Magnetic property of Mn_3O_4 nanowires prepared by electrospinning

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Mn_3O_4 nanowires were prepared by electrospinning followed by H_2 reduction. XRD patterns showed the samples were tetragonal phase with the average grain size of about 24.7 nm. The diameter of Mn_3O_4 nanowires was about 100 nm and the nanowires were porous ones. The magnetic properties of the samples presented obvious the feature of ferromagnetism at 5 K and a small coercivity. The porous and magnetic features mike that the nanowires can be used as the filtration for the separation of the magnetic-active particles.

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1. Introduction

Manganese has many oxidation states and can form many different oxides, such as MnO, Mn_3O_4, Mn_2O_3, Mn_5O_8 and MnO_2, so it has tremendous potential in wide range of technical applications – catalysis, electrode materials, molecular adsorptions, gas-sensing devices, magnetic storage media, solar energy conversion, etc. [1-6]. Among them, the hausmannite phase, Mn_3O_4 is one of the most stable oxides of manganese and posses the ferromagnetism and electrochromic properties [7-9]. In particular, materials fabricated on a nanoscale can exhibit better phonic, optical, magnetic, thermal, and electrical properties than bulk materials. A number of methods were reported to fabricate nanostructured Mn_3O_4, for example, thermal decomposition, mild solution method, hydrothermal process, γ-ray irradiation, and so on [9-13]. Electrospinning is the most attractive because of its convenience, simplicity, and low cost in very recent years, which can also spin a variety of one-dimension materials at micro- and even nanoscale [14-16].

In this paper, Mn_3O_4 nanowires are prepared by electrospinning method. The structure and magnetic properties have been characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and superconducting quantum interference device (SQUID).

2. Experimental

In the first step, 0.5 g Manganese acetate ($C_4H_6MnO_4{\cdot}4H_2O$) (analytical reagent, > 98%) was dissolved into 2 ml Deionized water by magnetic stirring 5 minutes. Second, 0.17 g Polyvinyl Alcohol (PVA) was added to this solution, followed by magnetic stirring for about 1 h. The mixed solution was loaded into a syringe equipped with a stainless needle with the diameter of 0.6 mm. A stainless steel grid plate was used to collect the electrospun nanowires. The distance between the tip of the needle and the collector is 20 cm. Upon applying a high voltage of 20 kV to the needle, a fluid jet ejected. The solvent evaporated and the charged nanowires were deposited on the collector. After dried by leaving in air for ~24 h, the collected nanowires were annealed at 450 °C for 4 h in air. Finally, the nanowires were annealed in H_2 atmosphere at the pressure of 160 Pa and at the temperature of 600 °C for 6 h.

The structure of the samples was characterized by X-ray diffraction (XRD) (Philips, Regiku D/max-IIIC) using Cu Kα ray (wavelength 1.5404 nm) at the grazing incidence angle of 1º. Field emission scanning electron microscopy (FESEM) (Hitachi, S-4800) was utilized to observe the morphology of the samples. Variable-temperature magnetization measurements under a magnetic field of 200 Oe and under both zero-field-cooled (ZFC) and field-cooled (FC) conditions were performed on a Quantum Design SQUID MPMS XL-7 (SQUID) from 300 K down to 5 K. The dc hysteresis loops were collected on the same SQUID in magnetic fields from 50000 to -50000 Oe at 5 K.

3. Results and discussion

Fig. 1 shows XRD patterns of the samples before annealed in H_2 atmosphere. All observed peaks agree very well with JCPDS file 76-0150 and reveals that the sample

presents a cubic phase Mn_2O_3. The average grain size of Mn_2O_3 nanowires estimated by Scherrer formula is about 18.8 nm. After high temperature H_2 reduction, the sample presents a tetragonal phase Mn_3O_4 (hausmannite structure) with the lattice constants of a = 5.760 Å and c = 9.444 Å, and seems also to contain a little amorphous phase, as shown in Fig. 2. The result is consistent with other results [1, 9] and the values of the bulk materials (JCPDS card #24-0734). The average size of the grains is about 24.7 nm. There is obviously no metallic phase in the samples after a long time reduction, so it can be inferred that Mn_3O_4 is very stable and can be applied in harsh environment. In addition, although the O content in the sample reduces, the grain instead grows. It implied that the re-crystalline happens during the H_2 reduction.

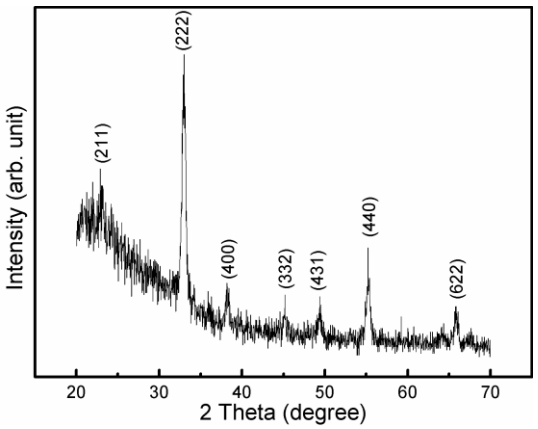

Fig. 1. XRD patterns of Mn_2O_3 nanowires.

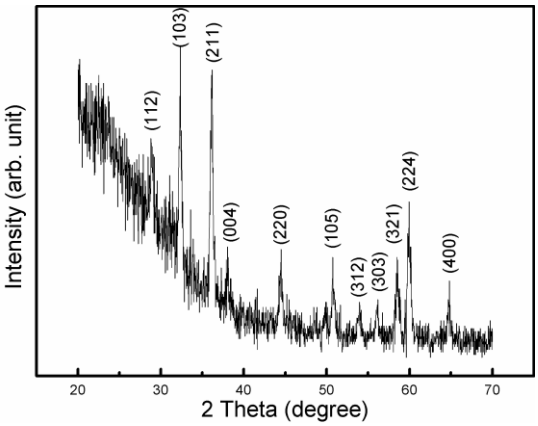

Fig. 2. XRD patterns of Mn_3O_4 nanowires.

FESEM imagine of Mn_3O_4 nanowires is shown in Fig. 3. It can be seen that Mn_3O_4 nanowires are not very compact and porous, and the surface is not smooth. The nanowires are straight and about 100 nm in diameter. This morphology may be related to the evaporation of the solvents, the decomposing and removing of the organic phase via calcinations, the oxygen escape and the re-crystallization in the high temperature H_2 reduction. The porous structure can increase the surface area of Mn_3O_4 nanowires. Increasing of surface area is favor to many applications, such as absorption, filtration, catalysis, fuel cells, and solar cells [17].

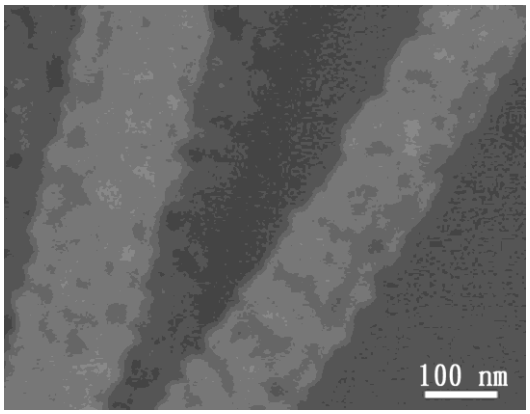

Fig. 3. FESEM imagine of Mn_3O_4 nanowires.

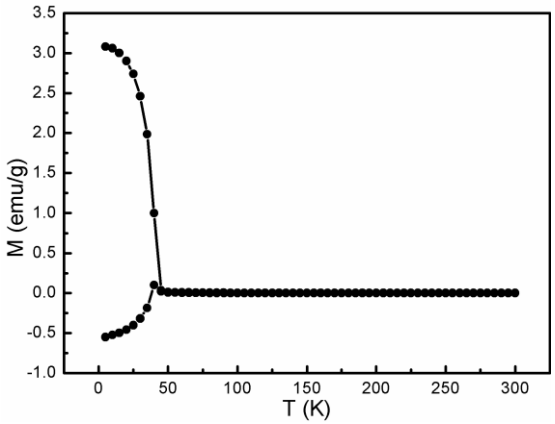

Fig. 4. ZFC-FC curve of Mn_3O_4 nanowires at 200 Oe.

M-T curves of Mn_3O_4 nanowires were measured in field cooled (FC) and zero field cooled (ZFC) conditions with an external field of 200 Oe, as shown in Fig. 4. The curve indicates that the FC curve exhibits an obvious deviation from the ZFC curve until 40 K, revealing that the Curie temperature (T_c) of the sample is 40 K. This value is close to the bulk value of Mn_3O_4. In the FC measurements, the magnetization shows weak temperature dependence at lower temperature and obviously decreases until reaching the T_c. In contrast, the ZFC results show low magnetization in the low temperature region but increases obviously at a certain temperature. This special temperature matches T_c at a low external field. From Fig. 4, it can be known that the individual Mn_3O_4 nanowires is paramagnetic at room temperature, and exhibit ferromagnetic under 40 K. Fig. 5 shows the representative hysteresis curve of Mn_3O_4 nanowires at 5 K, which shows the coercivity of Mn_3O_4 nanowires is 33.6 Oe and the saturation magnetization of the sample is 4.92 emu/g. The saturation magnetization is smaller than the single crystal

Mn_3O_4 nanowires [18]. This can be ascribed to the Mn_3O_4 nanowires prepared by electrospinning method is polycrystalline and porous ones, and the crystal boundary and other defect make the saturation magnetization smaller than the single crystal samples. This result also indicates the ferromagnetic property of Mn_3O_4 nanowires at low temperature. The porous and magnetic features of the sample mike that they can be used as the filtration to separate effectively the magnetic-active particle through the application of an external magnetic field [17].

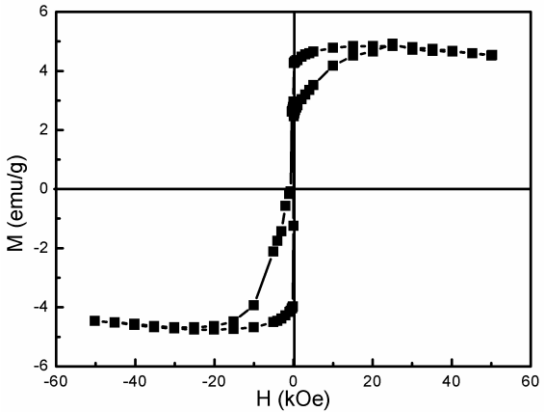

Fig. 5. M-H curve of Mn_3O_4 nanowires at 5 K.

4. Conclusion

In summary, Mn_2O_3 nanowires were prepared by the electrospinning method followed by annealing in air. After the further H_2 reduction, Mn_3O_4 nanowires were obtained. Mn_3O_4 nanowires were tetragonal phase with a diameter of about 100 nm. The samples were porous, which mike them have many potential application. The magnetic properties of the samples were measured by SQUID and presented obviously ferromagnetic at the low temperture.

Acknowledgements

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References

[1] P. Zhang, Y. Zhan, B. Cai, C. Hao, J. Wang, C. Liu, Z. Meng, Z. Yin, Q. Chen, Nano Res. **3**, 235 (2010).
[2] Y. F. Han, F. X. Chen, Z. Y. Zhong, K. Ramesh, L. W. Chen, E. Widjaja, J. Phys. Chem. B **110**, 24450 (2006).
[3] A. E. Fischer, K. A. Pettigrew, D. R. Rolison, R. M. Stroud, J. W. Long, Nano Lett. **7**, 281 (2007).
[4] L. Liu, H. Liang, H. Yang, J. Wei, Y. Yang, Nanotechnology **22**, 015603 (2011).
[5] J. Liu, J. Essner, J. Li, Chem. Mater. **22**, 5022 (2010).
[6] Z. H. Wang, D. Y. Geng, W. J. Hu, W. J. Ren, Z. D. Zhang, J. Appl. Phys. **105**, 07A315 (2009).
[7] A. E. Berkowitz, G. F. Rodriguez, J. I. Hong, K. An, T. Hyeon, N. Agarwal, D. J. Smith, E. E. Fullerton, Phys. Rev. B **77**, 024403 (2008).
[8] T. Maruyama, Y. Osaki, J. Electrochem. Soc. **142**, 3137 (1995).
[9] S. Thota, B. Prasad, J. Kumar, Mater. Sci. Eng. B **167**, 153 (2010).
[10] W. Chen, N. Wang, L. Liu, Y. Cui, X. Cao, Q. Chen, L. Guo, Nanotechnology **20**, 445601 (2009).
[11] X. Fang, X. Lu, X. Guo, Y. Mao, Y. Hu, J. Wang, Z. Wang, F. Wu, H. Liu, L. Chen, Electrochem. Commun. **12**, 1520 (2010).
[12] H. Dhaouadi, A. Madani, F. Touati, Mater. Lett. **64**, 2395 (2010).
[13] Y. Hu, J. Chen, X. Xue, T. Li, Mater. Lett. **60**, 383 (2006).
[14] S. V. Fridrikh, J. H. Yu, M. P. Brenner, G. C. Rutledge, Phys. Rev. Lett. **90**, 144502 (2003).
[15] J. Zhao, H. Duan, Z. Ma, L. Liu, E. Xie, J. Optoelectron. Adv. Mater. **10**, 3029 (2008).
[16] Y. Su, B. Lu, Y. Xie, Z. Ma, L. Liu, H. Zhao, J. Zhang, H. Duan, H. Zhang, J. Li, Nanotechnology **22**, 285609 (2011).
[17] D. Li, Y. Xia, Adv. Mater. **16** ,1151 (2004).
[18] S. Sambasivam, G. J. Li, J. H. Jeong, B. C. Choi, K. T. Lim, S. S. Kim, T. K. Song, J. Nanopart. Res. **14**, 1138 (2012).

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