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Synthesis and optimization of barium manganate nanofibers by electrospinning

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Abstract

Barium manganate nanofibers were successfully synthesized for the first time after heat treatment of composite nanofibers of polyvinyl pyrrolidone (PVP), barium acetate and manganese acetate using electrospinning technique. Different PVP concentrations were used and the results show that PVP concentration had played important role in the formation, uniformity, homogeneity and particularly in the reduction of nanofibers diameter. Crystal structure, microstructure, elemental analysis and surface morphology were studied using X-ray diffraction analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. X-ray diffraction results show that at low temperature there is no crystallinity in the fibers sample and at ~400 °C formations of barium manganate crystalline phase starts and finally at 700 °C all the nanofibers became single phase. The first two high intensity peaks (1 0 1) and (1 1 0) give an average crystallite size of about 20 nm. The scanning electron micrographs show that the morphology of the fibers is smooth and uniform at low temperature and become slightly porous at intermediate temperature and finally at high temperature of 700 °C the fibers become highly porous, shrank and their average diameter reduced from ~400 nm to about 100 nm. These fibers are made of grains with sizes ranging from 15 to 30 nm. Energy dispersive X-ray spectroscopy and Fourier transform infra-red results are also in good agreement with XRD and SEM results.

Keywords: B. Nanocomposites; B. Fibers; B. Porosity; Electrospinning

1. Introduction

Ceramic materials have high corrosive resistance and high chemical erosion which makes them useful in many fields of technology [1]. In recent years, one-dimensional ceramic materials such as nanorods, nanotubes, nanowhiskers, and nanofibers, etc., have attracted great interest because of their superior electrical, magnetic, optical, thermal, gas sensing and catalytic properties that arise from the difference in surface morphology and size effect as compared to their bulk counterparts [2]. Among these nanostructures, nanofibers have many potential applications owing to their high porous structure, low density and high surface to volume ratio [3,4]. Electrospinning is one of the simplest, versatile, time and cost effective technique used for the synthesis of ultrafine, continuous and uniform diameter nanofibers of polymers, composites and ceramics [5,6]. An important feature of this technique is that the electrospun nanofibers mats are suggested for membrane-based applications in environmental science, catalysis, and energy technology [1]. Shao et al. [7] have reported for first time the formation of ceramic nanofibers by electrospinning technique in 2002. The technique has been used successfully by many research groups for the synthesis of varieties of ultrafine ceramic nanofibers, e.g., $BaTiO_3$, $LaMnO_3$, $LaFeO_3$, $ZnFe_2O_4$, $Pb(Zr_{0.5}Ti_{0.5})O_3$, etc., [5,8–11].

To the best of our knowledge synthesis of $BaMnO_3$ nanofibers has not been reported. In this paper, we report the successful synthesis of continuous, porous, and uniform diameter nanofibers of $BaMnO_3$ with the effect of temperature and PVP concentration using electrospinning technique.

2. Experimental

Barium acetate and manganese acetate were used as the starting materials for the synthesis of $BaMnO_3$ nanofibers. We

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dissolved 1.2772 g of $Ba(CH_3COO)_2$ and 1.2254 g of $Mn(CH_3COO)_2{\cdot}4H_2O$ in 6 ml acetic acid and stirred for 10–15 min. Polyvinyl pyrrolidone (PVP, $M_w \approx 1{,}300{,}000$) of 0.1, 0.5, 1.0, 1.5 and 2.0 g each was dissolved in 13.5 ml ethanol and stirred for 10–15 min. After stirring, both solutions were mixed and the final mixture was thoroughly stirred at room temperature for 16 h to get a homogeneous and viscous mixture. The mixture was then loaded in 20 ml plastic syringe of 25 gauge stainless steel needle. DC power supply of 10 kV was used with its positive terminal connected to the needle and negative terminal connected to the collector electrode covered by aluminum foil to collect nanofibers on it. The distance between aluminum foil and tip of the needle was fixed at 8 cm. A continuous jet of composite nanofibers was produced at 10 kV voltage and PVP concentration of 2.0 g. The composite nanofibers were annealed at 100, 400 and 700 °C for 3 h each to remove PVP and other volatile components completely. In all annealing processes, temperature of the furnace was varied at 2 °C per minute in air atmosphere.

X-ray diffraction (XRD) patterns were recorded using Rigaku Geiger flux instrument equipped with Cu-Kα ($\lambda = 0.1504$ nm) radiation. The size and morphology of $BaMnO_3$ fibers were characterized by JEOL JSM-5910 scanning electron microscope (SEM). Energy dispersive X-ray (EDX) spectrograph was recorded for the elemental analysis to investigate the phase purity of $BaMnO_3$ nanofibers using INCA 200 EDS, attached with SEM. Fourier transform infra-red (FT-IR) spectra of samples were recorded using Nicolet 6700 FT-IR spectrometer at a resolution of 6 cm^{-1}.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of barium manganate nanofibers after annealing at 100, 400 and 700 °C were shown in Fig. 1(a), (b) and (c), respectively. Fig. 1(d) shows the standard XRD pattern of single phase 2H-$BaMnO_3$, JCPDS card no. 26-0168. In Fig. 1(a) the XRD pattern is amorphous type which means that barium manganate phase is not formed at 100 °C. However, at 400 °C the high intensity peaks of $BaMnO_3$ crystalline phase appeared and became more prominent and clear at 700 °C without any impurity peak which is an indication of formation of single phase $BaMnO_3$. Lattice constants *a* and *c* have values, 5.6843 Å and 4.805 Å, respectively, as calculated from XRD pattern in Fig. 1(c). XRD pattern and the values of lattice parameters match well with the JCPDS card no. 26-0168 shown in Fig. 1(d). The average crystallite size of sample annealed at 400 °C for 3 h was ~17 nm, calculated using Scherrer formula. As the annealing temperature was increased to 700 °C the average crystallite size increased to ~20 nm.

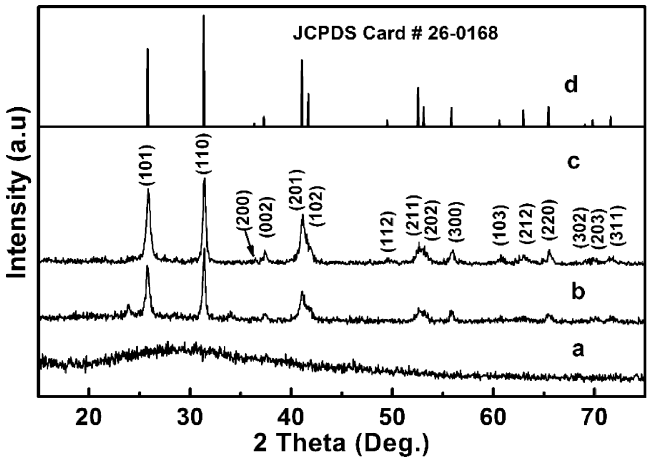

Fig. 1. XRD patterns of samples annealed at (a) 100 °C; (b) 400 °C; (c) 700 °C, and (d) JCPDS card no 26-0168, standard phase of $BaMnO_3$.

3.2. SEM and EDX analysis

SEM images in Fig. 2 shows the effect of PVP concentration on the synthesis, uniformity and homogeneity of $BaMnO_3$ fibers. In all experiments the amount of precursors and other experimental parameters were kept constant. Effect of PVP concentration on formation of nanofibers is summarized in Table 1. For PVP concentration of 0.1 g, no fibers were formed. For PVP concentration of 0.5 g, non-uniform fibers of diameters up to 5 μm were formed. When the concentration of PVP was increased the diameter of fibers was reduced and fibers became more uniform as compared with the fibers with low PVP concentration. Finally, at 2.0 g PVP concentration highly uniform, homogeneous and low diameter nanofibers were formed as shown in Fig. 2(d).

Fig. 3(a)–(c) shows the SEM images of $BaMnO_3$ nanofibers after annealing at 100, 400 and 700 °C, respectively. At 100 °C (Fig. 3(a)) the fibers have uniform diameter and smooth surface. At 400 °C (Fig. 3(b)) some portion of PVP was decomposed and the surface morphology of the nanofibers became coarse and as a result of reaction between barium acetate and manganese acetates, crystalline grains of $BaMnO_3$ were formed on the surfaces of these nanofibers. At 700 °C (Fig. 3(c)) the PVP was completely removed and highly porous

Table 1
Effect of PVP concentration of synthesis of uniform nanofibers.

Exp.	PVP (g)	Stirring time (h)	Results
1	0.10	16	No fibers were formed
2	0.50	16	Non-uniform fibers of diameter ranges from ~1 to 5 μm were formed
3	1.00	16	Uniform fibers of two different diameters (~0.7 μm and ~3 μm) were formed
4	1.50	16	Uniform fibers of diameter ranges from ~ 300 to ~ 400 nm were formed
5	2.00	16	Highly uniform fibers were formed of average diameter ~100 nm after annealing at 700 °C

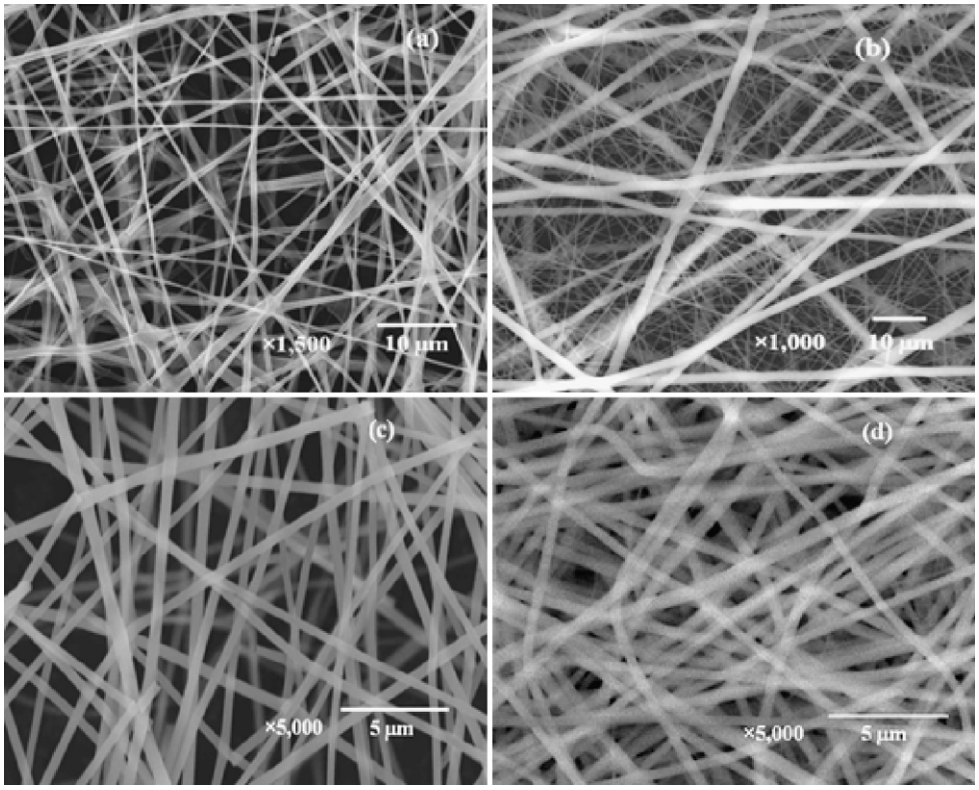

Fig. 2. SEM images showing the effect of PVP concentration on as synthesized nanofibers.

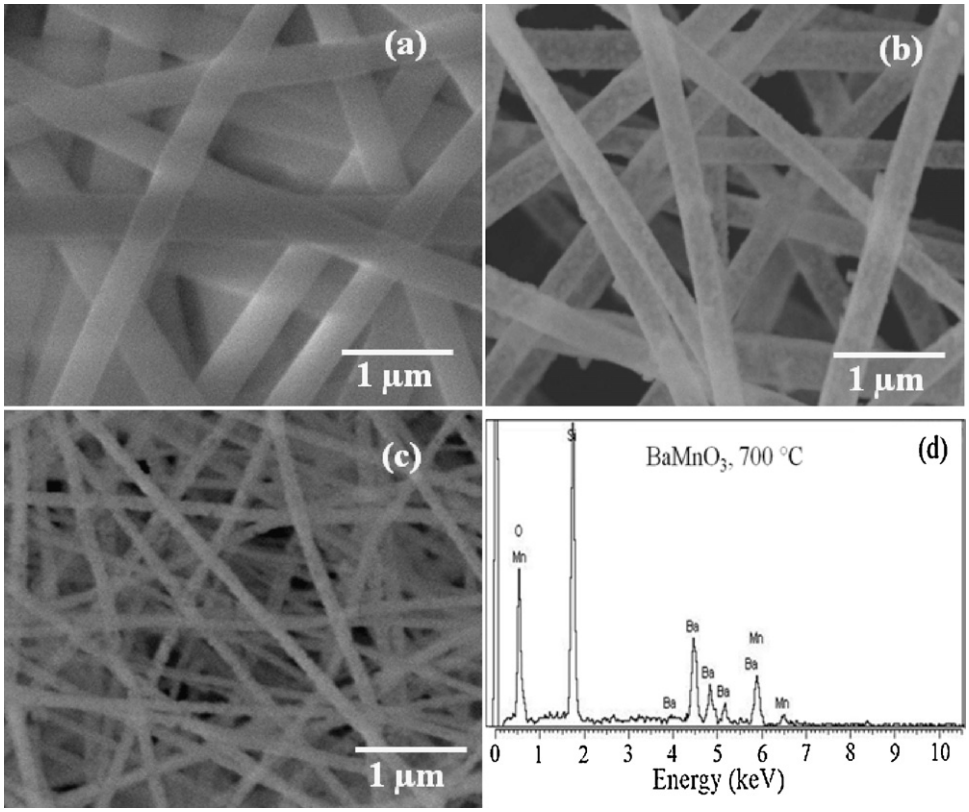

Fig. 3. SEM images of samples annealed at (a) 100 °C; (b) 400 °C; (c) 700 °C; (d) EDX of $BaMnO_3$ nanofibers annealed at 700 °C.

polycrystalline single phase $BaMnO_3$ nanofibers were formed. The diameter of $BaMnO_3$ nanofibers was reduced to ~100 nm. $BaMnO_3$ were composed of small grains with sizes in the range of 15–30 nm, in good agreement with the XRD results. Fig. 3(d) shows the EDX spectra of $BaMnO_3$ nanofibers annealed at 700 °C on Si wafer. In the EDX pattern, all peaks correspond to Ba, Mn and O, except Si peak, indicate formation of barium manganate. Si peak appeared because fibers were deposited on Si wafer for EDS analysis. EDS also support the formation of $BaMnO_3$ crystalline phase in the XRD pattern as shown in Fig. 1(c).

3.3. FT-IR analysis

Fig. 4(a)–(c) shows the FT-IR spectra of samples annealed at 100, 400 and 700 °C, respectively. Fig. 4(a) shows the FTIR spectrum of PVP/$Ba(CH_3COO)_2$/$Mn(CH_3COO)_2$ composite nanofibers. In this spectrum all peaks correspond to PVP since no formation of $BaMnO_3$ crystal structure has occurred at this temperature. It has been suggested that PVP act as a capping agent of different ionic species such as barium (II) and manganese (IV) via strong ionic bonds between amide group in PVP and metal ions [12]. These immobilized metallic ions in the polymeric chains of PVP form a well distributed solid solution of the metal oxide during annealing process. First two broaden peaks, in Fig. 4(a), at about 3431 cm^{-1} and 2944 cm^{-1} were due to the stretching vibration of hydroxyl group (υ_{O-H}) (OH or H_2O) and Carbon–Hydrogen (υ_{C-H}) bond, respectively. While the other three dominant peaks at about 1649, 1420 and 1269 cm^{-1} are due to the stretching vibration of $\upsilon_{C=O}$, C–H (υ_{C-H}) bond and C–N (υ_{C-N}) (or C–O (υ_{C-O})) bond, respectively [2]. As we annealed the sample at 400 °C, just above the decomposition point of PVP, $BaMnO_3$ lattice formation starts as indicated by the XRD result in Fig. 1(b). At 700 °C (Fig. 4(c)) all the PVP peaks vanished, indicating the full decomposition of PVP from the sample and four new peaks appeared at about 663, 600, 531 and 501 cm^{-1} that matches well with the data published in the literature [13] and corresponds to the stretching vibration of metal–oxide (M–O) bonds in $BaMnO_3$. FTIR results are in good agreement with the XRD and SEM results as shown in Figs. 1 and 3, respectively.

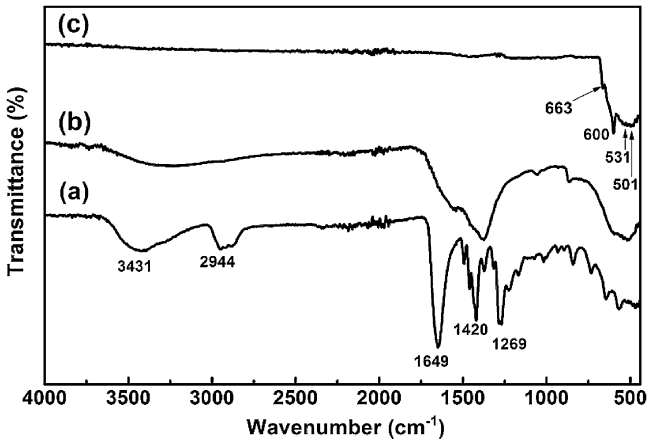

Fig. 4. FT-IR spectra of the samples annealed at (a) 100 °C; (b) 400 °C; and (c) 700 °C.

4. Conclusions

Barium manganate porous nanofibers of diameter about 100 nm were successfully synthesized from the heat treatment of PVP/$Ba(CH_3COO)_2$/$Mn(CH_3COO)_2$ composite nanofibers using electrospinning technique. Results show that PVP concentration had played an important role in the formation, uniformity, homogeneity and particularly in the reduction of diameter of nanofibers when other parameters were kept constant. The effect of temperature on crystal structure and morphology of nanofibers was also studied using XRD, SEM, EDS and FT-IR techniques. XRD and FT-IR results showed that at low temperature there is no crystallinity in the fibers sample and when the annealing temperature increased to ~400 °C hexagonal phase of $BaMnO_3$ began to appear and finally at 700 °C single phase $BaMnO_3$ was formed. SEM results showed that the fibers were smooth and uniform at low temperature and as the temperature of the fibers was increased to 400 °C the fibers became slightly porous and shrank in diameter. Finally, at 700 °C the fibers became highly porous and their diameter was reduced to about 100 nm. These porous nanofibers are expected to have applications in sensing and catalysis.

Acknowledgments

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