

## Preparation of Mn<sub>3</sub>O<sub>4</sub> Nanofibres via An Electrospinning Technique

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**Abstract:** Thin PVA/manganese acetate composite fibres were prepared by using sol-gel processing and electrospinning technique. After calcinations of the above precursor fibres, Mn<sub>3</sub>O<sub>4</sub> nanofibres with a diameter of 50-200 nm could be successfully obtained. The fibres were characterized by SEM, FT-IR, XRD. The results showed that the crystalline phase and morphology of nanofibres were largely influenced by the calcination temperature.

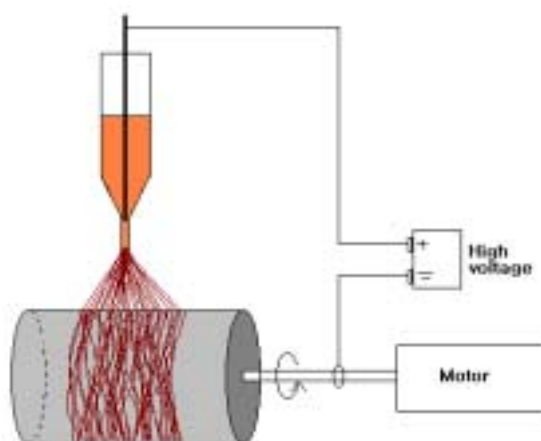
**Keywords:** PVA/manganese acetate composite, Mn<sub>3</sub>O<sub>4</sub> nanofibres, PVA.

Trimanganese oxide (Mn<sub>3</sub>O<sub>4</sub>), widely used as electrode materials<sup>1,2</sup>, is a catalyst for the decomposition of nitrogen oxides, selective reduction of nitrobenzene and so on<sup>3-5</sup>. It is also used for preparing the soft magnetic materials such as manganese zinc ferrite, which is useful for magnetic cores in transformers for power supplies<sup>6,7</sup>. A few methods of the preparation of nanocrystalline powder and films of these materials were reported<sup>8-10</sup>. However, to our knowledge, there have been no reports on the preparation of the nanofibres of manganese oxides. We have obtained the electrospun fibres of PVA/manganese acetate composite by using sol-gel processing and electrospinning technique. The nanofibres of Mn<sub>3</sub>O<sub>4</sub> were got by calcination of the precursor fibres at 1000 °C. In this paper, we report the details. 20.0 g aqueous PVA (M<sub>n</sub> 80,000) solution of 10 wt% was dropped slowly into the solution of manganese acetate (1.0 g Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and 1.5 g H<sub>2</sub>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. Then, it was contained in a plastic capillary. As shown in **Figure 1**, 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 aluminium foil, served as counter electrode. A voltage of 20 kV was applied to the solution and a dense web of fibres was collected on the aluminium foil.

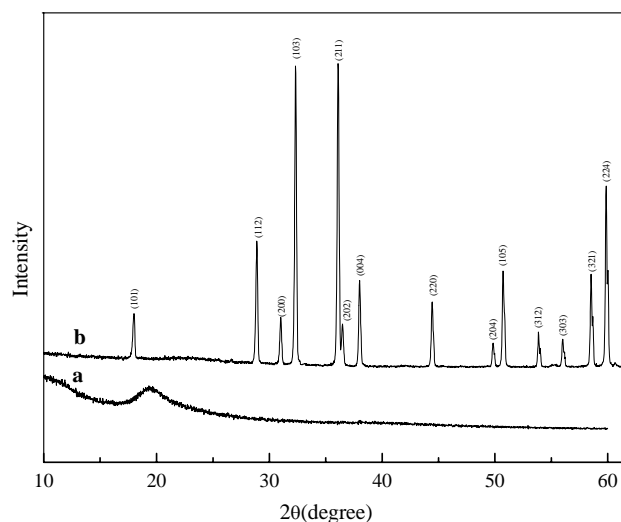
The fibres thus formed were dried initially for 12 h at 70 °C under vacuum, and then calcined at 1000 °C at a rate of 240 °C h<sup>-1</sup> and remained 10 h at the required temperature

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**Figure 1** Scheme of the electrospinning process.

IR results showed that all the organic groups could be removed completely from PVA/manganese acetate composite fibres after calcination at 1000 °C, and three new peaks around 417  $\text{cm}^{-1}$ , 535  $\text{cm}^{-1}$ , and 638  $\text{cm}^{-1}$  assigned to  $\nu_{\text{Mn-O}}$  of  $\text{Mn}_3\text{O}_4$  phase<sup>11</sup> appeared, indicating that the fibres obtained at this temperature were pure inorganic  $\text{Mn}_3\text{O}_4$  species. The XRD results in the next section also supported this suggestion.

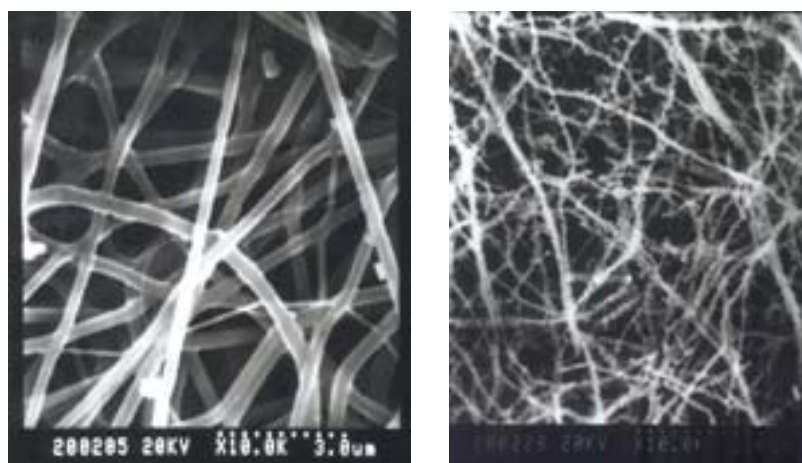
**Figure 2** XRD results for (a) PVA/manganese acetate composite fibres; (b) calcination at 1000 °C.

**Figure 2** gave the XRD curve for various fibres samples. As showed in **Figure 2** (a), there existed a broad peak around  $2\theta = 20^\circ$ , corresponding to the (101) plane of PVA semi-crystalline<sup>12</sup> in PVA/manganese acetate composite fibres. This result indicated that the crystallinity of PVA was largely influenced by the presence of manganese

acetate in the PVA/manganese acetate composite fibres, saying that there might be some interaction between PVA and manganese acetate molecules. Notably, after the PVA/manganese acetate composite fibres were calcined at 1000°C (**Figure 2(b)**), crystalline peak of PVA disappeared, fourteen 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 Mn<sub>3</sub>O<sub>4</sub> (JCPDS card 24-734). As compared with the IR results, the products obtained at 1000 °C were pure Mn<sub>3</sub>O<sub>4</sub> fibres.

It can be seen from **Figure 3**, that the nanofibres of Mn<sub>3</sub>O<sub>4</sub> with alveolate surface and small diameters (50-200 nm) were prepared after calcination of the PVA/manganese acetate composite fibres at 1000 °C.

**Figure 3** Scanning electron microscopy photographs.



(a) PVA/manganese acetate fibres

(b) calcination at 1000 °C

### Conclusion

The nanofibres of Mn<sub>3</sub>O<sub>4</sub> phase, with diameters of 50-200 nm, were prepared by using the electrospun thin fibres of PVA/manganese acetate composites as precursor and through calcination treatment. This technique might open a new door to prepare nanofibres of inorganic materials. By modifying the parameters of sol-gel or electrospinning processing, one could also expect to be able to make nanofibres of inorganic materials with smaller diameter.

### Acknowledgments

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