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ARTICLE

Facile Hydrothermal Synthesis of MnOOH Nanorods and Their Application

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Abstract: Single crystal manganese oxyhydroxide (MnOOH) nanorods were prepared under the condition of no extra template or surfactant by a simple hydrothermal route using potassium permanganate ($KMnO_4$) as Mn source, water and N-methyl pyrrolidone (NMP) as mixed solvent. By adjusting the reaction temperature, reaction time and the volume ratio of H_2O/NMP, MnOOH nanorods with lengths up to 20 μm and square cross-sections of edge lengths in the range of 50~400 nm were be facilely prepared. The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and Fourier transformed infrared spectroscopy (FTIR). The formation mechanism of MnOOH nanorods was preliminarily discussed based on the Ostwald's ripening process. Furthermore, Mn_2O_3 nanorods were obtained by calcination of MnOOH nanorods. Results show that the morphologies of MnOOH nanorods and Mn_2O_3 nanorods are almost the same.

Key words: manganese oxyhydroxide; Mn_2O_3; synthesis; nanorod

Manganese oxyhydroxide (MnOOH) has drawn great attention due to its potential applications in catalysts for redox reactions[1,2]. Meanwhile, it can be easily transformed into several different manganese oxides, such as Mn_3O_4[3,4], MnO_2[5,6], and Mn_2O_3[5], which find potential applications in catalysis and supercapacitors[6-8]. Many methods including solvothermal/hydrothermal routes[9-11], electro-chemical deposition[2,12], and solution-based routes[13-15], have been explored to synthesize the MnOOH with various morphologies, such as branched architectures[10,16], microrods or nanorods[3,17,18], nanowires[15,19,20], multi-pods[11,21], fibers[22,23], and nanowhiskers[24]. Although a great deal of effort has been made and some successes have been achieved, the synthesis of MnOOH with controllable phase, shape, and size, especially the preparation of one-dimensional (1D) MnOOH in a controlled way still faces a big challenge for the material scientists. Moreover, the performance of MnOOH in many fields could be potentially enhanced by processing MnOOH into 1D nanostructure[1,2,15]. In the present paper, we reported the synthesis of MnOOH nanorods by a simple hydrothermal route under mild conditions based on the redox between $KMnO_4$ and NMP without extra surfactant or template. The NMP, a kind of water-soluble compound, is not only reactant, but also crystal growth modifier. MnOOH nanorods were achieved by simply tuning the hydrothermal reaction conditions including the volume ratio of H_2O/NMP, reaction temperature and reaction time. The experiment results showed that the volume ratio of H_2O/NMP, reaction temperature and reaction time were crucial factors in determining the morphologies of final products. The formation mechanism of MnOOH nanorods was preliminarily discussed based on the Ostwald's ripening process. Furthermore, uniform Mn_2O_3 nanorods were achieved by calcination of MnOOH nanorods at 500 °C.

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1 Experiment

Potassium permanganate ($KMnO_4$, AR), N-methyl pyrrolidone (NMP), and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. The water used in the whole experiment was thrice-distilled water.

MnOOH nanorods were synthesized via a facile hydrothermal process as follows. 0.20 g of $KMnO_4$ was dissolved in the mixture of NMP and thrice-distilled water (the total volume of the mixture was 15.0 mL). After stirring vigorously, the resultant system was transferred to a 25 mL Teflon-lined pressure vessel, stainless steel autoclave. The autoclave was sealed and heated in an oven at a given temperature for different time. The reaction time was varied from 2 h to 36 h in order to optimize the morphologies of the samples. The pressure vessel was allowed to cool to room temperature naturally after the dwell time. The precipitate was collected by centrifugation and washed with water and ethanol for several times, and then the precipitate was dried in air.

MnOOH nanorods obtained from the above hydrothermal process were put into a crucible, and then, it was transferred into a muffle furnace. The temperature of muffle furnace was raised to 500 °C and held for 4 h. Finally, the black powder was collected.

XRD analyses were performed on a Bruker D8 Advance diffractometer with Cu Kα radiation. SEM images were obtained with a HITACHI-3400s. TEM images were observed on a Tecnai-12 transmission electron microscopy operating at 120 kV. HRTEM characterization was performed with a FEI Tecnai G2 F30 S-TWIN field-emission transmission electron microscopy operating at 300 kV. FTIR spectrum was obtained using a Nicolet 200 Model Fourier transformed infrared spectroscopy at ambient temperature.

2 Results and Discussion

2.1 XRD of MnOOH nanorods

A typical XRD pattern of as-prepared MnOOH nanorods is shown in Fig.1. The sharpness of the peaks implies that the sample is well crystallized. All of the reflections in Fig.1 can be readily indexed to a monoclinic phase of MnOOH with lattice constants a = 0.530 nm, b = 0.527 nm, and c = 0.530 nm, which are compatible with literature values (JCPDS No. 41-1379)[9,17,20]. And no peak of impurities could be found from this pattern. The XRD result preliminarily indicates that high purity MnOOH nanorods can be obtained through the hydrothermal route based on the redox between $KMnO_4$ and NMP in water.

2.2 Microstructure and morphology of MnOOH nanorods

The overview morphology of as-prepared MnOOH is shown in Fig.2a, which indicates that the sample is composed of a large quantity of MnOOH nanorods with lengths up to around 20 μm. It is interestingly observed that an individual MnOOH nanorod owns a cross-section of square shape. Fig.2b shows a typical TEM image of as-prepared MnOOH nanorods. As shown in Fig.2b, MnOOH nanorods with high aspect ratios are obtained on a large scale. Their diameter are 50~400 nm and the lengths is up to 15 μm. To further analyze the structure of MnOOH nanorods, we have obtained HRTEM image of a single nanorod as shown in Fig.2c. The inset in Fig.2c shows the enlarged view of the square region to identify the lattice planes of formed MnOOH nanorods. The lattice fringe is clearly seen in Fig.2c, indicating that the nanorod is well crystallized. The spacings of the neighboring lattice fringes are found to be 0.225 and 0.287 nm, which correspond to

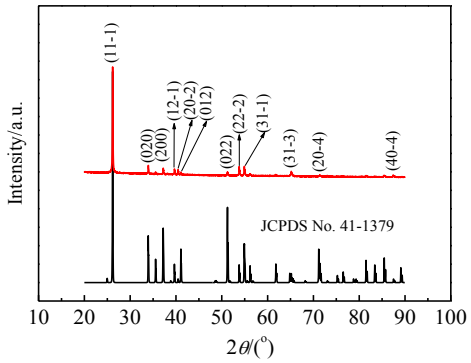

Fig.1 XRD pattern of MnOOH nanorods

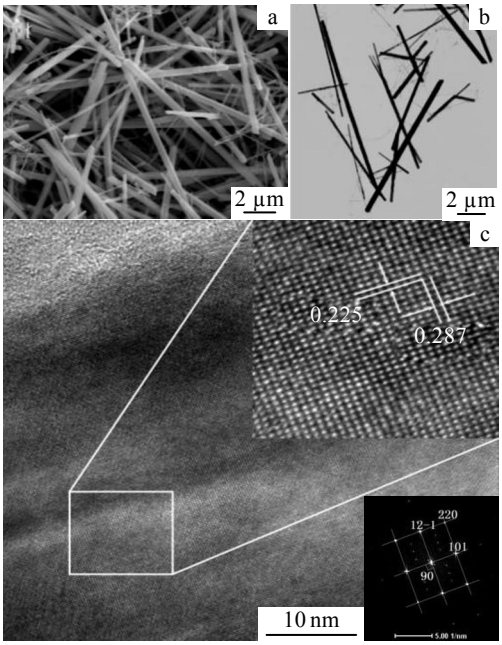

Fig.2 SEM image (a), TEM image (b), HRTEM image and FFT pattern (c) for MnOOH nanorods synthesized at 120 °C with the volume ratio H_2O/NMP of 14.0