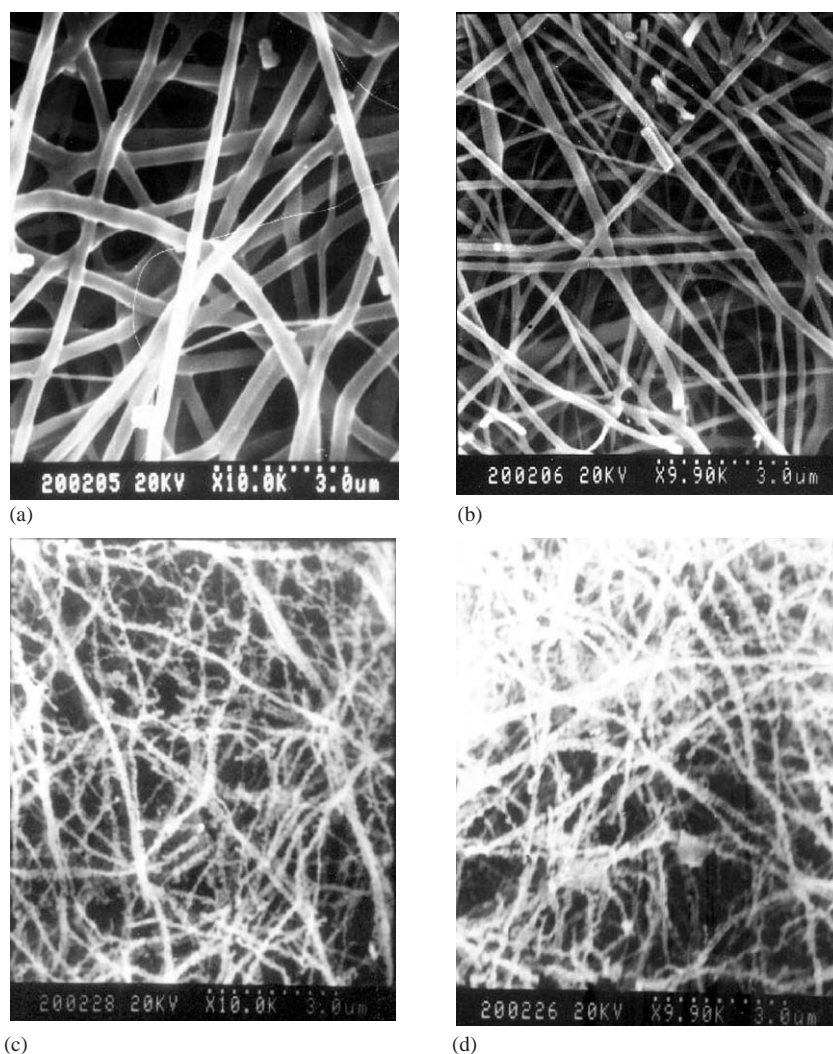


Fig. 4. Scanning electron microscopy photographs of various fiber samples: (a) PVA/manganese acetate composite fibers; (b) calcinations at 300°C; (c) calcinations at 700°C; and (d) calcinations at 1000°C.

### 3.3. Wide-angle X-ray diffraction

Fig. 3 gave the WAXD curve for various fiber samples. As showed in Fig. 3(a), there existed a broad peak around  $2\theta = 20^\circ$ , corresponding to the (101) plane of PVA semi-crystalline [32] in PVA/manganese acetate composite fibers. This result indicated that the crystallinity of PVA was largely influenced by the presence of manganese acetate in the PVA/manganese acetate composite fibers, saying that there might be some interaction between PVA and manganese acetate molecules. Notably, after the PVA/manganese acetate composites fibers were calcined at  $300^\circ\text{C}$  (Fig. 3(b)), crystalline peak of PVA disappeared, and some unknown crystalline phase appeared with the reflection peaks around  $2\theta = 28.8^\circ$ ,  $32.3^\circ$ ,  $36.1^\circ$ ,  $44.5^\circ$ ,  $51.8^\circ$ ,  $59.8^\circ$ , respectively. When increasing calcination temperature to  $700^\circ\text{C}$  (Fig. 3(c)),  $\text{Mn}_2\text{O}_3$  crystalline phase appeared with  $2\theta = 23.3^\circ$  (211),  $33.4^\circ$  (222),  $38.7^\circ$  (400),  $45.5^\circ$  (332),  $49.5^\circ$  (431),  $53.5^\circ$  (521),  $55.3^\circ$  (440),  $57.2^\circ$  (433),  $60.9^\circ$  (611), respectively, which were close to those reported in the JCPDS card (01-1061). When the calcination temperature reached to  $1000^\circ\text{C}$  (Fig. 3(d)), 14 reflection peaks appeared with  $2\theta = 18.0^\circ$ ,  $28.9^\circ$ ,  $31.0^\circ$ ,  $32.3^\circ$ ,  $36.1^\circ$ ,  $36.4^\circ$ ,  $37.9^\circ$ ,  $44.4^\circ$ ,  $49.8^\circ$ ,  $50.7^\circ$ ,  $53.8^\circ$ ,  $56.0^\circ$ ,  $58.5^\circ$ ,  $59.8^\circ$ , respectively, which could be indexed to the tetragonal phase of  $\text{Mn}_3\text{O}_4$  (JCPDS card 24-734). As compared to the IR results, the products obtained at  $700^\circ\text{C}$  were pure  $\text{Mn}_2\text{O}_3$  fibers, and which obtained at  $1000^\circ\text{C}$  were pure  $\text{Mn}_3\text{O}_4$  fibers.

### 3.4. Scanning electron microscopy (SEM)

The SEM photographs of PVA/manganese acetate composite fibers and the fibers calcined at  $300$ – $1000^\circ\text{C}$  were shown in Fig. 4. It can be seen that the surface of PVA/manganese acetate composite fibers (Fig. 4(a)) was smooth due to the amorphous nature of PVA and manganese acetate composites. Upon calcination at  $300^\circ\text{C}$  (Fig. 4(b)), the diameters of fibers became smaller due to the decomposition of PVA. However, after increasing calcination temperatures to  $700^\circ\text{C}$  and  $1000^\circ\text{C}$  (Fig. 4(c) and (d)), nanofibers of  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ , with alveolate surface and small diameters of  $50$ – $200$  nm, were prepared.

## 4. Conclusion

For the first time, nanofibers of  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  phase, with diameters of  $50$ – $200$  nm, were prepared by using the electrospun thin fibers of PVA/manganese acetate composites as precursor and through calcination treatments. This route might open a new door to making nanofibers of inorganic materials. By modifying the parameters of sol–gel or electrospinning processing, one

could also expect to be able to make nanofibers of inorganic materials with smaller diameter.

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## References

- [1] R.E. Cavicchi, R.H. Silsbe, *Phys. Rev. Lett.* 52 (16) (1984) 1435.
- [2] P. Ball, G. Li, *Nature* 355 (1992) 761.
- [3] J. Hu, M.Y. Ouyang, C.M. Lieber, *Nature* 399 (1999) 48.
- [4] D.S. Xu, G.L. Guo, L.L. Gui, Y.Q. Tang, E.J. Shi, E.X. Jin, *Appl. Phys. Lett.* 75 (1999) 481.
- [5] J.R. Heath, P.J. Kuekes, R.S. Snyder, Williams, *Science* 280 (1998) 717.
- [6] S. Iijima, *Nature* 354 (1991) 56.
- [7] A.M. Morales, C.M. Lieber, *Science* 279 (1998) 208.
- [8] C.R. Martin, *Science* 266 (1994) 1961.
- [9] W. Han, S. Fan, Q. Li, Y. Hu, *Science* 277 (1997) 1287.
- [10] Y.D. Wang, C.L. Ma, X.D. Sun, H.D. Li, *Inorg. Chem. Commun.* 5 (2002) 75.
- [11] W.S. Shi, Y.F. Zheng, N. Wang, C.S. Lee, S.T. Lee, *Adv. Mater.* 13 (2001) 591.
- [12] Z.W. Pan, Z.R. Dai, E.L. Wang, *Science* 291 (2001) 1947.
- [13] S.W. Liu, J. Yue, A. Gedanke, *Adv. Mater.* 13 (2001) 656.
- [14] C.L. Shao, H.Y. Kim, J. Gong, B. Ding, D.R. Lee, *Mater. Lett.* 57 (9–10) (2003) 1579.
- [15] C.L. Shao, H.Y. Kim, J. Gong, D.R. Lee, *Nanotechnology* 13 (2002) 635.
- [16] H.Q. Dai, J. Gong, H.Y. Kim, D.R. Lee, *Nanotechnology* 13 (2002) 674.
- [17] J.C.Z. Nardi, *J. Electrochem. Soc.* 132 (1985) 1787.
- [18] L. Sanchez, J. Farcy, J.P. Pereira-Ramos, L. Hernan, J. Morales, J.L. Tirado, *J. Mater. Chem.* 6 (1996) 37.
- [19] T. Yamashita, A. Vannice, *J. Catal.* 163 (1996) 158.
- [20] W.M. Wang, Y.N. Yang, Z. Jiayu, *Appl. Catal. A* 133 (1995) 81.
- [21] A. Maltha, H.F. Kist, B. Brunet, J. Ziolkowski, H. Onishi, Y. Iwasawa, V. Ponc, *J. Catal.* 149 (1995) 356.
- [22] V.V. Pankov, *Ceram. Int.* 14 (1998) 87.
- [23] Y. Fujioimura, *Jpn. Kokai Tokyo Koho JP 08,310,857*, May 1995.
- [24] W.X. Zhang, C. Wang, X.M. Zhang, Y. Xie, Y.T. Qian, *Solid State Ionics* 117 (1999) 331.
- [25] O.Yu. Gorbenko, I.E. Graboy, V.A. Amelichev, A.A. Bosak, A.R. Kaul, B. Guttler, V.L. Svetchnikov, H.W. Zandbergen, *Solid State Commun.* 124 (2002) 15.
- [26] L.W. Guo, D.L. Peng, H. Makino, K. Inaba, H.J. Ko, K. Sumiyama, T. Yao, *J Magn Magn Mater* 213 (2000) 321.
- [27] N. Koji, Y. Tomonori, I. Kenji, S. Fumio, *J. Appl. Polym. Sci.* 74 (1999) 133.
- [28] N. Chikako, S. Takeo, Y. Toshio, S. Masataka, *Fuel* 77 (1998) 321.
- [29] Y. Liu, W. Ren, L.Y. Zhang, X. Yao, *Thin Solid Films* 353 (1999) 124.
- [30] B. Gillot, M. El Guendouzi, M. Laarj, *Mater. Chem. Phys.* 70 (2001) 54.
- [31] F.A. Alsagheer, M.A. Hasan, L. Pasupulety, M.I. Zaki, *J. Mater. Sci. Lett.* 18 (1999) 209.
- [32] Y. Nishio, R.S. Manley, *Macromolecules* 21 (1988) 1270.