One-step Route to Single-crystal γ-Mn_3O_4 Nanorods in Alcohol–Water System

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(Received January 15, 2004; CL-040057)

A one-step low-temperature alcohol–water thermal route has been developed to synthesize single-crystal γ-Mn_3O_4 nanorods with diameters of 50–120 nm, and lengths of up to several tens micrometers. high-resolution transmission electron microscopic observations show that the axial direction of the as-prepared nanorods is perpendicular to the normal direction of the (101) lattice planes of the tetragonal γ-Mn_3O_4.

Hausmannite Mn_3O_4, a normal spinel, has been used as a catalyst for several processes, e.g., the oxidation of methane and carbon monoxide,[1,2] the decomposition of nitrogenoxides,[3] the selective reduction of nitrobenzene,[4] and the catalytic combustion of organic compounds at temperatures of 373–773 K.[5] Considerable attention has been focused on the lithiation of $LiMnO_2$ prepared from Mn_3O_4 for rechargeable lithium batteries.[6,7] Pure form of Mn_3O_4 has been applied as one of the raw materials in the manufacture of professional grade ferrites.[8]

Mn_3O_4 is often synthesized by the high-temperature calcination (at about 1000 °C) of all oxides, hydroxides, hydroxyoxides, or oxysalts of manganese.[9] Low temperature approaches mainly include sol–gel process[10] and controlled oxidation of aqueous suspension of $Mn(OH)_2$.[9,11] Recently, Zhang and co-workers[12] have reported a low-temperature solvothermal method to synthesize nanocrystalline Mn_3O_4. Wang and co-workers[13] have synthesized single-crystal Mn_3O_4 nanowires in NaCl flux at 850 °C. Herein, for the first time, we report a one-step low-temperature alcohol–water thermal route to synthesize one-dimensional (1-D) γ-Mn_3O_4 nanorods. The prepared nanorods may have new potential applications in catalysts, lithium batteries, and so on, due to the smallest dimention structures of the 1-D system.

All the reagents used in our experiments were of analytical purity from Shanghai Chemicals Co. (China). In a typical procedure, 2 mmol $KMnO_4$, 3 mmol Na_2SO_3, and 44-mL alcohol–water solution with a volume ratio of 1:1 of anhydrous alcohol and distilled water, were put into a Teflon liner stainless steel autoclave of 50 mL capacity. The autoclave was closed tightly and kept at 140 °C for 10–12 h, then allowed to cool to room temperature. A reddish-brown powder was collected, washed with distilled water, and finally dried in a vacuum at 60 °C for 4 h.

X-ray powder diffraction (XRD) patterns were recorded on a Japan Rigaku D/max-γA X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The IR spectra were recorded using a Nicolet 750 Magna-IR spectrameter. Transmission electron microscopy (TEM) images were taken with a Hitachi Model H-800 transmission electron microscope. High-resolution electron transmission microscopy (HRTEM) images were obtained with a JEOL-2010 transmission electron microscope.

Typical XRD pattern of the as-prepared samples is shown in Figure 1a. All strong and sharp diffraction peaks can be perfectly indexed to the tetragonal phase [space group: $I4_1/amd$ (141)] of γ-Mn_3O_4 with calculated lattice constant $a = 5.764(2)$ Å, $c = 9.461(3)$ Å, which are consistent with the literature values of $a = 5.762$ Å, $c = 9.469$ Å (JCPDS 24-0734). In addition, the IR spectrum (Figure 2) of the same sample displayed four main bands (632.7, 595.9, 531.1, 411.9 cm^{-1}) in the region 1000–400 cm^{-1}, similar to those reported for this solid.[14,15] These indicate that pure-phase γ-Mn_3O_4 products are obtained under current synthetic conditions.

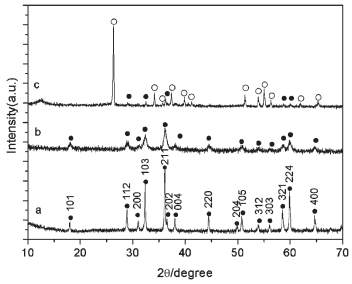

Figure 1. XRD patterns of samples prepared under different conditions (a) 22-mL anhydrous alcohol and 22-mL distilled water, (b) 44-mL anhydrous alcohol, (c) 44-mL distilled water. ● γ-Mn_3O_4, ○ γ-MnOOH.

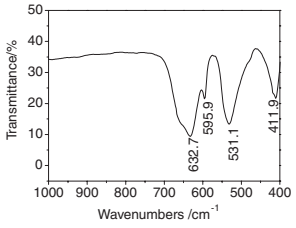

Figure 2. Infrared spectrum of the same sample as Figure 1a.

TEM images of the as-prepared γ-Mn_3O_4 samples (shown in Figures 3a and 3b) show that the sample dispersed on the TEM grids exhibits rod-shape, with diameters of 50–120 nm and lengths of up to several tens micrometers. Electron diffraction (ED) pattern (inset in Figure 3b) obtained from a single nanorod confirms that the as-prepared nanorods are single crystals of tetragonal γ-Mn_3O_4, which is in agreement with XRD and IR spectrum results.

Figure 3f shows a representative HRTEM image of a single nanorod with a diameter of about 60 nm. The clear lattice fringes further confirm that the nanorod is single crystal. The fringe spacing is about 4.94 Å, which is close to the separation between the (101) lattice planes. This means that the axial direction of the as-prepared nanorods is perpendicular to the normal direction of

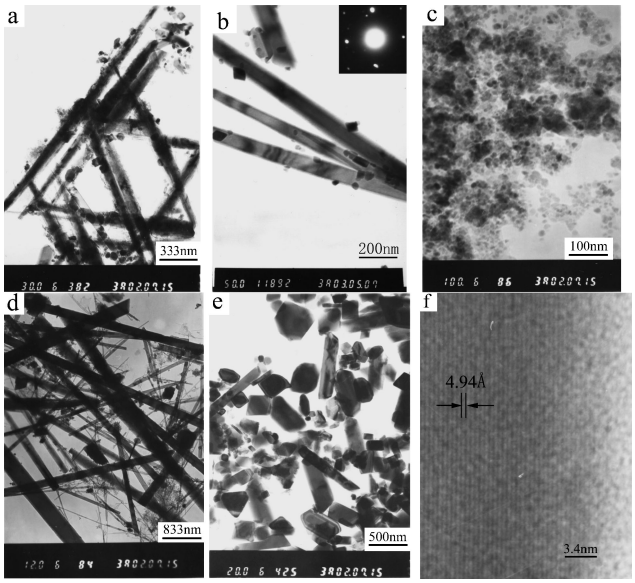

Figure 3. Typical TEM images samples prepared under different conditions (a) (b) 22-mL anhydrous alcohol and 22-mL-distilled water, (c) 44-mL anhydrous alcohol, (d) 44-mL distilled water, (e) 6 mmol Na_2SO_3, 44-mL-distilled water, (f) HRTEM image of a single as-prepared γ-Mn_3O_4 nanorod.

the (101) lattice planes of the tetragonal γ-Mn_3O_4.

It is known that $KMnO_4$ can be reduced by Na_2SO_3 or alcohol to different valence manganese compounds under certain conditions. Trying to investigate the possible formation process of 1D γ-Mn_3O_4 nanorods, several comparative experiments have been arranged. When adding 44-mL anhydrous alcohol without distilled water and keeping the other conditions unchanged, the dark purplish product is characterized as γ-Mn_3O_4 nanocrystal with particle size of about 10 nm (XRD shown in Figure 1b and TEM in Figure 3c). The reaction can be similarly formulated as Eq 3. When adding 44 mL-distilled-water without anhydrous alcohol, a black powder was obtained. The XRD image (Figure 1c) shows that the main phase of this powder is γ-MnOOH (JCPDS 74-1632), with a small amount of γ-Mn_3O_4. The TEM image (Fig. 3d) shows that the sample mainly exhibits rod-shape. The overall reaction is formulated as:

$$KMnO_4 + 2Na_2SO_3 + H_2O \longrightarrow MnOOH + 2Na_2SO_4 + KOH \quad (1)$$

When adding 6 mmol Na_2SO_3, and 44-mL-distilled water without anhydrous alcohol, the obtained sample is pure-phase γ-Mn_3O_4 by XRD analysis (similar to Figure 1a). However, only short rod-shape and diamond-shape were observed from the TEM image (Figure 3e). This indicates that intermediate product, MnOOH, can be further reduced to γ-Mn_3O_4. The overall reaction is formulated as:

$$6KMnO_4 + 13Na_2SO_3 + 3H_2O \longrightarrow 2Mn_3O_4 + 13Na_2SO_4 + 6KOH \quad (2)$$

According to previous works[11,12,15,16] and our experiment results, we believe that the overall reaction of the γ-Mn_3O_4 nanorods can be formulated as:

$$6KMnO_4 + 7Na_2SO_3 + 6CH_3CH_2OH \longrightarrow 2Mn_3O_4 + 7Na_2SO_4 + 6CH_3CHO + 6KOH + 3H_2O \quad (3)$$

In Eq 3, although H_2O presented not as a reactant but as a product, the above comparative experimental results showed that Na_2SO_3, alcohol (which may serves as solvent and reducing agent) and water all played important role in the formation of the γ-Mn_3O_4 nanorods. The above comparative experiments also strongly imply that γ-MnOOH nanorods may be formed as intermediate product and play a key role on the formation of γ-Mn_3O_4 nanorods. A possible reaction process under our experiment conditions may be described as following: $KMnO_4$ is first reduced by Na_2SO_3 to form γ-MnOOH nanorods by reaction (1), then the newly formed γ-MnOOH nanorods can be further converted to γ-Mn_3O_4 nanorods under our Na_2SO_3–alcohol reductive conditions, in which the newly formed γ-MnOOH nanorods may serve as in-situ sacrificed template. Thus, the γ-Mn_3O_4 nanorods form.

In summary, we have developed a one-step low-temperature alcohol–water thermal route to synthesize single-crystal γ-Mn_3O_4 nanorods with diameters of 50–120 nm, and lengths of up to several tens micrometers. The possible formation process of γ-Mn_3O_4 nanorods has been discussed according to the comparative experiment results.

This work was financial support from the National Natural Science Funds and the 973 Projects of China.

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Published on the web (Advance View) June 7, 2004; DOI 10.1246/cl.2004.804