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Nucleation site and mechanism leading to growth of bulk-quantity Mn_3O_4 nanorods

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We report a simple and effective method for the generation of bulk-quantity nanorods of manganese oxide, Mn_3O_4, under surroundings of a suitable surfactant and alkaline solution. It is found that the Mn_3O_4 nanorod is smooth, straight, and that the geometrical shape is structurally perfect, which is produced with lengths from several hundreds nanometers to a few micrometers, and diameters range from 10 nm to 30 nm. We amazedly found that the dripping speed of the NaOH solution plays an important role in formation of bulk-quantity Mn_3O_4 nanorods. The difference of dripping speed of the NaOH solution leads to a large difference of Mn_3O_4 morphologies, which is observed in the transmission electron microscopy images. The growth of the Mn_3O_4 nanorods is suggested first to follow a self-catalyzed solution-liquid-solid mechanism. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1923753]

One-dimensional nanostructures have stimulated great interest among materials scientists because of their peculiar properties and potential applications.[1] Considerable efforts have been devoted to report on the bulk-quantity synthesis of nanorods or nanowires using arc discharge,[2] laser ablation,[3] template,[4] solution,[5] vapor-liquid-solid,[6] and other methods.[7] Artificial nanostructured materials have potential technical applications because of their distinctive optical, mechanical, electrical, acoustic, and magnetic properties.[8] Manganese oxide is an important catalyst for removing carbon monoxide and nitrogen oxide from waste gas, and is also used to produce soft magnetic materials such as manganese zinc ferrite.[9] Various manganese oxides have aroused attention due to their catalysis, ion-exchange, electrochemical, molecular adsorption, and magnetic properties. These materials have also attracted interest recently as an electrochromic material of anodic coloration since they have a reversible color change from brown (colored state) to yellow (bleached state).[10]

Mn_3O_4 is known to be an active catalyst in several oxidations and reductions, and can be used as a catalyst for the oxidation of methane and carbon monoxide[11] or the selective reduction of nitrobenzene.[12] More important, catalytic applications of different polymorphs of Mn_3O_4 (hausmannite) (Ref. 13) have been extended to the combustion of organic compounds at temperatures of the order of 373–773 K. These combustion catalytic technologies are of interest in relation to several air-pollution problems, allowing the limitation of the emission of NO_x and volatile organic compounds from waste gases of different origins.[14] The discovery of Mn_3O_4 nanorods may provide us with another kind of manganese oxide with different characteristics.

Mn_3O_4 nanorods were prepared by chemical liquid homogeneous precipitation method, which has been employed to synthesize this nanorod by chemical reaction processes using reactants: $MnCl_2 \cdot 4H_2O$, NaOH, and H_2O_2. Here, the H_2O_2 solution was used as an oxidant, and a surfactant, $C_{18}H_{29}NaO_3S$, was added to the reaction mixture to prevent the growing of nanoparticles. The fabrication can be described in detail as follows: An appropriate amount of $MnCl_2 \cdot 4H_2O$ was dissolved in distilled water, 2.5 M H_2O_2 solution, and an appropriate amount of surfactant $C_{18}H_{29}NaO_3S$ were added to the $MnCl_2$ solution, respectively. Then, 2.5 M NaOH solution was dripped into the above system quickly or very slowly, respectively. The heating temperature was set at 200 °C for the chemical reaction and the growth of Mn_3O_4 nanocrystals. After the reaction, the solution became a suspension, immovably keeping it for 2 h, the precipitation occurred. The reaction equation is:

$$3MnCl_2 + H_2O_2 + 6NaOH \rightarrow Mn_3O_4 + 6NaCl + 4H_2O.$$

The precipitation was separated and dried at 100 °C. After grinding, it was put into a muffle furnace for heating at 200 °C for 2 h, and a pure Mn_3O_4 black powder was obtained.

Raman scattering measurements were obtained by backscattering geometry with a SPEX-1403 laser Raman spectrometer. The excitation source was an argon-ion laser operated at a wavelength of 514.5 nm in the backscattering configuration and a low incident power to avoid thermal effects. X-ray diffraction (XRD) was performed with a Philips X'pert diffractometer using Cu $K\alpha$ radiation (1.5418 Å) in reflection geometry. Proportional counter with an operating voltage of 40 kV and a current of 40 mA was used. XRD patterns were recorded at a scanning rate of $0.05°/s^{-1}$ in the 2θ ranges from 15 to 65°. A Philips CM20 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV was used to determine the grain size distribution of the Mn_3O_4 nanocrystals. High-resolution TEM (HRTEM) images of Mn_3O_4 nanorods were obtained with a JEOL-2010 HRTEM with a point-to-point resolution 1.94 Å operating at 200 kV, and with the energy-dispersive x-ray spectroscopy (EDS). This approach requires neither complex apparatus and sophisticated techniques nor templates, as usually needed in other methods. Our findings indicate that other nanorods or nanowires may be manipulated by using this simple technique, and might provide insight into the new opportunities to control material fabrication.

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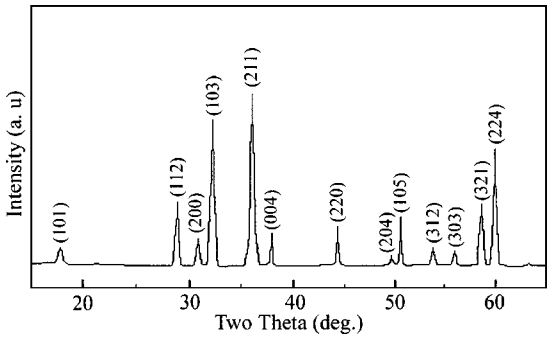

FIG. 1. A typical XRD pattern of the sample prepared by the dripping speed of the NaOH solution was faster under a heating temperature at 200 °C for 2 h, which was obtained using Cu $K\alpha$ radiation (1.5418 Å).

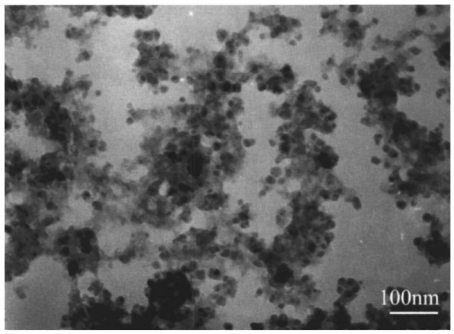

FIG. 3. A typical TEM bright-field image of clusters of Mn_3O_4 nanoparticles, where the nanoparticles formed in the dripping speed of the NaOH solution was very slow.

We amazedly found that the dripping speed of the NaOH solution plays an important role in formation of bulk-quantity Mn_3O_4 nanorods. Figure 1 shows the XRD pattern of sample prepared by the dripping speed of the NaOH solution was faster under a heating temperature at 200 °C for 2 h. All of the diffraction peaks can be indexed to the tetragonal hausmannite structure (space group: I41/amd) of Mn_3O_4 with lattice constants $a=5.762$ Å and $c=9.470$ Å, which are consistent with the standard values for bulk Mn_3O_4. No characteristic peaks of impurities, such as other forms of manganese oxides, were detected.

The TEM bright-field image [Fig. 2(a)] shows that a typical distribution in morphology for the sample prepared by the dripping speed of the NaOH solution was faster under a heating temperature at 200 °C for 2 h. It is evident that the samples consist of bulk quantity of one-dimensional nanorods with lengths from several hundreds nanometers to a few micrometers, and diameters range from 10 nm to 30 nm. TEM image reveals that the Mn_3O_4 nanorod is smooth, straight, and that the geometrical shape is structurally perfect. The chemical composition of the nanorods was determined by EDS to be close to Mn_3O_4.

HRTEM studies provide further insight into the microstructural characterizations of these Mn_3O_4 nanorods. Figure 2(b) is a typical HRTEM image of a single Mn_3O_4 nanorod with about 9 nm in width and larger than 200 nm in length. The profile of the fringes implies that the geometrical shape of this nanostructure is likely to be a nanorod, where the smooth and straight of the nanorod is evident. With a change in the dripping speed of the NaOH solution, a large difference was observed in the TEM images. Figure 3 shows the TEM image of Mn_3O_4 nanoparticles under the dripping speed of the NaOH solution is very slow, and the heating-temperature at 200 °C for 2 h as compared to Fig. 2(a). This indicates the dripping speed of the NaOH solution is a crucial factor in the preparation of Mn_3O_4 nanorods. It determines the chemical reaction rate, which has important effect on the growth of the Mn_3O_4 nanorods. As seen in Fig. 3, there are many small particles of a roughly spherical shape. The contrast of the particles in different regions of the TEM image indicates different densities, which may be related to the grain sizes.

Figure 4 exhibits the Raman spectra of the sample prepared by the dripping speed of the NaOH solution was faster under a heating temperature at 200 °C for 2 h. Three peaks at 657.8, 370.4, and 316.5 cm^{-1} were observed, in agreement with literature reference values for Mn_3O_4.[15] The peak at 656 cm^{-1} is characteristic of the Raman spectrum of Mn_3O_4,

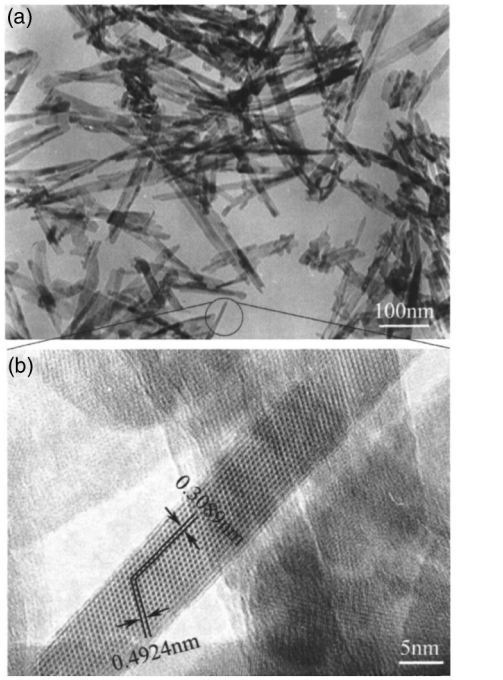

FIG. 2. (a) A typical TEM bright-field image of clusters of Mn_3O_4 nanorods. (b) An HRTEM image of the single Mn_3O_4 nanorod shown in (a), where the nanorod formed in the dripping speed of the NaOH solution was faster under a heating temperature at 200 °C for 2 h.

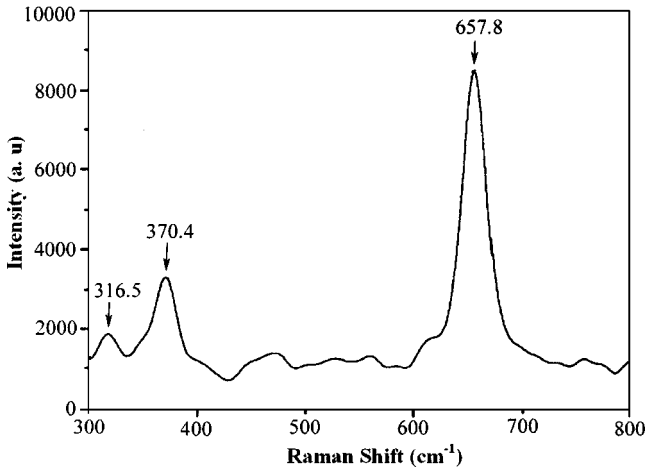

FIG. 4. Raman spectra of Mn_3O_4 nanorods, which was prepared by the dripping speed of the NaOH solution, was faster under heating temperature at 200 °C for 2 h.

which was found on mineralogical hausmannite, as well as the chemically prepared sample or commercial powder. This peak was typical of a spinel structure.

The formation process of the Mn_3O_4 nanorods could be divided into two stages from a chemical reaction point of view. In the first stage, the starting materials $MnCl_2$ and H_2O_2 were dispersed into the surroundings of a suitable surfactant. In the second stage, $MnCl_2$ was oxidized by H_2O_2 to Mn_3O_4 in a suitable alkaline solution. Here, the appropriate concentration NaOH solution was introduced into the above system. Although the chemical reaction was rather simple, the formation of the Mn_3O_4 nanorod would involve a very complicated process, because the nanorods can only be formed under a faster dripping speed of the NaOH solution. We can reasonably speculate about the Mn_3O_4 nanorod formation process as follows: The $MnCl_2$ is carried by the processing surfactants and contacts H_2O_2 under a heating temperature at 200 °C, where it deposits in the form of a liquid droplet. The liquidized $MnCl_2$ then reacts with H_2O_2—when the NaOH solution is dripped quickly into the system—and forms Mn_3O_4, which further serves as some seeds (nucleation sites) for Mn_3O_4 nanorod growth. The above growth is most likely to be controlled by the solution-liquid-solid (SLS) mechanisms.[16] However, interestingly, in the present SLS growth of the Mn_3O_4 nanorods, no additional transition metals are added as catalysts; it is, therefore, proposed first that the formation of the Mn_3O_4 nanorods undergoes a self-catalyzed SLS growth process. The $MnCl_2$ not only acts as the reactant but also provides an energetically favored site for the oxidation of H_2O_2. The newly formed Mn_3O_4 functions as a nanorod seed, which further grows to an Mn_3O_4 nanorod in the presence of $MnCl_2$ and H_2O_2. The size and, hence, the uniformity of the Mn_3O_4 nanorods are predefined by the size of the liquid $MnCl_2$ droplets.

In conclusion, we have prepared bulk-quantity Mn_3O_4 nanorods that depend on the faster dripping speed of the NaOH solution under a heating temperature at 200 °C for 2 h. The synthetic procedures may offer the following advantageous features for the fabrication of transition metal oxide nanorods. First, this method is simple, effective, and reproducible. Second, highly crystalline nanorods are obtained directly. Third, no additional transition metals are added as catalysts for the formation of nanorods. The growth of the nanorods is suggested first to follow a self-catalyzed SLS mechanism. When suitable synthetic parameters, such as reaction temperature and time, are chosen, it is reasonable to expect that this method can be extended to obtain other transition metal oxide nanorods or nanowires.

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