



## The effects of high magnetic field on the morphology and microwave electromagnetic properties of MnO<sub>2</sub> powder

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### ARTICLE INFO

#### Article history:

Received 11 December 2009

Received in revised form

14 April 2010

Accepted 17 April 2010

Available online 28 April 2010

#### Keywords:

Manganese dioxides

High magnetic field

Chain shape

Electromagnetic properties

### ABSTRACT

MnO<sub>2</sub> with a sea urchin-like ball chain shape was first synthesized in a high magnetic field via a simple chemical process, and a mechanism for the formation of this grain shape was discussed. The as-synthesized samples were characterized by XRD, SEM, TEM, and vector network analysis. The dielectric constant and the loss tangent clearly decreased under a magnetic field. The magnetic loss tangent and the imaginary part of the magnetic permeability increased substantially. Furthermore, the theoretically calculated values of reflection loss showed that the absorption peaks shifted to a higher frequency with increases in the magnetic field strength.

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### 1. Introduction

Shape- and size-controlled dispersible inorganic nanocrystals such as metals, semiconductors, and metal oxides, have been the subject of intensive research because of their potential applications in electronics, photonics, and catalysis [1,2]. They are also ideal subjects for research on optical, electrical, magnetic, microwave electromagnetic, mechanical properties, and the interdependence of these characteristics on morphology and size confinement [3–5]. Consequently, particles with novel shapes and sizes have become especially interesting.

In this context, manganese dioxides and their derivative compounds have attracted special attention. Their outstanding structural flexibility, in combination with their novel chemical and physical properties has paved the way for their wide use as catalysts [6], molecular sieves [7], and Li/MnO<sub>2</sub> batteries materials [8]. The different crystallographic structural forms of MnO<sub>2</sub> that exist in nature, such as the  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and other types [9], are generally believed to be responsible for their unique properties. For example, Bach et al. have pointed out that the electrochemical properties of MnO<sub>2</sub> are strongly dependent on parameters such as powder morphology, crystalline structure, or bulk density [10].

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Several research groups have investigated the MnO<sub>2</sub> with different crystalline structures. They have successfully prepared nanorods [1,11–13], nanofibers [14,15], cuneiforms [2], microspheres [16], and nanowires [17] of  $\alpha$ -MnO<sub>2</sub>,  $\beta$ -MnO<sub>2</sub>,  $\gamma$ -MnO<sub>2</sub>, and  $\delta$ -MnO<sub>2</sub>. Manganese oxide resembling a “sand rose” with large blades was synthesized by Beaudrouet [18]. Nest-like hierarchical architecture of manganese oxide was studied by Liu et al. [19]. Cheng et al. [20] synthesized a 2-D hexagonal star-like  $\beta$ -MnO<sub>2</sub>. Zhang et al. [21] obtained hollow octahedral of manganese oxides. However, most of these studies used the method of hydrothermal synthesis to obtain manganese oxides without any external field, and there are only a few research papers on the hydrothermal synthesis under the high magnetic field. One of these is by Zhong and the co-author [22], which focused only on the electrochemistry property of the prepared MnO<sub>2</sub> powder. The microwave electromagnetic characteristics of the prepared MnO<sub>2</sub> under the high magnetic field were not dealt with.

Many researchers have synthesized other materials in high magnetic field and obtained good morphology. Gong et al. [23] were able to fabricate Ni fibers of different lengths by applying external magnetic fields. Polyaniline with an open-ramified rod-like pattern was obtained under the high magnetic field by Duan [5]. External magnetic fields can therefore be viewed as important components of synthetic processes for generation of unusually shaped materials.

In the present paper, manganese oxide with the sea urchin-like ball chain shape was first synthesized in a high magnetic field, and the microwave electromagnetic characteristics of the

prepared  $\text{MnO}_2$  were also studied firstly. Moreover, a mechanism for formation of the observed grain shape by a high magnetic field was discussed.

## 2. Experimental

All chemical reagents were commercially available and were used as-received without further purification. Manganese sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) and ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) were purchased from the Dalian Shenlian Chemical Reagent, Co. (China). The procedures of a typical synthesis are described below.

### 2.1. Synthesis

A solution of  $\text{MnSO}_4$  was prepared by dissolving 5.1 g in 100 mL distilled water. The obtained solution was stirred until the solution was transparent, then 17.1 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was added and stirring was continued for another 30 min at room temperature. The transparent solution was then transferred to a glass test tube and heated at 70 °C for 4 h in a high magnetic field, at selected magnetic field strengths of 1, 3, 5 or 8 T. Subsequently, the glass test tube was allowed to cool to room temperature. The black products were filtered off, washed several times with distilled water and absolute ethanol, and then dried under vacuum at 60 °C for 24 h. The product, a black powder, was collected for characterization.

### 2.2. Characterization

Phase identifications were performed by the X-ray powder diffraction (SHIMADZU, XRD-6000, 40 kV/30 mA) with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm) in the  $2\theta$  range of 10° to 100° in steps of 0.04°, using the detector technique for measuring intensities. Microstructural features of the  $\text{MnO}_2$  were observed by electron microscopy (SEM, JSM-5600LV). Transmission electron microscope (TEM) images, high resolution TEM (HRTEM) images, and selected area electron diffraction (SAED) patterns were generated using a TECNAI G<sup>2</sup>20 S-Twin TEM.

The measurements of complex relative permittivity and permeability versus frequency were carried out by reflection/transmission technology using an Agilent 8722ES network analyzer. The as-obtained  $\text{MnO}_2$  was dispersed in molten paraffin wax, and the uniform mixtures were molded into toroid-shaped samples of 7.00 mm outer diameter and 3.00 mm inner diameter. The specimens, consisting of 30 wt%  $\text{MnO}_2$  powders, were measured at 2–18 GHz. The microwave absorption properties of the  $\text{MnO}_2$ /paraffin wax samples were calculated according to the transmit line theory.

## 3. Results and discussion

### 3.1. Morphology analysis

A series of experiments were carried out by varying the magnetic field strength, and the morphologies of the resulting  $\text{MnO}_2$  products obtained were examined by SEM and TEM. Figs. 1 and 2 show the SEM and TEM images with inserted diffraction patterns and the HRTEM images prepared in the present study. The five samples corresponding to Fig. 1 and Fig. 2 (a–e) were obtained at 70 °C for 4 h with the magnetic field strengths of 0, 1, 3, 5, and 8 T, respectively. As can be seen in Fig. 1 and 2 (a), sea urchin-like microspheres can be observed in the precipitated sample. At the magnetic field strength of 1 T, the microspheres

began to form sea urchin-like ball chain structures (Fig. 1 and 2 (b)), but this was not very pronounced. With magnetic field strengths of 3 to 8 T, the sea urchin-like ball chain pattern became more evident (Figs. 1 and 2 (c–e)). From Fig. 1, the effect of high magnetic field on the microspheres size was only slightly, but it is obvious from Fig. 2 that the particle size of the sample 3 T is smaller and more uniform than others. The inserted diffraction pattern images in Fig. 2 show that the crystallization degree of the  $\text{MnO}_2$  in a high magnetic field was improved effectively compared with that without high magnetic field. And the HRTEM images provide more detailed structural information about the stick on the surface of the micro-sphere, showing the apparent lattice fringes of the crystal. But the influence of the high magnetic field on lattice fringes of the crystal is not very evident.

One possible mechanism for the formation of the sea urchin-like ball chain shape is the following. The original sea urchin-like microspheres were arrayed randomly in the absence of a high magnetic field. Nevertheless, the microspheres arrayed themselves along a given direction under the external magnetic field (Fig. 1 (c–e)). This is because, for any kind of crystals, differences in the arrangement and the density of the atomic structure will result in differences in the magnetic susceptibilities of the same crystal at different crystallographic orientations. Small size microspheres arrayed along the direction of their maximum magnetic susceptibility (which is also along the magnetic field) were equivalent to small magnetic bodies. Consequently, they assembled to form the sea urchin-like ball chain shaped.

### 3.2. Phase structure and compositional analysis

According to Fig. 3, the  $\alpha$ - $\text{MnO}_2$  and  $\gamma$ - $\text{MnO}_2$  are the major  $\text{MnO}_2$  products, and all of the diffraction peaks can be indexed to tetragonal and orthorhombic structures (PDF# 721982, PDF# 822169, PDF# 721983 and PDF# 731539). The broadened diffraction peaks indicate that the crystalline size of the samples is small and that the crystallinity is not yet ideal. Further more, it is obvious that the crystalline nature and percentage of  $\alpha$ - and  $\gamma$ -phase  $\text{MnO}_2$  in each sample are different from the X-ray results, which show that the high magnetic field has a significant effect on the crystalline nature and the phase structure.

### 3.3. Electromagnetic properties

The complex permittivity, permeability, and their loss tangent represent the dielectric and magnetic properties of an absorbing material. The real parts ( $\epsilon'$  and  $\mu'$ ) of complex permittivity and permeability symbolize the storage capability of electric and magnetic energy. The imaginary parts ( $\epsilon''$  and  $\mu''$ ) represent the loss of electric and magnetic energy [24]. The loss tangent ( $\text{tg}\delta$ ) represents the loss properties of incidence electromagnetic wave in the microwave absorber. In terms of microwave absorption, the imaginary parts and the loss tangent are expected to be larger.

Fig. 4 shows the relatively complex permittivity and permeability of the five samples in the frequency range 2–18 GHz. As shown in Fig. 4 (a), the  $\epsilon'$  values for the five samples declined from 9.29, 9.39, 7.77, 4.64 and 5.06 to 5.26, 5.29, 5.03, 3.38 and 3.72, respectively, with increasing frequency in the 2–18 GHz range. All of the  $\epsilon''$  values for the five samples also exhibited a decrease from 3.43, 3.72, 2.54, 0.93 and 1.04 to 2.20, 2.27, 1.64, 0.75 and 0.83, respectively, as frequency was increased from 2 to 18 GHz. Increases in magnetic field strength from 0 to 8 T resulted in decreases in  $\epsilon'$  values of the samples, except for 8 T and  $\epsilon''$  values, decreased. Fig. 4 (b) shows that the  $\mu'$  and  $\mu''$  values of samples, except for 3 and 5 T, were almost constant, with less variation throughout the whole frequency range. All  $\mu' \approx 1.04$  and

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