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Letter

Morphology-controlled synthesis and characterization of $MnWO_4$ nanocrystals via a facile, additive-free hydrothermal process

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A B S T R A C T

Single-crystal $MnWO_4$ nanowires were successfully prepared for the first time via a simple hydrothermal method without any surfactants. The as-prepared products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution transmission electron microscopy (HRTEM). The effect of pH value, precursor, and reaction temperature on the formation of $MnWO_4$ nanocrystals was investigated. The precursor was found to be vital to the formation of $MnWO_4$ nanowires. It is rational to expect that one-dimensional nanostructures of other tungstates may also be synthesized by this simple method.

1. Introduction

One-dimensional nanostructures, such as nanowires, nanorods, nanotubes, have attracted a lot of attention because of their promising applications in physics and fabrication of nanoscale electronic and photonic devices [1–4]. One-dimensional nanostructures are the lowest dimensional anisotropic structures that can be used for the efficient transport of electrons and optical excitations [5]. Therefore, the ability to precisely prepare one-dimensional nanostructures is an important goal of materials science. Recently, manganese tungstate ($MnWO_4$) has been extensively explored because of its potential applications in photocatalysts, optical fibers, humidity sensors, photoluminescence and multiferroic materials [6–8]. Up to date, $MnWO_4$ crystallites with different morphologies, such as nanoplates, nanoflowers, nanococoons, nanoparticles, nanorods, and nanofibres [9–16], have been successfully prepared. However, it is still a significant challenge for material researchers to synthesize $MnWO_4$ nanowires. Although $MnWO_4$ nanowires have been successfully prepared by the assistance of a polycarbonate template [17], the obtained $MnWO_4$ nanowires were polycrystalline.

In this paper, we report the morphology-controlled synthesis of single-crystal $MnWO_4$ nanowires by a simple hydrothermal method without any templates or surfactants, which would be of fundamental importance in investigating the correlation between morphology and basic physical properties. Furthermore, the effect of pH value, precursor, and reaction temperature on the formation of $MnWO_4$ nanocrystals was studied. To the best of our knowledge, this is the first time that single-crystal $MnWO_4$ nanowires have been reported.

2. Experimental

All the chemicals were analytical grade purity. In a typical experiment, Na_2WO_4, $MnCl_2$, K_2CO_3, and KOH were used as the starting materials. Firstly, equimolar amounts Na_2WO_4 and $MnCl_2$ were separately dissolved in distilled water to form aqueous solutions. Then, the Na_2WO_4 solution was slowly added to $MnCl_2$ solution by constant stirring. Finally, the mixed precipitate solution was transferred into a 50 ml stainless-steel autoclave for a hydrothermal treatment. The autoclave was sealed, heated to 150 °C and held for 3 h, and then cooled to room temperature naturally. The resultant precipitates were centrifuged, washed with distilled water, and dried naturally for characterization. The effect of precursors and pH values of Na_2WO_4 solution on the formation of $MnWO_4$ was investigated. The pH value of Na_2WO_4 solution was adjusted to 14 and 7, respectively. In addition, the effect of $C_{14}H_{10}MnO_4$ and $MnCO_3$ as precursors on the formation of $MnWO_4$ crystals was also investigated. Especially, the present precursor $MnCO_3$ was prepared by the hydrothermal method at 120 °C for 3 h using K_2CO_3 and MnC_2O_4 as raw materials. And other reaction conditions were unchanged.

X-ray diffraction was performed on an X-ray diffractometer (D8 Focus, Germany) using CuKα radiation. Transmission electron microscope (TEM) images were taken with a JEOL, 200CX TEM by using an acceleration voltage of 160 kV. High-resolution TEM (HRTEM) images were obtained on a JEOL-2010 HRTEM using an acceleration voltage of 200 kV.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples synthesized by the hydrothermal method using $MnCl_2$ and Na_2WO_4 as precursors at 150 °C for 3 h with different pH values. As displayed in Fig. 1a, there is no $MnWO_4$ phase to come into being in the case of pH5. When the pH value was increased to 7 and 14, all the diffraction peaks can be indexed to a pure phase $MnWO_4$ with a monoclinic structure, which is in good agreement with the literature value (JCPDS: 13–0434). The sharp diffraction peaks suggest that well-

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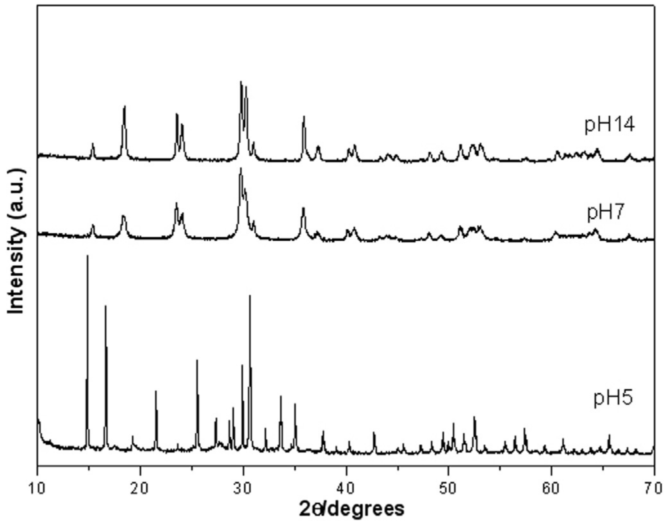

Fig. 1. Powder X-Ray diffraction patterns of the as-prepared samples prepared by the hydrothermal method using $MnCl_2$ and Na_2WO_4 as precursors at 150 °C for 3 h with different pH values: (a)5, (b)7, and (c)14, respectively.

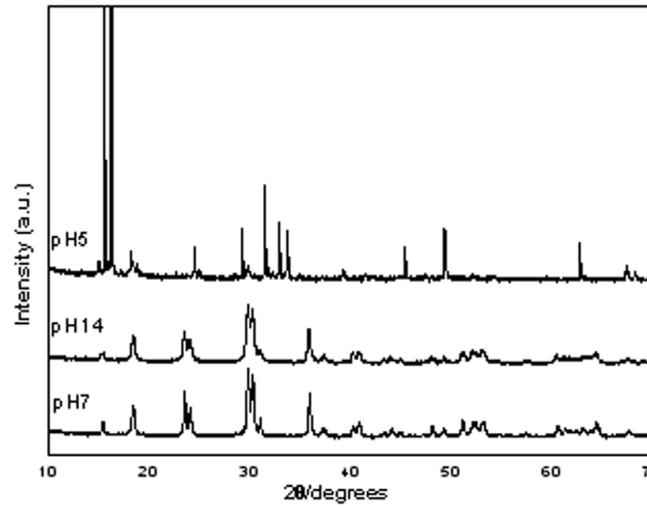

Fig. 3. Powder X-Ray diffraction patterns of the as-prepared samples synthesized by the hydrothermal method using $C_{14}H_{10}MnO_4$ and Na_2WO_4 as precursors at 150 °C for 3 h with different pH values: (a)5, (b)7, and (c)14, respectively.

crystallized $MnWO_4$ crystallites could be easily obtained by the present hydrothermal process.

Fig. 2 illustrates the TEM images of the $MnWO_4$ samples synthesized by the hydrothermal method using $MnCl_2$ and Na_2WO_4 as precursors at 150 °C for 3 h with different pH values. In the case of pH7 (Fig. 2a), it shows that the particles are uniformly distributed and exhibit a rod like structure with lengths of 50 nm and widths of 20 nm. As displayed in Fig. 2b, increasing the pH values would promote the evolution and growth of the $MnWO_4$ nanorods. The rod-like shape of the as-prepared $MnWO_4$ is similar to that of the $MnWO_4$ nanorods obtained by Almeida et al. [12,13].

The effect of pH values on the formation of $MnWO_4$ crystals was investigated, and $C_{14}H_{10}MnO_4$ and Na_2WO_4 were used as precursors by the hydrothermal method. As illustrated in Fig. 3a, almost no phase of $MnWO_4$ could be detected in the case of pH5. Combined with the above XRD results (Fig. 1a), it is found that acid condition would not favor the formation of $MnWO_4$ phase in the present hydrothermal process. When the pH value was increased to 7 and 14, as shown in Fig. 3b and c, all the diffraction peaks could be readily assigned to a pure phase of well-crystallized $MnWO_4$ with a monoclinic structure, well consistent with the literature data (JCPDS: 13–0434). Fig. 4 depicts the corresponding TEM image of the $MnWO_4$ crystals obtained by the hydrothermal method using $C_{14}H_{10}MnO_4$ and Na_2WO_4 as precursors. As shown in Fig. 4a,b, the as-prepared $MnWO_4$ powders consist of uniform rod-like particles when pH value was 7 and 14, respectively. The shape of the resultant $MnWO_4$ crystals is similar to that of the results in Fig. 2a,b, indicating that the precrusors $MnCl_2$ and $C_{14}H_{10}MnO_4$ bring similar influence on the crystallization and evolution of $MnWO_4$ crystals.

The influence of precursors on the formation of $MnWO_4$ crystals was further investigated. In the present experiment, $MnCO_3$ powders were first prepared. Fig. 5a shows the representative XRD patterns of the samples prepared by the hydrothermal method at 120 °C for 3 h using K_2CO_3 and MnC_2O_4 as raw materials. All the diffraction peaks can be perfectly indexed to the pure rhombohedral phase of $MnCO_3$ (JCPDS Card No. 44–1472). Fig. 5b,c displays the representative XRD patterns of the samples prepared by the hydrothermal method using Na_2WO_4 and the obtained $MnCO_3$ powders as precursors at 150 °C for 3 h with different pH values. All the diffraction peaks can be indexed to the monoclinic structure of $MnWO_4$, matching well the reported data (JCPDS: 13–0434). No peaks of impurities, such as $MnCO_3$, could be detected in the patterns, revealing that the high purity of monoclinic phase $MnWO_4$ could be successfully synthesized using $MnCO_3$ and Na_2WO_4 as precursors. Furthermore, the relative intensity of the reflection of (100) was much stronger than that of bulk materials in the JCPDS card (JCPDS: 13–0434). Such phenomenon suggests that the as-synthesized $MnWO_4$ crystals have a preferred orientation along the (100) planes, which was further demonstrated below by high-resolution transmission electron microscope (HRTEM).

Fig. 6 displays the TEM images of the $MnWO_4$ samples

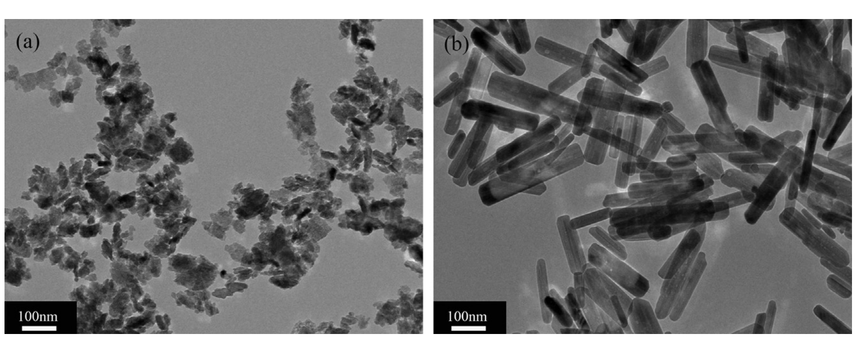

Fig. 2. TEM images of the as-prepared $MnWO_4$ samples prepared by the hydrothermal method using $MnCl_2$ and Na_2WO_4 as precursors at 150 °C for 3 h with different pH values: (a) 7 and (b)14, respectively.