COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Rational synthesis of α-MnO_2 single-crystal nanorods

Xun Wang and Yadong Li*

Department of Chemistry, Tsinghua University, Beijing 100084, Peoples' Republic of China. E-mail: ydli@tsinghua.edu.cn

Received (in Cambridge, UK) 3rd January 2002, Accepted 27th February 2002
First published as an Advance Article on the web 12th March 2002

α-MnO_2 single-crystal nanorods with diameters 20–80 nm and lengths up to 6 μm have been prepared through a low-temperature liquid-phase comproportionation method, which involves no catalysts or templates and may be adjusted to prepare α-MnO_2 single-crystal nanorods in large scale.

In recent years, there has been considerable interest in the fabrication of one-dimensional (1-D) nanostructured materials such as Bi,[1] WS_2,[2] MX_2 (M = Mo or W, X = S or Se)[3] nanotubes, semiconducting oxides nanobelts,[4] and GaN,[5] InP,[6] Ge,[7] W[8] nanowires, for their potential uses in mesoscopic research and in the development of nanodevices. However, comparatively few studies, to the best of our knowledge, have been carried out concerning the preparation of MnO_2 1-D nanostructures. Here, we report the synthesis of α-MnO_2 single-crystal nanorods with diameters 20–80 nm and lengths ranging between 2 and 6 μm.

MnO_2 exists in many polymorphic forms (such as α, β, γ and δ). They are different in that the basic unit [MnO_6] octahedra are linked in different ways; the α-type is constructed from double chains of [MnO_6] octahedra forming 2 × 2 tunnels (Fig. 1).[9] Owing to its specific properties α-MnO_2 is a traditionally attractive material for various industrial applications.[10] Recently, α-MnO_2 has been intensively examined as an electrode material for lithium batteries,[11] and also as a molecular sieve.[12] Various methods have been applied to prepare α-MnO_2, including acid treatment of Li_2MnO_3,[13] thermal treatment of $(NH_4)_xMn_8O_{16}$[14] and ozone oxidation of $MnSO_4$.[15] However, the above synthetic routes only lead to bulk α-MnO_2, and the synthesis of α-MnO_2 1-D nanostructures remains as a challenge to material scientists.

Templates or catalysts have been widely used to grow 1-D nanostructures,[5,7] in which templates are used to confine the growth of wires, while catalysts may act as the energetically favorable sites for the adsorption of reactant molecules. However, the introduction of templates or catalysts to the reaction system will greatly complicate the process, and increase the production cost, and thus increase the difficulty for scale-up production of 1-D nanostructures. It would thus be of value to find techniques without involving templates or catalysts. Recent studies, for example, the preparation of Bi,[1] WS_2[2] nanotubes, W[8] nanowires, *etc*., suggest that it is possible to prepare 1-D nanostructures based on the nature of the crystal growth. Initiated by such a notion, we have developed a low-temperature liquid-phase comproportionation method to prepare α-MnO_2 single-crystal nanorods, in the absence of templates or catalysts.

The chemical reaction we employed can be formulated as shown in eqn. (1)

$$3MnSO_4 + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4 \quad (1)$$

which comprises two half reactions, eqns. (2) and (3):

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e \ (E^0 = 1.23 \text{ V}) \quad (2)$$

$$MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O \ (E^0 = 1.695 \text{ V}) \quad (3)$$

On the basis of the values of E^0, the standard Gibbs free energy change ΔG^0 of reaction (1) could be estimated to be −269.2 kJ mol^{-1}, implying a very strong tendency for this reaction to progress towards completion.

Analytical grade hydrate manganese sulfate ($MnSO_4 \cdot H_2O$, 0.2 g) and potassium permanganate(VII) ($KMnO_4$, 0.5 g) were placed in distilled water at room temperature to form a mixed solution, which was then transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 140 °C for 12 h. After the reaction was complete, the resulting brownish-black solid product was filtered off, washed with distilled water to remove ions possibly remaining in the final products, and finally dried at 100 °C in air.

The phase purity of the products were examined by X-ray diffraction (XRD) using a Bruker D8-advance X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å), using an operation voltage and current of 40 kV and 40 mA, respectively. All the reflections of the XRD pattern in Fig. 2 can be readily indexed to a pure tetragonal phase [space group: *I*4/*m* (no. 87)] of α-MnO_2 with lattice constants a = 9.7847 Å and c = 2.8630 Å (JCPDS 44-0141). The XRD pattern indicates that pure α-MnO_2 can be obtained under the current synthetic conditions.

The morphology of the products was further examined with transmission electron microscopy [TEM, Hitachi (Tokyo, Japan) H-800]. As shown in Fig. 3A, all α-MnO_2 samples

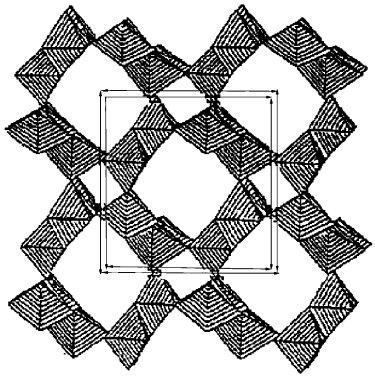

Fig. 1 The structure of α-MnO_2.

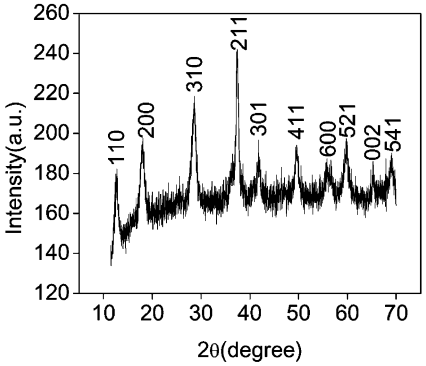

Fig. 2 XRD patterns of α-MnO_2.

DOI: 10.1039/b111723h

dispersed on the TEM grids show rod-like morphology with diameters 20–80 nm and lengths in the range 2–6 μm. Electron diffraction patterns of α-MnO_2, taken from a single rod, are consistent with the single crystalline nature of a bulk sample, and can be indexed to the reflections of tetragonal α-MnO_2 [1$\bar{1}$1] (Fig. 3B).

The whole process, with a product yield repeatedly above 95% (based on Mn) and involving no catalysts or templates, may be easily adjusted to prepare α-MnO_2 single-crystal nanorods on a large scale. The temperature and the reactant molecular ratio play an important role in determining the morphology and crystallographic form of the products, based on our experimental results. The growth mechanism of single-crystal nanorods is worth further systematic study. This simple solution synthetic route has the potential to be developed as a general method for the preparation of other 1-D nanostructured materials.

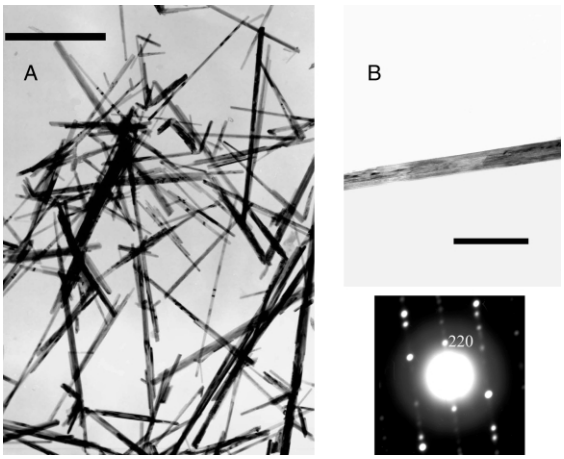

Fig. 3 A, TEM image of α-MnO_2 (scale bar = 1 μm); B, TEM image of an α-MnO_2 single rod (scale bar = 200 nm) and the corresponding electron diffraction pattern of α-MnO_2 [1$\bar{1}$1].

This work was supported by the NSFC and the State Key Project of Fundamental Research for Nanomaterials and Nanostructures.

Notes and references

1 Y. D. Li, J. W. Wang, Z. X. Deng, Y. Y. Wu, X. M. Sun, D. P. Yu and P. D. Yang, *J. Am. Chem. Soc*., 2001, **123**, 9905.
2 Y. D. Li, X. L. Li, R. R. He, J. Zhu and Z. X. Deng, *J. Am. Chem. Soc*., 2002, **124**, 1411.
3 (*a*) R. Tenne, L. Margulis, M. Genut and G. Hodes, *Nature*, 1992, **360**, 444; (*b*) Y. Feldman, E. Masserman, D. J. Srolovita and R. Tenne, *Science*, 1995, **267**, 222; (*c*) R. Tenne, M. Homyonfer and Y. Feldman, *Chem. Mater*., 1998, **10**, 3225.
4 Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, 2001, **291**, 1947.
5 W. Q. Han, S. S. Fan, Q. Q. Li and Y. D. Hu, *Science*, 1997, **277**, 1287.
6 X. F. Duan, Y. Huang, Y. Cui, J. F. Wang and C. M Lieber, *Nature*, 2001, **409**, 66.
7 A. M. Morales and C. M. Lieber, *Science*, 1998, **279**, 208.
8 Y. D. Li, X. L. Li, Z. X. Deng, B. C. Zhou, S. S. Fan, J. W. Wang and X. M. Sun, *Angew. Chem., Int. Ed*., 2002, **41**, 333.
9 M. M. Thackeray, *Prog. Solid State Chem*., 1997, **25**, 1.
10 (*a*) T. Ohzuku, M. Kitagawa, K. Sawai and T. Hirai, *J. Electrochem. Soc*., 1992, **138**, 360; (*b*) Q. Feng, H. Kanoh, Y. Miyai and K. Ooi, *Chem. Mater*., 1995, **7**, 148; (*c*) P. Strobel, J. Vicat and D. T. Qui, *J. Solid State Chem*., 1984, **55**, 67.
11 Y. Shao-Horn, S. A. Hackney, C. S. Johnson and M. M. Thackeray, *J. Electrochem. Soc*., 1998, **145**, 582.
12 Y. Tanaka, M. Tsuji and Y. Tamaura, *Phys. Chem. Chem. Phys*., 2000, **2**, 1473.
13 M. H. Rossouw, D. C. Liles and M. M. Thackeray, *Mater. Res. Bull*., 1992, **27**, 221.
14 Y. Muraoka, H. Chiba and T. Atou, *J. Solid State Chem*., 1999, **144**, 136.
15 N. Kijima, H. Yasuda, T. Sato and Y. Yoshimura, *J.Solid State Chem*., 2001, **159**, 94.