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Synthesis of monodispersed single-crystal compass-shaped Mn_3O_4 via gamma-ray irradiation

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Abstract

Monodispersed and uniform single-crystal compass-shaped (80 nm in middle width and 200 nm in length) Mn_3O_4 (hausmannite) have been successfully prepared in a surfactant solution system by a simple reduction–oxidation method at room temperature and under ambient pressure. The reactions contain two steps: first, Mn^{2+} is reduced into Mn atoms by γ-ray irradiation; then, Mn atoms are oxidized into Mn_3O_4 in air. The possible growth mechanism has also been proposed.

Keywords: Nanocrystals; Compass-shaped; Raman spectrum

1. Introduction

Metal-oxide nanocrystals are expected to find useful applications in catalysis, energy storage, magnetic data storage, sensors, and ferrofluids [1–4]. In particular, manganese oxides are important materials due to their wide-range applications, such as high-density magnetic storage media, catalysts, ion exchange, molecular adsorption, electrochemical materials, varistors and solar energy transformation [5–11]. One of the manganese oxides, Mn_3O_4, has been widely used as the main source of ferrite materials, which have extensive application in electronic and information technologies. This material has also attracted interest as an active catalyst for the reduction of nitrobenzene or oxidation of methane [12–14]. Most of the applications require pure and well-dispersed chemically stable nanoparticles of Mn_3O_4 having a uniform size and shape [15].

Mn_3O_4 is often synthesized by high-temperature calcinations (at about 1000 °C) of all oxides, hydroxides, hydroxyoxides, or oxysalts of manganese [16]. Low-temperature approaches mainly include sol–gel process and controlled oxidation of aqueous suspension of $Mn(OH)_2$ [17]. Recently, Zhang and co-workers have reported a low-temperature solvothermal method to synthesize nanocrystalline Mn_3O_4 [18]. Wang and co-workers have synthesized single-crystal Mn_3O_4 nanowires in NaCl flux at 850 °C [19]. Yang and co-workers have reported a one-step low-temperature alcohol–water thermal route to synthesize one-dimensional (1-D) Mn_3O_4 nanorods at 140 °C [20].

Herein, we provide a novel approach to prepare monodispersed and uniform single-crystal compass-shaped Mn_3O_4 nanocrystals in a surfactant solution through a simple reduction–oxidation method at room temperature and under ambient pressure by γ-ray.

2. Experimental details

In a typical experiment, analytically pure $MnSO_4 \cdot H_2O$ (0.846 g) and cetyltrimethylammonium bromide (CTAB 2.0 g) were dissolved into 50 ml distilled water under intensive stirring for 0.5 h at room temperature. To scavenge some oxidative radicals such as •OH produced during γ-ray irradiation and maintain the reductive atmosphere of the system, isopropyl alcohol (15 ml), a scavenger of oxidative radicals, was also added into the system. Then the mixed solution was irradiated in a field of 2.22×10^{15} Bq ^{60}Co γ-ray source with an absorption

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dose of 80 kGy at a dose rate of 50 Gy/min. After irradiation, the produced black precipitates were collected by centrifugalized emulsion, placed in air for 24 h, washed with distilled water and ethanol several times, and dried in air at room temperature. The yield of the reaction is 0.238 g and the conversion ratio of the reaction is about 20%.

3. Results and discussion

The phase of the as-prepared product was identified by X-ray powder diffraction (XRD) pattern, shown in Fig. 1. XRD pattern was recorded by a Philip X'Pert PRO SUPER γA rotation anode with Cu Kα radiation (λ=1.54187 Å) at 25 °C. In each XRD pattern, all the reflection peaks can be indexed to that of the corresponding pure phases tetragonal hausmannite Mn_3O_4 (JCPDS card 01-1127, a=5.75 Å and c=9.42 Å). However, since the XRD patterns of γ-Mn_2O_3 and Mn_3O_4 are very similar, it is difficult to distinguish the two phases simply from XRD patterns.

In order to make sure no impurity such as γ-Mn_2O_3 in products, more convincing evidence of pure Mn_3O_4 is provided by the Raman spectrum (Fig. 2). Raman spectrum was recorded at room temperature with a LABRAM-HR Confocal Laser MicroRaman Spectrometer. The Raman spectrum of the product is clearly with three peaks at 314.6, 363.8 and 653.5 cm^{-1}, which is the characteristic signature of hausmannite Mn_3O_4, thus indicating the formation of well-crystallized Mn_3O_4 [21].

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the sample are shown in Fig. 3. TEM images were taken on a Hitachi Model H-800 instrument with a tungsten filament using an accelerating voltage of 200 kV and the HRTEM image was recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. TEM images (at low magnification Fig. 3a and at high magnification in Fig. 3b) reveal that the sample consists entirely of monodispersed and uniform compass shape with 80 nm in middle width and 200 nm in length. Fig. 3c shows a representative HRTEM image of a single nanocompass. The clear lattice fringes further confirm that the nanocompass is a single crystal. The fringe spacing is about 0.49 nm, which is close to the separation between the (101) lattice planes. This means that the axial direction of the as-prepared nanocompasses is perpendicular to the normal direction of the (101) lattice plane of the tetragonal hausmannite Mn_3O_4. Electron diffraction (ED) pattern (inset in Fig. 3c) obtained from a single nanocompass also confirms that the as-prepared products are

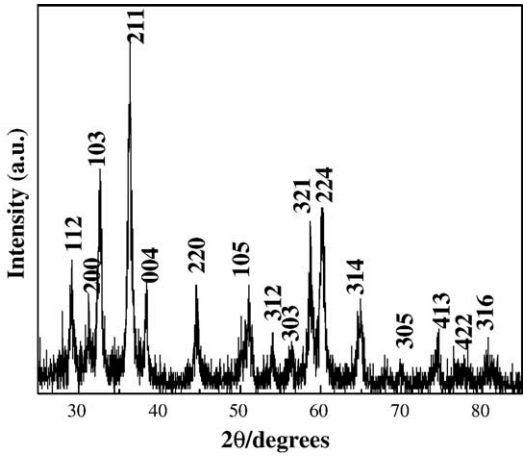

Fig. 1. XRD pattern of the as-prepared compass-shaped Mn_3O_4.

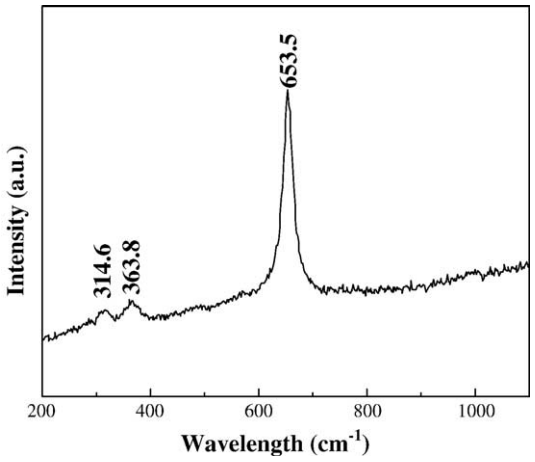

Fig. 2. Raman spectrum of the as-prepared compass-shaped Mn_3O_4.

single crystals of tetragonal hausmannite Mn_3O_4, which is in agreement with the XRD pattern result.

A possible formation process of the compass-shaped Mn_3O_4 nanocrystals was suggested according to the designed route. First, many active products were generated during the radiolysis of water:

$$H_2O \rightsquigarrow e^-_{aq},\ H_3O^+,\ H\bullet,\ H_2,\ \bullet OH,\ H_2O_2. \quad (1)$$

Here, the symbol ($\rightsquigarrow$) stands for irradiation and e^-_{aq} represents hydrated electron. Among these active products, the hydrated

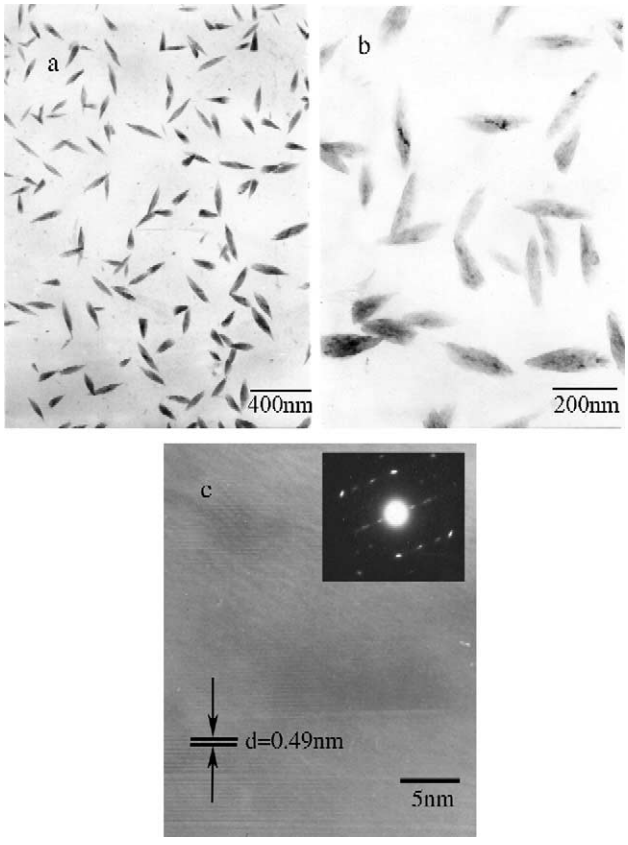

Fig. 3. TEM images of the as-prepared compass-shaped Mn_3O_4 (a) at low magnification and (b) at high magnification. (c) HRTEM image of a single as-prepared Mn_3O_4 nanocompass.

electron and the hydrogen atom were strong reductive particles. They could reduce Mn^{2+} into Mn atoms. Meanwhile, some oxidative particles such as hydroxyl radicals could prevent the Mn atoms from producing and must be scavenged, so isopropyl alcohol was introduced into the system. Although the hydrogen atoms could be also scavenged by isopropyl alcohol, the reducing reaction was not affected since Mn^{2+} was reduced mainly by the hydrated electron:

$$Mn^{2+} + 2e^{-}_{aq} \rightarrow Mn. \quad (2)$$

Second, the yielded Mn atoms were very active, so they only could exist in the reducing conditions. During the reduction of Mn, a layer-shaped structure existing in the CTAB solution could be attacked only along certain directions by the hydrated electrons [22]. Thus, it was possible that the produced Mn particles had a certain shape. When these Mn particles were treated in air, they were quickly oxidized by oxygen in air. Thus, the compass-shaped Mn_3O_4 nanocrystals were obtained.

$$3Mn + 2O_2 \rightarrow Mn_3O_4. \quad (3)$$

The whole reactions were chain reactions and the whole course was in the air. Thus, the O_2 of reaction is sufficient on account of H_2O_2 decomposability and in the air. When the little yield of Mn gained, Mn was oxidized to Mn_3O_4 at once. Eqs. (2) and (3) were persistent reactions. So, the yield of the reaction was higher than the estimate.

4. Conclusion

In summary, monodispersed and uniform compass-shaped (80 nm in middle width and 200 nm in length) Mn_3O_4 nanocrystals have been successfully prepared in CTAB solution system by a simple reduction–oxidation method at room temperature and under ambient pressure. The possible growth mechanism has also been proposed. The successful preparation of Mn_3O_4 nanocompasses in large scale under mild conditions could be of interest for both applications and fundamental studies.

Acknowledgments

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