Research Article

A Rational Self-Sacrificing Template Route to LiMn_2O_4 Nanotubes and Nanowires

Baojun Yang,¹ Xinsong Yuan,² and Duoli Chai¹

¹ Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering, School of Chemical Engineering, Hefei University of Technology, Hefei 230009, China

² Department of Chemistry and Chemical Engineering, Hefei Normal University, Hefei 230061, China

Correspondence should be addressed to Baojun Yang, lhmybigy@mail.ustc.edu.cn and Xinsong Yuan, yuanxinsong520@163.com

Received 5 April 2010; Accepted 11 July 2010

Academic Editor: William W. Yu

Copyright © 2011 Baojun Yang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Single-crystalline LiMn_2O_4 nanotubes and nanowires have been synthesized via a low-temperature molten salt synthesis method, using the prepared $\beta\text{-MnO}_2$ nanotubes and $\alpha\text{-MnO}_2$ nanowires as the precursors and self-sacrificing template. The materials were investigated by a variety of techniques, including X-ray powder diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HRTEM). The results indicate that the prepared LiMn_2O_4 nanotube and nanowire samples are both spinel phase, have lengths up to several micrometers and diameters of hundreds and tens of nanometers, respectively.

1. Introduction

One-dimensional (1D) nanomaterials, with their large surface areas and possible quantum confinement effects, exhibit distinct electronic, optical, chemical, and thermal properties [1]. Nanotubes and nanowires are always the focus of study of 1D nanomaterials, so the exploration of simple synthetic methods that can be generalized is a significant challenging field [2].

In recent years, the self-sacrificing template synthesis has been proved to be a facile and efficient route to nanotubes [3–6] and nanowires [7–9]. The idea of converting nanostructures of manganese dioxide to lithium manganese oxide has been described by several groups [10–15]. A sol-gel-AAO or polycarbonate membrane template strategy was used to synthesize LiMn_2O_4 nanotubes by Li et al. [16] and Li et al. [17] and LiMn_2O_4 nanowires by Zhou et al. [18] and Liu et al. [19]; an electrospinning technique was also utilized to prepare LiMn_2O_4 nanowires by Yu et al. [20] and Fu et al. [21]. Hosono et al. [22] reported a high temperature molten salt reaction to prepare LiMn_2O_4 nanowires at 450°C, using the prepared $\text{Na}_{0.44}\text{MnO}_2$ nanowires as a self-sacrificing template and converting $\text{Na}_{0.44}\text{MnO}_2$ nanowires to LiMn_2O_4 nanowires. However, to the best of our knowledge, a

simple route to 1D LiMn_2O_4 nanotubes and nanowires at low temperature has still rarely been reported. Herein, we report a low-temperature molten salt route to synthesize LiMn_2O_4 nanotubes and nanowires, using the prepared $\beta\text{-MnO}_2$ nanotubes and $\alpha\text{-MnO}_2$ nanowires as self-sacrificing templates.

2. Experimental Section

2.1. Synthesis Procedures. The precursor $\beta\text{-MnO}_2$ nanotubes were prepared following a procedure found in the literature [23]. In a typical process, 4 mmol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was dissolved in 10 mL of distilled water, and 4.5 mmol of PVP (K30, polymerization degree 360) was added slowly to it with vigorous stirring. When the solution clarified, 8 mL of aqueous solution containing 8 mmol of NaClO_3 was added to the above solution under continuous stirring. The resulting transparent solution was then transferred into a Teflon-lined stainless steel autoclave (20 mL) of 70% capacity of the total volume. The autoclave was sealed and maintained at 160°C for 10 h. After the reaction was completed, the autoclave was allowed to cool to room temperature naturally. The solid black precipitate was filtered, washed several times with

FIGURE 1: Typical XRD patterns of sample 1 (a) and sample 2 (b).

distilled water and absolute ethanol to remove impurities, and then dried at 50°C for 4 h.

The precursor α - MnO_2 nanowires were synthesized using the technique reported previously in [24]. In a typical process, 0.008 mol $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 0.02 mol $(\text{NH}_4)_2\text{SO}_4$, and 0.008 mol $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were put into distilled water at room temperature to form a homogeneous solution, which was then transferred into a 40 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 140°C for 12 h. After the reaction was completed, the resulting solid products were filtered, washed with distilled water to remove the remnant ions, and finally dried at 60°C for 4 h.

For the synthesis of LiMn_2O_4 nanotubes (noted as sample 1) and nanowires (noted as sample 2), 0.59 LiNO_3 –0.41 LiOH flux (melting point = 183°C) were used as lithium salts [25]. In a typical experimental procedure, 10 mmol MnO_2 powders (β - MnO_2 nanotubes or α - MnO_2 nanowires) and an appropriate amount (for example 100 mmol) of the flux were firstly mixed with a mortar and pestle, heated at $\sim 230^\circ\text{C}$ for ~ 10 h in air, and then air-cooled to room temperature. The resulting products were collected, washed repeatedly with distilled water, filtered, and finally dried in an oven at 60°C for 4 h.

2.2. Characterization. The samples were characterized by X-ray powder diffraction (XRD), which was recorded on a Japan Rigaku Dmax- γ A X-ray powder diffractometer with graphite-monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154056$ nm). The transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) pattern were captured on a Hitachi Model H-800 instrument at an acceleration voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images and Energy-dispersive X-ray spectrum (EDS) were obtained with a JEOL-2010 transmission electron microscope, employing an accelerating voltage of 200 kV. Field-emission scanning electron microscope (FESEM) images were taken on a field-emission microscope (JEOL JSM-6700F, 5 kV).

3. Results and Discussions

Figures 1(a) and 1(b) show the typical XRD patterns of sample 1 and sample 2. All of the intensive and sharp peaks can be readily indexed to the pure spinel structure of crystalline LiMn_2O_4 [space group: $Fd\bar{3}m$] (JCPDS 35-782).

TEM and FESEM images of the precursor MnO_2 nanotubes (Figures 2(a) and 2(e)) and nanowires (Figures 2(c) and 2(g)) indicate that the morphology and size of the prepared precursors are in good agreement with those in the studies in [23, 24]. Figures 2(b) and 2(f) show TEM and FESEM images of sample 1, from which, one can see that these LiMn_2O_4 nanotubes have diameters of hundreds of nanometers and lengths up to several micrometers, basically retain the morphology of the precursor MnO_2 nanotubes. Figures 2(d) and 2(h) show TEM and FESEM images of sample 2, which reveal that the LiMn_2O_4 nanowires have diameters of tens of nanometers and lengths up to several micrometers, and the morphology of the precursor MnO_2 nanowires is also mainly maintained. The above phenomenon suggests that the precursor MnO_2 nanotubes and nanowires may serve as self-sacrificing template for the formation of LiMn_2O_4 nanotubes and nanowires.

We have also characterized the as-synthesized LiMn_2O_4 nanotubes and nanowires using HRTEM, SAED, and EDS. A representative HRTEM image of a section of a single nanotube is shown in Figure 3(a). The discriminable lattice fringes illustrate that the prepared LiMn_2O_4 nanotubes are single crystals in the area shown. The lattice fringes, parallel to the axial direction of the nanotube, have spacing of 0.475 nm, which match well with the separations between the neighboring lattices of the (111) planes of cubic LiMn_2O_4 . This result indicates that the LiMn_2O_4 nanotube has preferential growth direction perpendicular to [111] direction. The clear and symmetrical spots in the corresponding SAED pattern also indicate that the single nanotube is single-crystalline in nature. The composition of the sample as calculated from the EDS analysis (Figure 3(b))

FIGURE 2: Typical TEM images of precursor MnO_2 nanotubes and nanowires (a and c) and sample 1 and 2 (b and d), FESEM images of precursor MnO_2 nanotubes and nanowires (e and g) and sample 1 and 2 (f and h).

gives an Mn : O atomic ratio of 1 : 2.08, which is close to the stoichiometry of LiMn_2O_4 . The HRTEM image (Figure 3(c)) taken from a single wire shows two sets of distinct fringe spacings of ca. 0.477 and 0.291 nm that match well with the separation between the $(1\bar{1}1)$ and (220) lattice planes of cubic LiMn_2O_4 , respectively, which indicate that the growth direction of the wire is along $[110]$ direction. The inset SAED pattern of the nanowire was recorded with the electron beam along the $[\bar{1}12]$ zone axis. It also demonstrates that this nanowire is single crystal and may have a growth direction of $[110]$. The composition of the nanowires as calculated from the EDS spectrum (Figure 3(d)) gives an Mn : O atomic ratio of 1 : 2.07, which is close to the stoichiometry of LiMn_2O_4 .

The specific formation mechanism of the LiMn_2O_4 nanotubes and nanowires is not yet clear and warrants further investigation. Concerning the formation mechanisms

for nanotubes and nanowires, we think that converting nanostructures of manganese dioxide to lithium manganese oxide is based on a lithiation reaction [10–12], and the 1D tubes and wires can be mainly retained in the present synthetic conditions.

The net lithiation reaction might be simply formulated by:

Xia et al. believe that the formation of Ag_2Se nanowires from Se nanowires is based on an in situ reaction and a straightforward transformation of Se nanowire template [7]. In our previous report of the synthesis of Bi_2O_3 nanotubes from Bi nanotubes [3] and Bi_2S_3 nanorods

FIGURE 3: HRTEM (a) and the associated EDS (b) image of a typical LiMn_2O_4 nanotube. The lower inset in (a) is the corresponding SAED pattern and the upper gives an enlarged view of the HRTEM image taken from the zone marked by the rectangle; HRTEM (c) and the associated EDS (d) image of a typical LiMn_2O_4 nanowire. The inset in (c) is the corresponding SAED pattern.

FIGURE 4: Schematic pictures of the net transition of $\beta\text{-MnO}_2$ nanotubes and $\alpha\text{-MnO}_2$ nanowires to LiMn_2O_4 nanotubes (a) and nanowires (b).

from Bi nanotubes [26], we have provided a rational self-sacrificing template mechanism. For the transformation of MnOOH nanorods to LiMn_2O_3 nanorods, Yang et al. [12] and Zhang et al. [13] have also given the similar explanations. Herein, we hypothesize that the conversion of the manganese dioxide nanotubes and nanowires to lithium manganese oxide nanotubes and nanowires might be simply described by the schematic pictures in Figures 4(a) and 4(b). However, the intermediate process and the specific mechanism of the formation of the LiMn_2O_4 nanotubes and nanowires are not yet clear and warrant further investigation.

4. Conclusions

In conclusion, we have synthesized spinel phase LiMn_2O_4 nanotubes and nanowires via a low-temperature lithiation reaction, using $\beta\text{-MnO}_2$ nanotubes and $\alpha\text{-MnO}_2$ nanowires as the precursors. Besides, we hypothesize that the formation process of the as-prepared LiMn_2O_4 nanotubes and nanowires is based on a self-sacrificing template converting mechanism. This method requires no complex apparatus or technique, and the conditions are mild, and the present

study may supply a general strategy to design and synthesize nanostructured oxide materials.

Acknowledgments

This paper was supported by Anhui Colleges and Universities Provincial Natural Science key research Projects (KJ2008A066) and Anhui Colleges and Universities Provincial Natural Science Research Project (KJ2010B174).

References

- [1] Y. Xia, P. Yang, Y. Sun et al., "One-dimensional nanostructures: synthesis, characterization, and applications," *Advanced Materials*, vol. 15, no. 5, pp. 353–389, 2003.
- [2] L. Li, Y.-W. Yang, G.-H. Li, and L.-D. Zhang, "Conversion of a Bi nanowire array to an array of Bi-Bi₂O₃ core-shell nanowires and Bi₂O₃ nanotubes," *Small*, vol. 2, no. 4, pp. 548–553, 2006.
- [3] B. Yang, M. Mo, H. Hu et al., "A rational self-sacrificing template route β -Bi₂O₃ nanotube arrays," *European Journal of Inorganic Chemistry*, no. 9, pp. 1785–1787, 2004.
- [4] J. Zhao, X. Wang, T. Sun, and L. Li, "In situ templated synthesis of anatase single-crystal nanotube arrays," *Nanotechnology*, vol. 16, no. 10, pp. 2450–2454, 2005.
- [5] C. Wu, S.-H. Yu, S. Chen, G. Liu, and B. Liu, "Large scale synthesis of uniform CuS nanotubes in ethylene glycol by a sacrificial templating method under mild conditions," *Journal of Materials Chemistry*, vol. 16, no. 32, pp. 3326–3331, 2006.
- [6] L. Pan, L. Pu, Y. Shi et al., "Synthesis of polyaniline nanotubes with a reactive template of manganese oxide," *Advanced Materials*, vol. 19, no. 3, pp. 461–464, 2007.
- [7] B. Gates, Y. Wu, Y. Yin, P. Yang, and Y. Xia, "Single-crystalline nanowires of Ag₂Se can be synthesized by templating against nanowires of trigonal Se," *Journal of the American Chemical Society*, vol. 123, no. 46, pp. 11500–11501, 2001.
- [8] G. H. Du and G. Van Tendeloo, "Cu(OH)₂ nanowires, CuO nanowires and CuO nanobelts," *Chemical Physics Letters*, vol. 393, no. 1–3, pp. 64–69, 2004.
- [9] G. H. Du, Z. Y. Yuan, and G. Van Tendeloo, "Transmission electron microscopy and electron energy-loss spectroscopy analysis of manganese oxide nanowires," *Applied Physics Letters*, vol. 86, no. 6, Article ID 063113, 3 pages, 2005.
- [10] M. Rossouw, A. de Kock, L. de Picciotto, M. Thackeray, W. David, and R. Ibberson, "Structural aspects of lithium-manganese-oxide electrodes for rechargeable lithium batteries," *Materials Research Bulletin*, vol. 25, no. 2, pp. 173–182, 1990.
- [11] T. Ohzuku, M. Kitagawa, and T. Hirai, "Electrochemistry of manganese dioxide in lithium nonaqueous cell. III. X-ray diffractational study on the reduction of spinel-related manganese dioxide," *Journal of the Electrochemical Society*, vol. 137, no. 3, pp. 769–775, 1990.
- [12] X. Yang, W. Tang, H. Kanoh, and K. Ooi, "Synthesis of lithium manganese oxide in different lithium-containing fluxes," *Journal of Materials Chemistry*, vol. 9, no. 10, pp. 2683–2690, 1999.
- [13] W. Zhang, Y. Liu, Z. Yang, S. Tang, and M. Chen, "Synthesis and characterization of nanostructured Li₂MnO₃ from nanostructured MnOOH precursors," *Solid State Communications*, vol. 131, no. 7, pp. 441–445, 2004.
- [14] J. Luo, L. Cheng, and Y. Xia, "LiMn₂O₄ hollow nanosphere electrode material with excellent cycling reversibility and rate capability," *Electrochemistry Communications*, vol. 9, no. 6, pp. 1404–1409, 2007.
- [15] F. Zhou, X. Zhao, Y. Liu, L. Li, and C. Yuan, "Size-controlled hydrothermal synthesis and electrochemical behavior of orthorhombic LiMnO₂ nanorods," *Journal of Physics and Chemistry of Solids*, vol. 69, no. 8, pp. 2061–2065, 2008.
- [16] X. Li, F. Cheng, B. Guo, and J. Chen, "Template-synthesized LiCoO₂, LiMn₂O₄, and LiNi_{0.8}Co_{0.2}O₂ nanotubes as the cathode materials of lithium ion batteries," *The Journal of Physical Chemistry B*, vol. 109, no. 29, pp. 14017–14024, 2005.
- [17] N. Li, C. J. Patrissi, G. Che, and C. R. Martin, "Rate capabilities of nanostructured LiMn₂O₄ electrodes in aqueous electrolyte," *Journal of the Electrochemical Society*, vol. 147, no. 6, pp. 2044–2049, 2000.
- [18] Y.-K. Zhou, C.-M. Shen, J. Huang, and H.-L. Li, "Synthesis of high-ordered LiMn₂O₄ nanowire arrays by AAO template and its structural properties," *Materials Science and Engineering B*, vol. 95, no. 1, pp. 77–82, 2002.
- [19] X. Liu, J. Wang, J. Zhang, and S. Yang, "Fabrication and characterization of Zr and Co co-doped LiMn₂O₄ nanowires using sol-gel-AAO template process," *Journal of Materials Science: Materials in Electronics*, vol. 17, no. 11, pp. 865–870, 2006.
- [20] N. Yu, C. Shao, Y. Liu, H. Guan, and X. Yang, "Nanofibers of LiMn₂O₄ by electrospinning," *Journal of Colloid and Interface Science*, vol. 285, no. 1, pp. 163–166, 2005.
- [21] Z.-W. Fu, J. Ma, and Q.-Z. Qin, "Nanostructured LiCoO₂ and LiMn₂O₄ fibers fabricated by a high frequency electrospinning," *Solid State Ionics*, vol. 176, no. 17–18, pp. 1635–1640, 2005.
- [22] E. Hosono, T. Kudo, I. Honma, H. Matsuda, and H. Zhou, "Synthesis of single crystalline spinel LiMn₂O₄ nanowires for a lithium ion battery with high power density," *Nano Letters*, vol. 9, no. 3, pp. 1045–1051, 2009.
- [23] D. Zheng, S. Sun, W. Fan et al., "One-step preparation of single-crystalline β -MnO₂ nanotubes," *The Journal of Physical Chemistry B*, vol. 109, no. 34, pp. 16439–16443, 2005.
- [24] X. Wang and Y. Li, "Synthesis and formation mechanism of manganese dioxide nanowires/nanorods," *Chemistry: A European Journal*, vol. 9, no. 1, pp. 300–306, 2003.
- [25] C.-H. Han, Y.-S. Hong, and K. Kim, "Cyclic performances of HT-LiCo_{0.8}Mn_{0.2}O₂ (M = Al, Ni) powders prepared by the molten salt synthesis method," *Solid State Ionics*, vol. 159, no. 3–4, pp. 241–247, 2003.
- [26] D. Chai, X. Yuan, B. Yang, and Y. Qian, "A rational route to synthesize Bi₂S₃ nanorods in large scale," *Solid State Communications*, vol. 148, no. 9–10, pp. 444–447, 2008.