J Mater Sci (2007) 42:9978–9982
DOI 10.1007/s10853-007-2054-3

Synthesis of γ-MnOOH nanorods and their isomorphous transformation into β-MnO_2 and α-Mn_2O_3 nanorods

**Fu Zhou · Xuemei Zhao · Cunguang Yuan ·
Hai Xu**

Received: 2 September 2006 / Accepted: 25 July 2007 / Published online: 6 September 2007

Abstract γ-MnOOH nanorods with different diameters were synthesized by a simple one-step polymer-assisted hydrothermal method using 50% (wt.%) $Mn(NO_3)_2$ solution and PEG-10000 as reagents. The diameters of as-synthesized γ-MnOOH nanorods were well controlled by simply varying the volume of the 50% $Mn(NO_3)_2$ solution. The calcination behavior of the as-synthesized γ-MnOOH nanorods was studied. Nanorods of β-MnO_2 and α-Mn_2O_3 were synthesized by calcination at 350 and 600 °C for 1 h respectively.

Introduction

Since the discovery of carbon nanotubes in 1991 [1], one-dimensional (1D) nanostructures have attracted increasing interest among science workers for their crucial role in future technological advances in electronics, optoelectronics, and memory devices [2–4]. A number of methods were applied to synthesize 1D nanostructures, such as vapor–liquid–solid (VLS) method, vapor–solid (VS) method, hydrothermal method, template-assisted method, microemulsion method and refluxing method [5–10]. Among them, due to its simplicity and effectiveness, hydrothermal method is widely applied to prepare 1D nanostructures.

For many years, manganese oxides and hydroxides have attracted special attention. Due to their outstanding structural flexibilities combined with novel chemical and physical properties, they are widely used as catalysts, molecular sieves, and Li/MnO_2 batteries. The crystallographic forms are generally believed to be responsible for their properties, and the controlled synthesis of manganese oxides and hydroxides has always been the focus of materials science and technology. Meanwhile, many efforts have been made to synthesize low-dimensional manganese oxides and hydroxides nanostructures. Li et al. has successfully synthesized nanorods and nanotubes of α-, β-, δ-MnO_2 by a common hydrothermal method based on the redox reactions of MnO_4^- and/or Mn^{2+} [11–13]. Zhang et al. have synthesized MnOOH nanorods by a solvothermal reduction reaction of $KMnO_4$ in the 2–10% ethanol solutions [14]. In their report, Mn_3O_4 and MnOOH with different morphologies were synthesized by varying the ethanol volume percent in the solvent and the reaction temperature. Xi et al. have prepared nanorods of MnOOH through the reduction of $KMnO_4$ with KI under hydrothermal conditions at 120 °C and studied the calcination behavior of the products to prepare β-MnO_2 nanorods [15]. Ooi et al. have also done a lot of works on the synthesis of manganese oxides and hydroxides nanostructures [16–18]. The electrochemical synthesis of manganese oxide nanoparticles has been reported by Ohsaka et al. [19]. But to the best of our knowledge, the synthesis of MnOOH nanorods by the oxidation of Mn^{2+} solutions is rarely reported.

Herein, we report a novel synthesis method to prepare uniform γ-MnOOH nanorods via the oxidation of Mn^{2+} solutions. PEG (Polyethylene glycol) is used as the polymer to assist the growth of MnOOH nanorods from the solution of $Mn(NO_3)_2$. The diameters of the γ-MnOOH nanorods were well controlled. The calcination behavior of

F. Zhou (✉) · C. Yuan
Department of Chemistry, China University of Petroleum,
Qingdao, Shandong 266555, P.R. China
e-mail: boksiczf@ustc.edu

X. Zhao · H. Xu
Center for Bioengineering and Biotechnology, China University
of Petroleum, Qingdao, Shandong 266555, P.R. China

the as-synthesized MnOOH nanorods was studied by thermo-gravimetric analysis. Uniform β-MnO_2 and α-Mn_2O_3 nanorods could be obtained after calcination at 350 and 600 °C for 1 h respectively. The as-prepared γ-MnOOH, β-MnO_2 and α-Mn_2O_3 nanorods might have wide use as precursors for the cathode materials in Li ion battery and as catalysis, electrochromic, and magnetic materials [20–25].

Experimental

All the reagents used in the experiments were purchased from commercial sources and were used as received without further purification. The synthesis process is as follows:

Synthesis of γ-MnOOH nanorods

Two gram of PEG-10000 was added to a fixed volume of 50% $Mn(NO_3)_2$ solution under magnetic stirring. Then the mixed solution was transferred into the 50 mL teflon-lined autoclave. Distilled water was added into the autoclave until 80% volume of the autoclave is filled. The mixture was magnetically stirred for around 60 min to get good homogeneity. Later the autoclave was sealed and maintained at 140 °C for 24 h, then the autoclave was cooled to room temperature naturally. Precipitate was collected and washed with distilled water and anhydrous alcohol for several times. The final product was dried in vacuum at 80 °C for 10 h.

Calcination preparation of β-MnO_2 and α-Mn_2O_3 nanorods

The as-synthesized γ-MnOOH was milled and put into quartz crucible. The crucible was then transferred into the furnace. The temperature of the furnace was raised to 350 and 600 °C respectively with a heating rate of 5 °C min^{-1} and maintained at the temperature for 1 h in air. The obtained powder was collected for characterization.

The X-ray diffraction was carried out on a Philiphs X'Pert Super diffractometer with graphite monochromatized CuKα radiation (λ = 1.54178 Å) in the 2θ range of 10–80°. The morphology of the products was examined by scanning electron microscope (SEM) using an X-650 microanalyzer. The TEM images were performed with a Hitachi 800 transmission electron microscopy with the accelerating voltage of 200 kV. The samples used for characterization were dispersed in absolute ethanol and were ultrasonicated before SEM, TEM tests. Thermal-gravimetric analysis (TGA) of the γ-MnOOH nanorods was carried out on a Shimadzu TA-50 thermal analyzer at a heating rate of 5 °C min^{-1} from room temperature to 800 °C.

Results and discussion

The XRD pattern of the hydrothermally synthesized product is shown in Fig. 1. All of the diffraction peaks can be indexed as a monoclinic phase of γ-MnOOH, which is in good agreement with the literature values (JCPDS 41-1379).

SEM images of the as-synthesized γ-MnOOH are shown in Fig. 2, revealing that the products constituted a number of uniform nanorods. Figure 2a showed the SEM images of the product using 5 mL 50% $Mn(NO_3)_2$ solution as reagents, the diameter of the nanorods is around 2–3 μm which reaches the micrometer range. When the quantity of $Mn(NO_3)_2$ solution used is reduced to 2 mL, the diameter of the nanorods reduces to around 100–200 nm, as is shown in Fig. 2b. It is clear that by simply controlling the quantity of the reagents, the diameters of the produced γ-MnOOH nanorods can be well controlled. Yin et al. have discovered the similar controlling process in their synthesis of silver nanoparticles [26].

The morphology and microstructure of the as-synthesized γ-MnOOH nanorods are further investigated by TEM and SAED tests, which is shown in Fig. 3. Figure 3a shows the TEM image of a typical microrod using 5 mL $Mn(NO_3)_2$ solution as reagents, which has diameter of 2 μm and length of tens of micrometers. In Fig. 3b, the product with 2 mL $Mn(NO_3)_2$ solution as reagents is characterized by TEM and SAED tests. The diameter of the γ-MnOOH nanorods reduces to around 100 nm and the

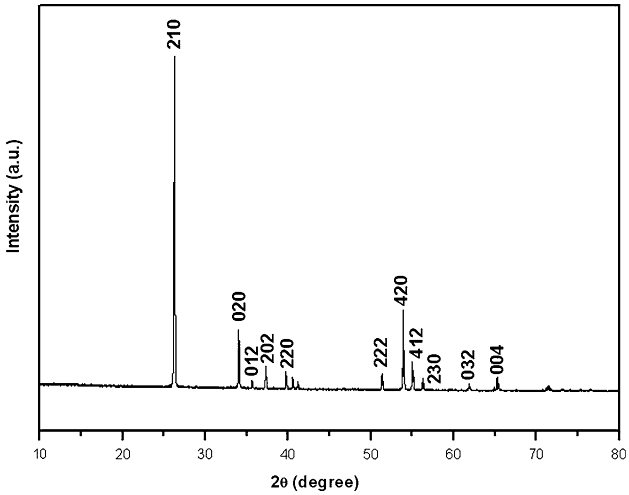


Fig. 1 XRD pattern of the as-synthesized γ-MnOOH nanorods

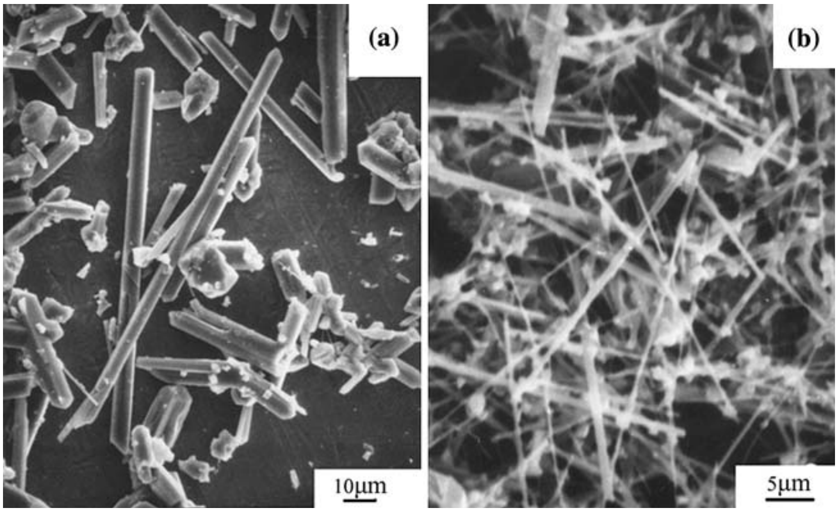


Fig. 2 SEM images of the as-synthesized γ-MnOOH nanorods (**a**) 5 mL $Mn(NO_3)_2$ solution as reagents; (**b**) 2 mL $Mn(NO_3)_2$ solution as reagents

length reaches several micrometers. The SAED pattern of γ-MnOOH nanorods (inset in Fig. 3b), which was taken from the single nanorod, indicates that the as-synthesized γ-MnOOH nanorods were well single crystallined.

PEG is the decisive factor in the successful synthesis of MnOOH nanorods in our experiments. We have done a comparative experiment without the participation of PEG-10000, and no product is obtained. The role of PEG in the formation of MnOOH nanorods may be explained as follows: Firstly, according to Pearson's results [27], the –O– of the ether group on the PEG chains has a strong basic property and possesses a pair of electrons, which facilitates the formation of MnOOH products in the hydrothermal conditions, thus the reaction temperature is lowered. Secondly, PEG is a nonionic polymer whose chain contains many hydrophilic (–O–) and hydrophobic ($–CH_2–CH_2–$) sites. And the chain has a high degree of flexibility in that the C–O bond is very easy to rotate. It is the high flexibility of the chains and its ability to be a donor of oxygen atoms that enable it to couple with Mn^{2+} ions and to form thermodynamically favorable polymer complex, which induces the successful growth of MnOOH nanorods under hydrothermal conditions.

The TGA curve of the as-synthesized γ-MnOOH nanorods is shown in Fig. 4. There are two main weight loss steps in the temperature range of 200–330 °C and 500–590 °C. The weight loss at 200–330 °C is about 1.956%, which is higher than the calculated weight loss of around 1.2% due to the decomposition of γ-MnOOH into β-MnO_2. This phenomenon could be attributed to the decomposition

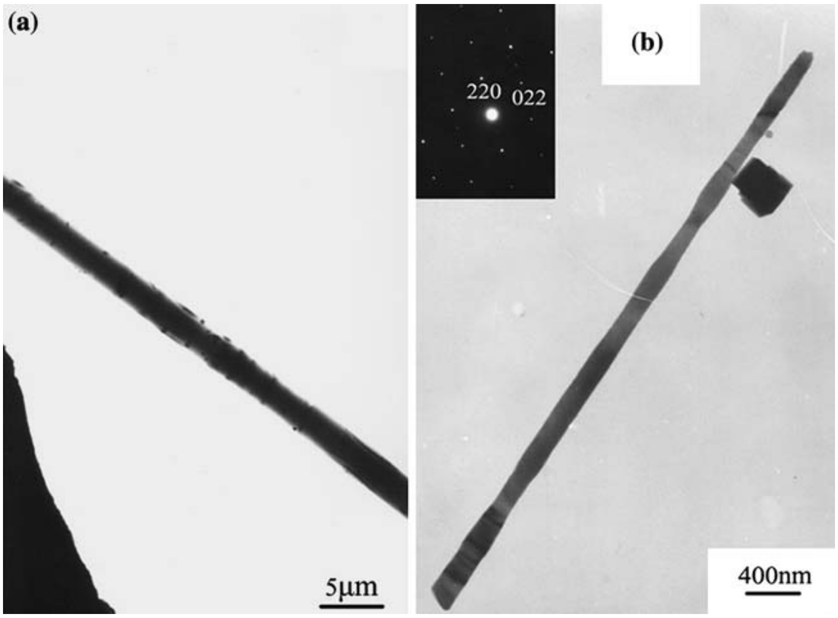


Fig. 3 TEM images of the as-synthesized γ-MnOOH nanorods (a) 5 mL $Mn(NO_3)_2$ solution as reagents; (**b**) 2 mL $Mn(NO_3)_2$ solution as reagents (inset: SAED pattern)

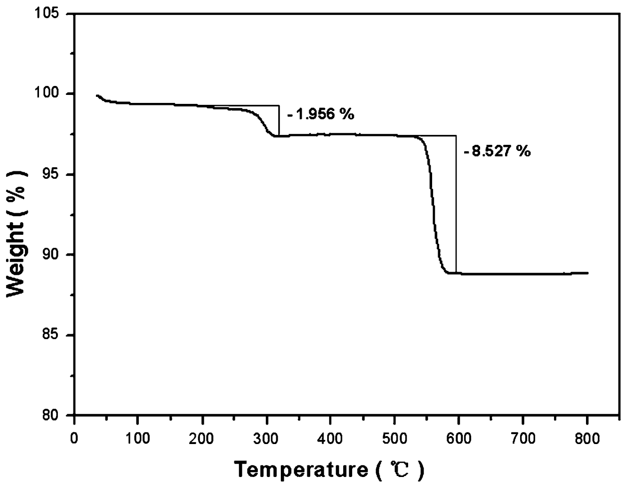


Fig. 4 TGA curve of the as-synthesized γ-MnOOH nanorods

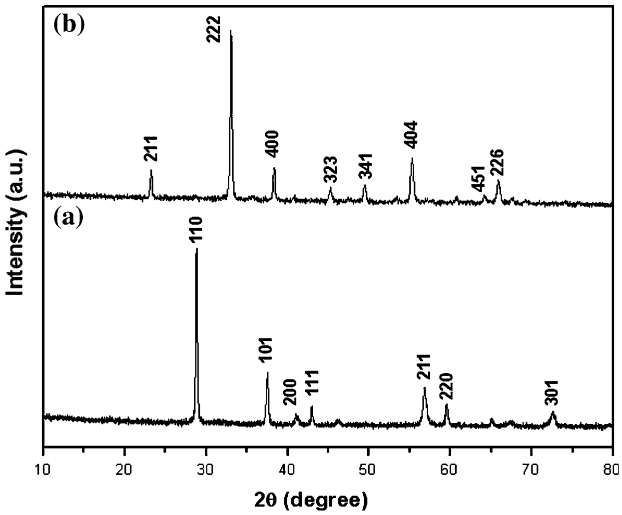


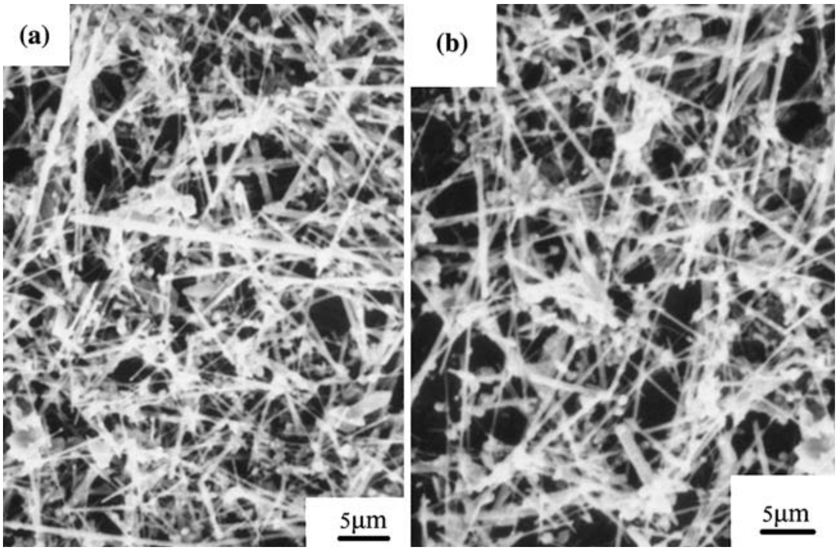
Fig. 5 XRD patterns of the calcination product of γ-MnOOH nanorods (**a**) product of calcination at 350 °C for 1 h; (**b**) product of calcination at 600 °C for 1 h

of the residual PEG-10000 in the γ-MnOOH nanorods, which is completely decomposed by the temperature of 265 °C [28]. In the temperature range of 500–590 °C, the weight loss reaches about 8.527%, which is also in good agreement with the calculated weight loss due to the further transformation of β-MnO_2 into α-Mn_2O_3. No more weight loss was observed from 600 °C to 800 °C, indicating that α-Mn_2O_3 phase is thermally stable at the temperature range of our TGA tests. According to the results of TGA tests, the calcination of γ-MnOOH in definite temperature range might lead to its transformation into β-MnO_2 and α-Mn_2O_3, which is very similar to the results reported in previous literatures [29, 30].

Figure 5 shows the XRD patterns of the products by calcining MnOOH nanorods for 1 h at 350 and 600 °C, respectively. The heating and cooling rate was controlled at 5 °C min^{-1}. Figure 5a shows the XRD pattern of the product calcined at 350 °C. All the diffraction peaks can be attributed to the pure phase of β-MnO_2 (JCPDS 24-0735). The XRD pattern of the 600 °C calcination product is shown in Fig. 5b, which corresponds well with the pure α-Mn_2O_3 phase (JCPDS 24-0508) with lattice constant $a = 9.410 \pm 0.005$ Å.

SEM images of the β-MnO_2 and α-Mn_2O_3 produced by calcining γ-MnOOH nanorods at 350 and 600 °C for 1 h were shown in Fig. 6. The morphology and microstructure of the γ-MnOOH nanorod precursors are well reserved in the calcined β-MnO_2 and α-Mn_2O_3 products and no obvious morphological difference is observed, indicating the transformation process between γ-MnOOH, β-MnO_2, and α-Mn_2O_3 is isomorphous.

Fig. 6 SEM images of the calcination products of γ-MnOOH nanorods (**a**) product of calcination at 350 °C for 1 h; (**b**) product of calcination at 600 °C for 1 h



The formation process for the γ-MnOOH, β-MnO_2, and α-Mn_2O_3 nanorods in this experiment can be described as follows:

$$4Mn(NO_3)_2(aq) + O_2(g) + 6H_2O(l) \xrightarrow[PEG-10000]{hydrothermal} 4\ \gamma\text{ - }MnOOH(s) + 8HNO_3 \tag{1}$$

$$4\gamma - MnOOH(s) + O_2(g) \xrightarrow[calcination]{350\,^{\circ}C} 4\ \beta\text{ - }MnO_2(s) + 2H_2O(g) \tag{2}$$

$$4\ \beta\text{ - }MnO_2(s) \xrightarrow[calcination]{600\,^{\circ}C} 2\ \alpha\text{ - }Mn_2O_3(s) + O_2(g) \tag{3}$$

Conclusion

In summary, γ-MnOOH nanorods were synthesized by a novel polymer-assisted low-temperature hydrothermal synthesis method. The calcination behavior of the γ-MnOOH nanorods was studied via TGA tests. Uniform nanorods of β-MnO_2 and α-Mn_2O_3 were synthesized by calcination of γ-MnOOH nanorods at definite temperatures. The as-synthesized nanorods might have great potential use as catalysts, battery materials, molecular sieves and so on.

References

1. Iijima S (1991) Nature 354:56
2. Han W, Fan SS, Li Q, Hu Y (1997) Science 277:1287
3. Coleman NRB, Morris MA, Spalding TR, Holmes JD (2001) J Am Chem Soc 123:187
4. Morales AM, Lieber CM (1998) Science 279:208
5. Duan XF, Lieber CM (2000) J Am Chem Soc 122:188
6. Pan ZW, Dai ZR, Wang ZL (2001) Science 291:1947
7. Li YD, Wang JW, Deng ZX, Wu YY, Sun XM, Yu DP, Yang PD (2001) J Am Chem Soc 123:9904
8. Dai H, Wong EW, Lu YZ et al (1995) Nature 375:769
9. Jiang XC, Xie Y, Lu J, Zhu LY, He W, Qian YT (2001) J Mater Chem 11:1775
10. Sun YG, Yin YD, Mayers BT, Herricks T, Xia YN (2002) Chem Mater 14:4736
11. Wang X, Li YD (2002) Chem Commun 7:764
12. Wang X, Li YD (2002) J Am Chem Soc 124(12):2880
13. Wang X, Li YD (2003) Chem Eur J 9(1):300
14. Zhang WX, Yang ZH, Liu Y, Tang SP, Han XZ, Chen M (2004) J Cryst Growth 263:394
15. Xi GC, Peng Y, Zhu YC, Xu LQ, Zhang WQ, Yu WC, Qian YT (2004) Mater Res Bull 39:1641
16. Yang XJ, Tang WP, Feng Q, Ooi K (2003) Cryst Growth Des 3(3):409
17. Liu ZH, Ooi K (2003) Chem Mater 15:3696
18. Yang XJ, Makita Y, Liu ZH, Sakane K, Ooi K (2004) Chem Mater 16:5581
19. El-Deab MS, Ohsaka T (2006) Angew Chem Int Ed 45:5963
20. Xia YY, Yoshio M (1995) J Power Sources 57(1–2):125
21. Nakamura H, Motooka K, Noguchi H, Yoshio M (1999) J Power Sources 81–82:632
22. Yoshio M, Nakamura H, Xia YY (1999) Electrochim Acta 45 (1–2):273
23. Ohsaka T, Mao LQ, Arihara K, Sotomura T (2004) Electrochem Commun 6(3):273
24. Mao LQ, Zhang D, Sotomura T, Nakatsu K, Koshiba N, Ohsaka T (2003) Electrochim Acta 48(8):1015
25. Mao LQ, Arihara K, Sotomura T, Ohsaka T (2004) Electrochim Acta 49(15):2515
26. Yin HB, Yamamoto T, Wada Y, Yanagida S (2004) Mater Chem Phys 83:66
27. Pearson PG (1968) J Chem Educ 45:581
28. Kim JG, Tai WP, Lee KJ, Cho WS (2004) Ceram Int 30:2223
29. Yang ZH, Zhang YC, Zhang WX, Wang X, Qian YT, Wen XG, Yang SH (2006) J Solid State Chem 179:679
30. Zhang WX, Yang ZH, Wang X, Zhang YC, Wen XG, Yang SH (2006) Catal Commun 7:408