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Synthesis of γ-MnO_2 single-crystalline nanobelts

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Abstract

High-quality γ-MnO_2 single-crystalline nanobelts have been synthesized by hydrothermal treatment of commercial γ-MnO_2 in NaOH aqueous solution. The products are characterized by X-ray diffractometer, scanning electron microscopy, and transmission electron microscopy. The width, thickness and lengths of γ-MnO_2 nanobelts are in the range of 80–100 nm, 10–20 nm, and several tens of micrometers, respectively. The influences of the reaction time, temperature, and medium on the morphologies of the resulting products have been investigated.

Keywords: Hydrothermal method; Manganese dioxide; Nanobelts; Single-crystal

1. Introduction

Manganese dioxide (MnO_2) materials are of considerable interest in technological applications in catalysts [1], ion sieves [2], and especially as electrode materials in Li/MnO_2 batteries [3,4] owing to their outstanding structural flexibility combined with novel chemical and physical properties. MnO_2 exists in many polymorphic forms (such as α, β, γ, and δ), which are different because the basic unit [MnO_6] octahedra are linked in different ways. Among them, γ-MnO_2 is the best known as an electrode material by the battery industry [5]. Recently, one-dimensional (1D) nanostructures have received considerable interest due to their diverse properties different from their bulk counterparts, such as high catalytic performance [6,7], high specific capacitance [8–10], and low magnetic transition temperature [11]. Different methods have been developed to synthesize 1D MnO_2 nanostructures. Wang and Li [12–14] have reported the hydrothermal synthesis of α- and β-MnO_2 nanowires/nanorods through the oxidation reaction of $MnSO_4$ by $(NH_4)_2S_2O_8$ or $KMnO_4$. Zheng et al. [15] have prepared β-MnO_2 nanotubes by a simple hydrothermal method through oxidizing $MnSO_4$ with $NaClO_3$ in the presence of poly(vinyl pyrrolidone). Wu et al. [16] have synthesized MnO_2 nanowires and nanotubes by cyclic voltammetric electrodeposition. Li et al. [17] have developed a solution-based catalytic route to fabricate α-MnO_2 hierarchical structures and β-MnO_2 nanorods and a coordination-polymer-precursor route to prepare γ-MnO_2 nanowires. In recent years, much attention has been paid to the synthesis of MnO_2 nanowires using commercial MnO_2 as raw material in water or ammonia solution [18,19]. Herein, we report a facile approach for the synthesis of γ-MnO_2 single-crystalline

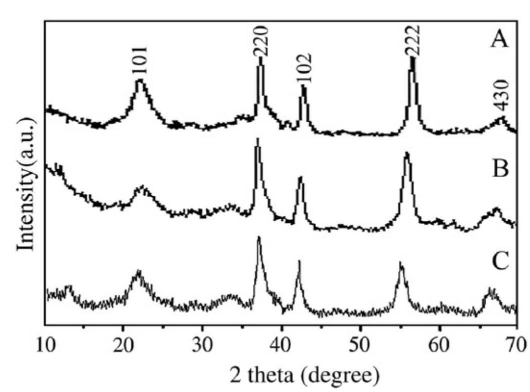

Fig. 1. XRD patterns of the initial MnO_2 precursor and the resulting products. (A) The initial MnO_2 precursor; (B) MnO_2 nanobelts synthesized at 180 °C for 48 h in NaOH aqueous solution; (C) MnO_2 nanowires synthesized at 180 °C for 96 h in LiOH aqueous solution.

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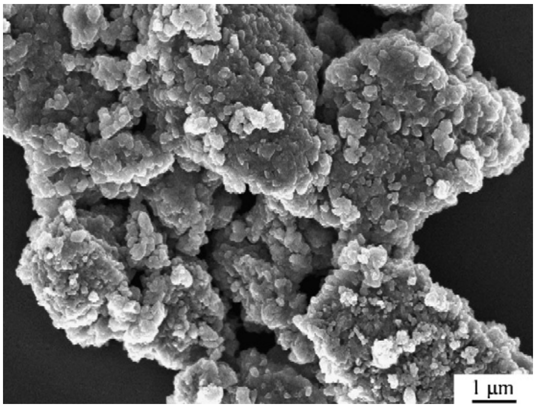

Fig. 2. SEM image of the commercial γ-MnO_2 powder before hydrothermal treatment.

nanobelts by hydrothermal treatment of commercial γ-MnO_2 in NaOH aqueous solution.

2. Experimental

2.1. Synthesis of γ-MnO_2 single-crystalline nanobelts

All the reagents used in our experiment are of analytical purity and are used without further purification. In a typical procedure, 1 mmol commercial γ-MnO_2 and 1 mmol NaOH were added into 50 mL distilled water. Then the solution was placed in a 100 mL autoclave with a teflon liner. The autoclave was maintained at 180 °C for 48 h, and then air cooled to room temperature. The resulting precipitates were collected and washed with distilled water several times, and then dried in air at 60 °C for 10 h.

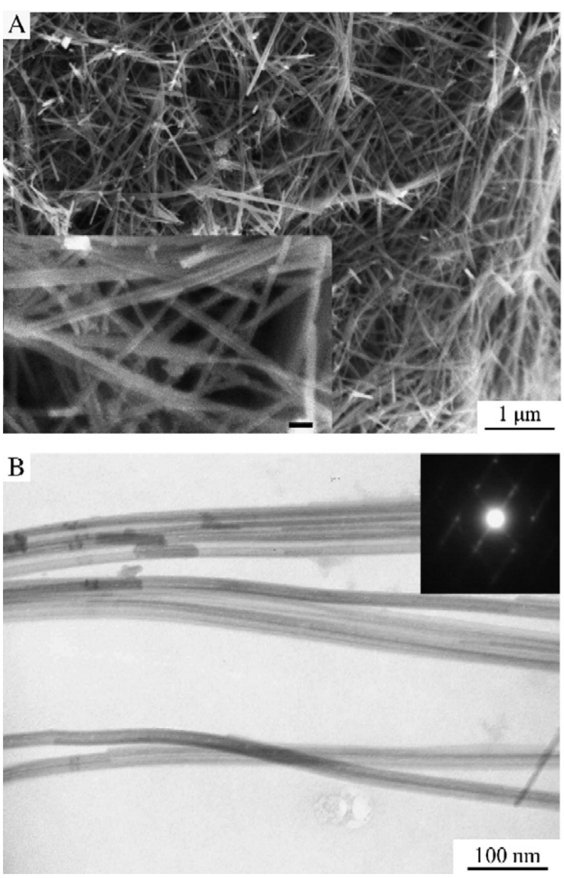

Fig. 3. SEM (A) and TEM (B) images of γ-MnO_2 single-crystalline nanobelts synthesized at 180 °C for 48 h in NaOH aqueous solution. The insets in A and B show a high magnification SEM image (scale bar = 100 nm) and a typical ED pattern taken from an individual nanobelt, respectively.

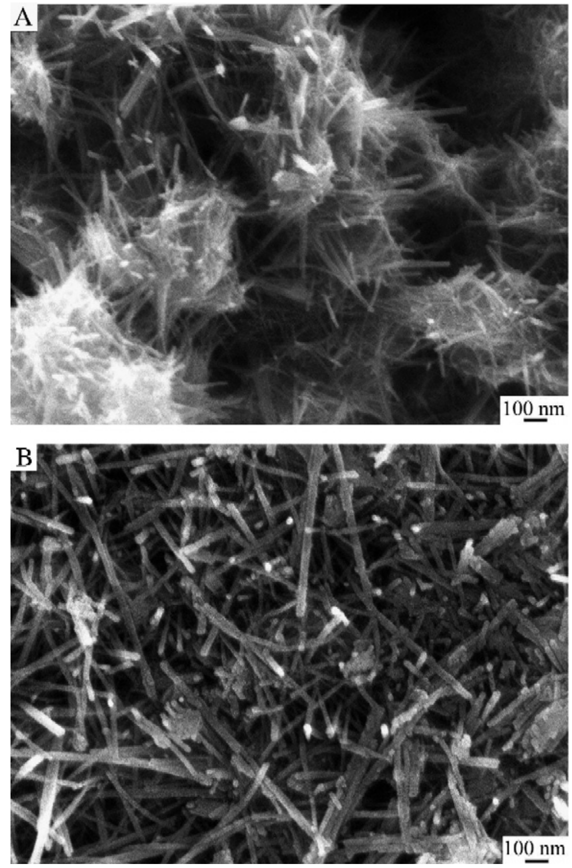

Fig. 4. SEM images of MnO_2 nanostructures synthesized under different conditions in NaOH aqueous solution. (A) 180 °C, 24 h and (B) 160 °C, 48 h.

2.2. Characterization

The crystal structures of the initial γ-MnO_2 precursor and the resulting products were characterized by an X-ray diffractometer (XRD, Rigaku D-max-γA XRD with Cu Kα radiation, $\lambda = 1.54178$ Å). The morphologies and sizes of the resulting products were observed by field-emission scanning electron microscopy (FE-SEM, JSM 6700F) and transmission electron microcopy (JEM-2000EX).

3. Results and discussion

Typical XRD patterns of the initial MnO_2 precursor and the resulting products are presented in Fig. 1. All the diffraction peaks in Fig. 1 can be indexed to the hexagonal γ-MnO_2 phase with lattice constants of $a = 9.66$ Å, and $c = 4.45$ Å [5,18]. No α, β-MnO_2 and MnOOH exist in the resulting products. The results reveal that the crystal structure of γ-MnO_2 is not changed before and after hydrothermal treatment in NaOH or LiOH aqueous solution.