

Fabrication and Characterization of Hexagonal SrMnO₃ Nanofibers by Electrospinning

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Abstract. SrMnO₃/Polyvinylpyrrolidone (PVP) composite nanofibers have been prepared successfully by electrospinning from Cerous(II) nitrate and Manganese(II) acetate tetrahydrate, after the heat treatment at 800 °C for 3 h, the hexagonal SrMnO₃ nanofibers was obtained. The effect of PVP concentration was investigated. The size and morphology, phase information, thermal properties of nanofibers were characterized by SEM, EDX, XRD, TGA, FT-IR, respectively.

1 Introduction

Electrospinning technique is extensively employed to synthesize some ultrafine, continuous and uniform diameter nanofibers of polymers, composites and ceramics for its advantages such as briefness, versatility, time saving and low cost [1, 2]. The method of electrospinning has some advantage such as high porous structure, low density and high specific surface area in synthesis of nanofibers. [3, 4]. The formation of ceramic nanofibers by electrospinning was firstly reported by Shao et al. [5] in 2002. As far, many one-dimensional ceramic materials have been synthesized by electrospinning such as BaTiO₃, YMnO₄, CaSnO₃, MgWO₄, etc., [2-12].

The SrMnO₃ is extensively used as antiferromagnetic insulator with a crystal structure of G-type[13,14]. Due to the special skeletal structure which was consisted of a three dimensional network of MnO₆ octahedra, the SrMnO₃ sample has some properties such as oxygen nonstoichiometry, electronic properties, thermochromism, etc [15].

SrMnO₃ powders have been synthesized with many methods such as high temperature solid-state reaction, coprecipitation [16], sol-gel, etc [17-20]. High temperature solid-state reactions need a very high temperature. Furthermore, obtained products with this technique are agglomerated in a big grain size. Coprecipitation and sol-gel processes can prepare nanopowders in a lower temperature. Nanofibers can be prepared *via* electrospinning combined with sol-gel process. As far as I know, the synthesis of SrMnO₃ nanofibers has never been reported. Recently, the mixture of inorganic and organic salts dissolving in Polyvinylpyrrolidone (PVP) as starting materials, inorganic-polymeric fibers was

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synthesized by electrospinning, the inorganic-polymeric fibers would transform into nanofibers by subsequent calcinations at high temperature. Here we report the synthesis and characterization of SrMnO₃ nanofibers for its future applications.

2 Experimental

Cerous(II) nitrate and Manganese(II) acetate tetrahydrate were used as the raw materials for the synthesis of SrMnO₃ nanofibers. PVP (MW = 1,300,000) was used as viscosity-controlling agent. 4 mmol Cerous(II) nitrate and 4 mmol Manganese(II) acetate tetrahydrate were dissolved in 3 mL deionized water, 11 mL ethanol aqueous and a certain amount of PVP was added and the solution was stirred for 12 h at room temperature, then homogeneous hybrid sol was obtained. The above precursor sol was loaded in 20 ml plastic syringe of 25 gauges with stainless steel needle. The distance between the spinneret and collector was fixed at 10 cm and the high-voltage supply was maintained at 15 kV. The spinning rate was controlled at 1.5 mL/h. inorganic-polymeric fibers was collected on the collector. These fibers were calcinated at a rate of 2 °C/min and remained 3 h at 800 °C in air atmosphere. Thus, hexagonal SrMnO₃ nanofibers was obtained.

X-ray diffraction (XRD) analysis were performed on Rigaku Geiger flux instrument equipped with Cu-K α (λ = 0.1506 nm) radiation, Scans were made from 10 ° to 70 ° at the speed of 3 °/min, and the step was 0.05°. The size and morphology of SrMnO₃ fibers were observed with JEOL JSM-6390 scanning electron microscope (SEM). Energy dispersive X-ray (EDX) spectrograph was recorded for the elemental analysis to investigate the phase purity of SrMnO₃ nanofibers using INCA 200 EDS, attached with SEM. Thermogravimetric analysis was carried out on TA Q50 in nitrogen atmosphere, and the temperature-rising rate was 10 °C/min. Fourier transformation infrared (FT-IR) spectroscopy was record on Perkin Elmer spectrum 100.

3 Results and Discussion

SEM and EDX Analysis. The results of SEM images (Fig. 1) show that the concentration of PVP had a significant effect on the formation, uniformity and homogeneity of nanofibers. The size and morphology has marked difference under the four conditions. Under 6%, non-uniform fibers with beaded structure are formed, reached 8%, the beaded structure disappears and the fibers become uniform. This is because that surface tension and viscosity are correspondingly increased, with increasing of PVP concentration. Resistance airflow tensile force and static electricity needing to overcome is becoming higher in the electrospinning process. For PVP concentration of 10%, the fibers are more uniform than that of low PVP concentration. These results are consistent well with the published literature [10, 11].

Fig. 2 (a-b) shows the SEM images of the sample before and after calcinations. In Fig. 2(a), the randomly oriented hybrid fibers with smooth surface and average diameter of 300~400 nm can be observed. After annealed at 800 °C (Fig. 2(b)), the fibrous structure is retained on the whole except that a small amount of fibers are broken during the calcinations process. And the average diameter is reduced to 150~200 nm due to the evaporation and decomposition of PVP and volatile components. The fibers surface becomes rough because of the decomposition of PVP and the formation of crystallites. SrMnO₃ nuclei also grow to form larger nanoparticles. Fig. 2(c) shows the EDX of SrMnO₃ nanofibers annealed at 800 °C. In the EDX pattern, all peaks are corresponding to Sr, Mn and O, except Au peak, indicate formation of strontium manganate. Au peak appears because Au is sprayed onto the nanofibers before scanning in order to get high quality

morphology images. The result shows that the SrMnO₃ nanofibers hold good purity after removal of PVP.

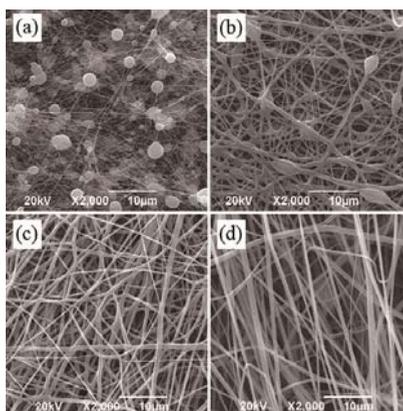


Fig. 1 SEM images of PVP/SrMnO₄ with different PVP concentration of (a) 4%, (b) 6%, (c) 8% and (d) 10%

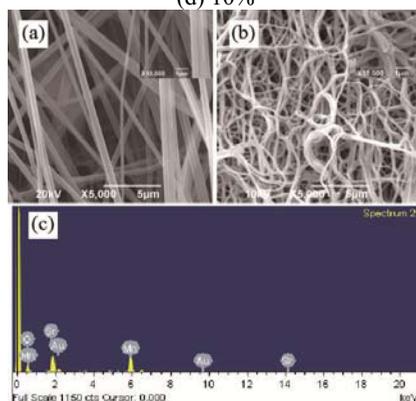


Fig. 2 SEM images of samples (a) before annealed, (b) annealed at 800 °C and (c) EDX of SrMnO₃ nanofibers annealed at 800 °C .

XRD Analysis. Fig. 3 shows the XRD pattern of SrMnO₃ nanofibers annealed at 800 °C. As indicated in Fig. 3, strong peaks are observed at $2\theta = 32.84^\circ$ associated with (110) planes. Other main diffraction peaks at $2\theta = 27.22, 35.19, 43.19, 48.90, 58.62, 60.17$ and 68.87° are assigned to the diffraction of (102), (103), (202), (203), (300), (213) and (220) crystal facets, respectively. All diffraction peaks show good consistency with JCPDS, Card No. 24-1213 of perovskite phase of SrMnO₃ [19]. A single hexagonal perovskite system was determined. No typical peak of polymer was observed in Fig. 3, indicated that PVP was decomposed and removed after the heat treatment at 800 °C.

Thermal Properties. The TGA curve of SrMnO₃/PVP composite nanofibers was shown in Fig. 4. The weight loss has 3 stages, The first weight loss is 11.4 % below 120 °C, which was caused by the loss of surface adsorbed and residual moisture [21-23]. The weight loss (~35.5 weight. %) between 250 and 400 °C is due to the evaporation of organic contents (PVP)[8, 11]. Similarly, the weight loss (~33.7 weight. %) during 400-700 °C is considered due to the decomposition of the organometallic precursor (manganese acetate) and strontium nitrate. The weight loss is completed below 700 °C and total weight loss is about 80.4%. Above 700 °C, no weight loss has been observed and the TGA curve becomes horizontal. The TGA curve result indicates that SrMnO₃ fibers sample can be fabricated at a temperature of 700 °C and above.

FT-IR Spectrum. Fig. 5(a)–(c) shows the FT-IR spectra of PVP, SrMnO₃/PVP

composite fibers and SrMnO₃ nanofibers, respectively. For PVP sample, the broad band around 3600–3200 cm⁻¹ corresponds to hydrogen bonded O-H stretching vibration. The triplet peaks present at 2954 cm⁻¹ corresponds to the asymmetric and symmetric C-H stretching vibrations of methyl groups (from acetate) [24]. While the other three dominant peaks at about 1654, 1442 and 1292 cm⁻¹ are due to the stretching vibration of C=O, C-H and C-N bond, respectively [25]. As shown in Fig. 5(b), the C=O stretching vibration characteristic peak red-shifts to 1652 cm⁻¹ in the composite fibers. The C-H stretching vibration peaks blue-shift to 2956 and 1444 cm⁻¹ respectively. The bands at 1425 cm⁻¹ in the PVP fibers disappears in the composite fibers and the stretching of C-N at 1292 cm⁻¹ is weakened. In Fig. 5(c), all the PVP peaks vanish, indicating that the PVP was full decomposed. Three new peaks appear at 765, 663, and 542 cm⁻¹. These new peaks are ascribed to the stretching vibration of metal-oxide (M-O) bonds in SrMnO₃, which matches well with the published literature [19]. FT-IR results are in good agreement with the SEM, XRD and TGA results.

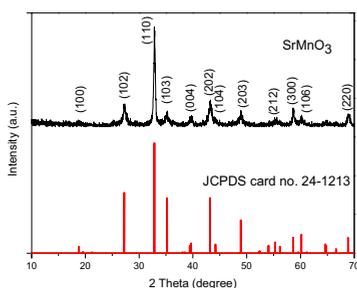


Fig.3 XRD patterns of samples annealed at 800 °C and (d) JCPDS card no 24-1213, standard phase of SrMnO₃.

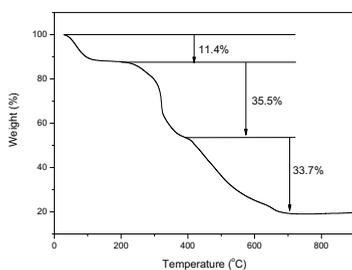


Fig. 4 TGA curve of SrMnO₃/PVP nanofibers.

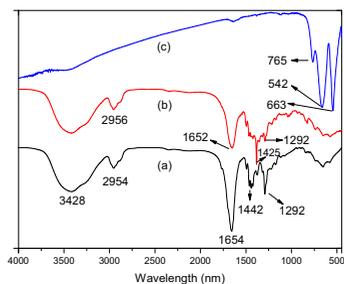


Fig.5 FT-IR spectrum of samples (a) PVP fibers, (b) SrMnO₃/PVP nanofibers, and (c) SrMnO₃ nanofibers.

4 Conclusions

SrMnO₃/PVP composite nanofibers with a diameter of 300~400 nm was successfully fabricated by electrospinning technique and pure hexagonal SrMnO₃ fibers of diameter of 150~200 nm was synthesized by the heat treatment of SrMnO₃/PVP composite nanofibers at 800 °C. PVP concentration plays an important role in the formation, uniformity and homogeneity of nanofibers, when the concentration reached 8%, the fiber became uniform. The SrMnO₃ fibers have hexagonal perovskite system structure which was determined by XRD. The EDX, XRD, TGA and FT-IR results indicated that PVP was decomposed and removed after the heat treatment at 800 °C.

References

1. J. Yuh, L. Perez, W.M. Sigmund, J.C. Nino: 'Sol-gel based synthesis of complex oxide nanofibers'. *J Sol-Gel Sci Technol*, 2007, 42, pp.323-329
2. J. Wang, X. Zheng, X. Dong, Z. Qu, G. Liu: 'Synthesis of LaMnO₃ Nanofibers via Electrospinning'. *Applied Physics Research*, 2009, 1, (2), pp. 30-36
3. X. He, R. Arsat, A.Z. Sadek, W. Wlodarski, K. Kalantar-zadeh, J. Li: 'Electrospun PVP fibers and gas sensing properties of PVP/36° YX LiTaO₃ SAW device'. *Sensors and Actuators B: Chemical.*, 2010,145,(2),pp. 674-679
4. X. Zhou, Y. Zhao, X. Cao, Y. Xue, D. Xu, L. Jiang, W. Su : 'Fabrication of polycrystalline lanthanum manganite (LaMnO₃) nanofibers by electrospinning'. *Materials Letters*, 2008, 62, (3), pp. 470-472
5. C. Shao, H. Kim, J. Gong, D. Lee: 'A novel method for preparing ultra-fine alumina-borate oxide fibres via an electrospinning technique'. *Nanotechnology*, 2002, 13, pp. 635-637
6. N. Zhang, Z.C. Zhang, J.G. Zhou: 'Synthesis of CaSnO₃ nanofibers by electrospinning combined with sol-gel'. *J Sol-Gel Sci Technol*. 2011, 58, (2), pp. 355-359
7. B. Sahoo, P.K. Panda: 'Preparation and characterization of barium titanate nanofibers by electrospinning'. *Ceramics International*, 2012, 38, (6), pp. 5189-5193
8. Z. Imran, S.S. Batool, M.Q. Israr, J.R. Sadaf, M. Usman, H. Jamil, M.Y. Javed, M.A. Rafiq, M.M. Hasan, O. Nur, M. Willander: 'Fabrication of cadmium titanate nanofibers via electrospinning technique'. *Ceramics International*, 2012, 38,(4), pp. 3361-3365
9. Y.X. Ye, H.Q. Fan, J. Li: 'Fabrication and texture evolution of hexagonal YMnO₃ nanofibers by electrospinning'. *Materials Letters*, 2010, 64, (3), pp. 419-421
10. G. George, S. Anandhan: 'Structural characterization of nano-crystalline Co₃O₄ ultra-fine fibers obtained by sol-gel electrospinning'. *J Sol-Gel Sci Technol.*, 2013, 67, (2), pp. 256-266
11. J. Chandradass, Hern Kim, Francis W. Y. Momade: 'Synthesis of ultrafine MgFe₂O₄ nanofibers via electrospinning using sol-gel precursor'. *J Sol-Gel Sci Technol.*, 2013, 65, (2), pp. 189-194
12. S. Wannapopa, T. Thongtem, S. Thongtema: 'Photoemission and energy gap of MgWO₄ particles connecting as nanofibers synthesized by electrospinning-calcination combinations'. *Applied Surface Science*, 2012, 258, (11), pp. 4971-4976
13. A. Sacchetti, M. Baldini, F. Crispoldi: 'Temperature dependence of the optical phonons in SrMnO₃ manganite: Evidence of a low-temperature structural transition in the hexagonal compound'. *Phys. Rev. B*, 2005, 72, (17), pp. 172407-172411

14. K. J. Lee and E. Iguchi: 'Electronic Properties of SrMnO_{3-x}'. *J. Solid State Chem.* 1995, 114, (1), pp. 242-248
15. J. Heiras, E. Pichardo, A. Mahmood: 'Thermochromism in (Ba,Sr)-Mn oxides'. *J. Phys. Chem. Solid*, 2002, 63, (4), pp. 591-595
16. A. M. Duprat, P. Alphonse, C. Sarda, A. Rousset, B. Gillot: 'Nonstoichiometry-activity relationship in perovskite-like manganites'. *Mater. Chem. Phys.*, 1994, 37, (1), pp. 76-81
17. H. Taguch, D. Matsuda, M. Nagao: 'Synthesis of Perovskite-Type (La_{1-x}Sr_x)MnO₃ (0<X<0.3) at Low Temperature'. *J. Am. Ceram. Soc.*, 1992, 75, (1), pp. 201-202
18. Y. Shimizu, T. Murata: 'Sol-Gel Synthesis of Perovskite-Type Lanthanum Manganite Thin Films and Fine Powders Using Metal Acetylacetonate and Poly(vinyl alcohol)'. *J. Am. Ceram. Soc.*, 1997, 80, (10), pp. 2702-2074
19. M. Khazaei, A. Malekzadeh, F. Amini, Y. Mortazavi, A. Khodadadi: 'Effect of citric acid concentration as emulsifier on perovskite phase formation of nano-sized SrMnO₃ and SrCoO₃ samples'. *Cryst. Res. Technol.*, 2010, 45, (10), pp. 1064-1068
20. J.Y. Junhan, L. Perez, W.M. Sigmund, C.N. Juan: 'Sol-gel based synthesis of complex oxide nanofibers'. *J Sol-Gel Sci Technol.*, 2007, 42, (3), pp. 323-329
21. S. Maensiri, M. Sangmanee, A. Wiengmoon: 'Magnesium Ferrite (MgFe₂O₄) Nanostructures Fabricated by Electrospinning'. *Nano. Res. Lett.*, 2009, 4, (3), pp. 221-228
22. U. Jianfeng, U. Donghui, I. Yujun: 'Fabrication and photocatalytic activity of ZnO-TiO₂ Nanofibers'. *Adv. Mater.*, 2011, 295-297, pp. 1978-1981
23. J.S. Lee, Y.I. Lee, H. Song, D.H. Jang, Y.H. Choa: 'Dielectric relaxation in bismuth layer-structured BaBi₄Ti₄O₁₅ ferroelectric ceramics'. *Curr. Appl. Phys.*, 2011, 11, (2), pp. 210-214
24. H.Y. Tian, W.G. Luo, X.H. Pu, P.S. Qiu, X.Y. He, A.L. Ding: 'Synthesis and analyses of thermal decomposition and microstructure of Sr-doped barium titanate alkoxide derived precipitates and thin films'. *Thermochim. Acta.*, 2000, 360, (1), pp. 57-62
25. C. Qizheng, D. Xiangting, W. Jinxian, L.I. Mei: 'Direct fabrication of cerium oxide hollow nanofibers by electrospinning'. *J. Rare Earths*, 2008, 26, (5), pp. 664-669