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One-step synthesis of Mn_3O_4 nanoparticles: Structural and magnetic study

América Vázquez-Olmos [a,*], Rocío Redón [a], Geonel Rodríguez-Gattorno [b], M. Esther Mata-Zamora [a], Francisco Morales-Leal [c], Ana L. Fernández-Osorio [d], José M. Saniger [a]

[a] *Centro de Ciencias Aplicadas y Desarrollo Tecnológico, México, DF 04510, Mexico*
[b] *Instituto de Física, México, DF 04510, Mexico*
[c] *Instituto de Investigación en Materiales, México, DF 04510, Mexico*
[d] *Facultad de Estudios Superiores, Cuautitlán-1, Universidad Nacional Autónoma de México, Coyoacán, México, DF 04510, Mexico*

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Abstract

One-step room-temperature synthesis of nanocrystalline Mn_3O_4 hausmannite, without heating posttreatment, was carried out from a simple dissolution of manganese(II) acetate in a mixture of N,N'-dimethylformamide (DMF) and water. Homogeneous nanocrystals like rods were obtained, with an average width and length of 6.6 ± 1.2 nm and 17.4 ± 4.1 nm, respectively, and a preferential growth along the $\langle 001 \rangle$ direction. Magnetization measurements on a powdered sample showed ferrimagnetic behavior at low temperatures. Under zero-field cooling (ZFC) measurement at 100 Oe, the observed blocking temperature (T_B) was 37 K.

Keywords: Nanoparticles; Hausmannite; Colloidal dispersion; Magnetic materials

1. Introduction

Manganese oxides are materials with a wide range of applications, such as batteries, catalysts, and electrochromic and magnetic materials [1–3]. In particular, Mn_3O_4 is known to be an effective and inexpensive catalyst to limit the emission of NO_x and CO, which provides a powerful method of controlling air pollution. This material has also attracted interest as an active catalyst for the reduction of nitrobenzene or oxidation of methane. It has been shown to be a corrosion-inhibiting pigment for epoxy–polyamide and epoxy–ester based primers and top coating [1,3,4]. Moreover, Mn_3O_4 has been used as one of the raw materials in the manufacture of soft magnetic materials such as manganese zinc ferrite, which is useful for magnetic cores in transformers for power supplies [5–7]. Nanometer-sized Mn_3O_4, with notable increased surface area and greatly reduced size, is expected to display better performance in these aspects of application.

Manganese oxides crystallize in several different structures with varied proportions of Mn in different oxidation states (+2, +3 and +4) [8]. Mn_3O_4 is an oxide with the normal spinel structure. The stable room-temperature phase is tetragonal hausmannite (space group $I4_1/amd$) with Mn^{3+} and Mn^{2+} ions occupying the octahedral and tetrahedral positions of the spinel structure, respectively. The octahedral symmetry is tetragonally distorted due to the Jahn–Teller effect on Mn^{3+} ions [9]. Mn_3O_4 is a model spinel compound for many experimental and theoretical investigations; however, the majority of these are related to the bulk material [8–13].

Usually, when heated to about 1000 °C in air, all oxides, hydroxides, carbonates, nitrates, and sulfates of manganese can form Mn_3O_4. In addition, it has also been re-

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[*] Corresponding author. Fax: +52 55 5622 8651.
E-mail address: amer@aleph.cinstrum.unam.mx (A. Vázquez-Olmos).

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ported that precipitated manganese dioxide can be reduced to Mn_3O_4 under a hydrogen atmosphere at 200 °C [3]. Furthermore, in the last decade, solution chemical synthesis techniques such as the sol–gel process and the solvothermal method have been employed to prepare hausmannite; however, these processes still require posttreatment at different temperatures [14]. Recently, Qian and co-workers [15] reported a one-step low-temperature (140 °C) synthesis of Mn_3O_4 nanorods in alcohol–water mixtures, using $KMnO_3$ as a starting manganese source and Na_2SO_3 as a reducing agent.

On the other hand, DMF and dimethyl sulfoxide (DMSO) have been proved to be very useful solvents in nanoparticle synthesis [16–21]. Their high dielectric constants allow charge separation, turning them into good solvents for ionic solids and polar or polarizable molecules.

Thus, herein we present a facile one-step process for the preparation of nanocrystalline Mn_3O_4 from $Mn(OAc)_2{\cdot}H_2O$ in DMF–H_2O (10%) at room temperature and its spectroscopic, structural, and magnetic study. The present contribution constitutes a very important advance in nanostructure Mn_3O_4 preparations, especially for those applications that require clean nanostructured materials.

2. Experimental

2.1. Materials

Manganese acetate tetrahydrate, $Mn(OAc)_2{\cdot}4H_2O$ (99% Aldrich), N,N'-dimethylformamide, DMF (99.8% Aldrich), and acetone, $CO(CH_3)_2$ (Fermont 99.7%), were purchased and used as received, without further purification. Ultrapure water (18 $M\Omega/cm$) was obtained from a Barnsted E-pure deionization system.

2.2. Synthesis

A quantity of 0.03063 g of $Mn(OAc)_2{\cdot}4H_2O$, was dissolved in DMF (22.5 ml) under vigorous stirring. After this, 2.5 ml of ultrapure water was added for the synthesis of colloidal Mn_3O_4 nanorods to get a final concentration of 5×10^{-3} M in 25 ml of DMF–H_2O (10%). The amber solution was stirred for a further 30 min and the resulting solution left to stand for 3 months to yield a dark brown precipitate, which was separated by centrifugation (16,000 rpm × 10 min) and washed with acetone.

2.3. Instruments

UV–visible absorption spectra, in colloidal dispersion and powder, were determined on an Ocean Optics USB2000 miniature fiber optic spectrometer. The Fourier transformed infrared (FTIR) spectroscopy was done in a Nicolet Nexus 670 FT-IR infrared spectrometer from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}, on a KBr wafer. The X-ray diffraction pattern was measured in D5000 Siemens equipment using Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å). Transmission electron microphotographs (TEM) were obtained in a JEOL 1200EXII instrument, operating at 60 kV, by deposition of a drop of the colloidal dispersion of Mn_3O_4 onto 200 mesh Cu grids coated with a carbon/collodion layer. High-resolution transmission electron microphotographs (HR-TEM) were obtained in a JEOL 2000F instrument, operating at 200 kV, using the same sample preparation as in TEM. The particle size distribution was determined from digitalized amplified micrographs by averaging the larger and smaller axis diameter measured in each particle. Morphology calculations of Mn_3O_4 crystal were done by the program SHAPE v7.1.2 (free demo from www.shapesoftware.com) based on simple geometric considerations according to Bravais–Friedel–Donnay–Harker (BFDH) methodology [22–24].

Magnetic measurements were performed on a SQUID Quantum Design magnetometer on powdered samples of Mn_3O_4 nanoparticles. The temperature was varied between 2 and 300 K according to zero-field-cooling (ZFC)/field-cooling (FC) procedure at 100 Oe, and the hysteresis loop was obtained at 5 K in a magnetic field of up to ±3 T.

3. Results and discussion

3.1. Spectroscopic study

The colloidal dispersion of Mn_3O_4 was monitored by UV–visible electronic absorption spectroscopy, as shown in Fig. 1. At the beginning the UV–visible spectrum of a freshly prepared solution of $Mn(OAc)_2{\cdot}4H_2O$ in DMF–H_2O(10%), exhibits a wide absorption band with an onset at 440 nm (Fig. 1b); 1 week later, this band becomes wider and the onset shifts to 558 nm (Fig. 1c). The spectrum remains unchanged after 3 months, when the Mn_3O_4 precipitates as a brown fine powder. The electronic absorption spectrum of the precipitate obtained by diffuse reflectance measurement (Fig. 1d) shows three well-defined regions, one going from 250 to 410 nm, another from 410 to 585 nm, and the last one finishing at 810 nm. The first portion is attributed to the allowed $O^{2-} \rightarrow Mn^{2+}$ and $O^{2-} \rightarrow Mn^{3+}$ charge transfer transitions, and the last two can be reasonably related to d–d crystal field transitions, ${}^3E_g(G) \leftarrow {}^3T_{1g}$, ${}^3A_{2g}(F) \leftarrow {}^3T_{1g}$, ${}^3A_{2g}(G) \leftarrow {}^3T_{1g}$, ${}^3T_{2g}(H) \leftarrow {}^3T_{1g}$, ${}^3T_{1g}(H) \leftarrow {}^3T_{1g}$, and ${}^3E_g(H) \leftarrow {}^3T_{1g}$, on octahedral Mn^{3+} species. This spectrum is similar to the one reported by Boyero et al. for the hausmannite phase [11].

The precipitate was analyzed by FTIR spectroscopy from 4000 to 400 cm^{-1}. The spectrum (Fig. 2) shows the characteristic absorption bands of υMn–O vibrations at 639, 532, and 409 cm^{-1}, together with a weak band at 1046 cm^{-1}, which can be attributed to υMn–O–H vibration. Finally, a broad band at 3423 and an other weak band at 1630 cm^{-1} were observed due to absorbed water. This FTIR spec-