Journal of Magnetism and Magnetic Materials 361 (2014) 161–165

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Hydrothermal synthesis, magnetic and electromagnetic properties of hexagonal Fe_3O_4 microplates

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ARTICLE INFO

Article history:
Received 20 December 2013
Received in revised form
11 February 2014
Available online 4 March 2014

Keywords:
Magnetite
2D material
Hydrothermal synthesis
Electromagnetic property

ABSTRACT

Magnetite (Fe_3O_4), with an inverse spinel structure, grows naturally in octahedral shape with eight equivalent {111} crystallographic planes. Here we demonstrated the successful morphology tuning of Fe_3O_4 microcrystal from the dominant octahedral shape to planar microplate shape by a facile hydrothermal method. The top and bottom surfaces of Fe_3O_4 microplates obtained under strongly alkaline and reductive conditions were bounded by {111} facets, and the formation of {111} twin planes was thought to be accountable for the anisotropic morphologies. The obtained Fe_3O_4 microplates delivered saturation magnetization (M_s) of 96.6 emu/g and coercivity (H_c) of 50 Oe. We also measured the electromagnetic properties of Fe_3O_4 microplates for possible applications as filler for electromagnetic wave absorption coatings.

1. Introduction

As an extreme anisotropic structure with high in-plane diameter-to-thickness ratio, two-dimensional (2D) micro-/nanomaterials (e.g., sheets, plates, disks and flakes) have attracted tremendous attention in the past few years [1–4]. Recent investigations have revealed that 2D micro-/nanomaterials show marvelous shape-dependent physical and chemical properties, being endowed with broad potential applications ranging from electronics and catalysis to energy conversion and storage [5–9]. Generally, the 2D crystals can be obtained by hindering/promoting specific growth directions using suitable ligands, such as citrate [10] and fluoride [11], which might preferentially absorb on certain crystallographic facets. The most successful utilization of the above approach is the preparation of noble metal nanocrystals (Ag [12,13], Au [14,15], Pd [16], etc.), and other cases including TiO_2 [11], $LiFePO_4$ [17], etc.

Magnetite (Fe_3O_4), with an inverse spinel structure, has attracted enormous attention because of its broad applications, such as magnetic resonance imaging (MRI) [18,19], drug delivery [20], energy storage [21,22], etc. Fe_3O_4 micro-/nanocrystals grow naturally in octahedral shape [23,24] due to the inherent face-centered cubic (*fcc*) structure, which allows different surface energies (γ) for different crystallographic facets in the order of $\gamma(110) > \gamma(100) > \gamma(111)$ [25]. The exposed facets of magnetite octahedra are eight equivalent {111} crystallographic planes. By using various approaches to engineer the crystal surfaces, the high energy facets are possible to be exposed, yielding different polyhedral-shaped crystals, such as truncated octahedron [26], cubes [27,28], and rhombic dodecahedron [29,30]. Nevertheless, there are only a few reports concerning the fabrication of Fe_3O_4 2D micro-/nanomaterials with anisotropic morphology. For example, Zhang et al. [31] and Liu et al. [32] reported the solvothermal synthesis of Fe_3O_4 nanoplates using diglycol and ethylenedimine as solvents and reducing agents, respectively. Li et al. [33] demonstrated a supercritical fluid technique to prepare hexagonal Fe_3O_4 nanoplatelets using ferrocene as a Fe source and sc-CO_2 as both a solvent and a oxygen source at 650–750 °C. An ultrasonic irradiation method was also developed to prepare Fe_3O_4 nanoplates with high efficiency [34]. Recently, Gu et al. [35] also prepared ultrathin Fe_3O_4 nanoplates by Schikorr reaction, which involves the ageing of ferrous hydroxide under anaerobic conditions.

In this work, we demonstrated that hexagonal-shaped Fe_3O_4 microplates with edge length of about 5.5 μm can be prepared using a facile hydrothermal process. Crystal twinning was suggested to be accountable for the formation of Fe_3O_4 microplates. In addition, the magnetic and electromagnetic properties of the Fe_3O_4 microplates were also investigated.

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http://dx.doi.org/10.1016/j.jmmm.2014.02.092
0304-8853

2. Experimental section

2.1. Synthesis

Fe_3O_4 microplates were prepared by a facile hydrothermal method under strongly alkaline and reductive conditions. In a typical procedure, 2 mmol $K_3Fe(CN)_6$ was dissolved into 20 ml deionized water, and then 72 mmol NaOH was added. The mixture was magnetically stirred at room temperature to form a homogeneous solution. Then, 10 ml $N_2H_4 \cdot H_2O$ was gently added to the above solution. The obtained colorless mixture was transferred into a Teflon-lined stainless steel autoclave with 40 mL capacity. The autoclave was maintained at 140 °C for 6 h, and allowed to cool to room temperature naturally. The obtained dark precipitates were collected by centrifugation, washed with deionized water and ethanol several times and then were dried in vacuum at 60 °C for 12 h.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected using a Rigaku D/Max-γB diffractometer with Cu Kα radiation. The morphology and structures of the products were characterized by using a field-emission scanning electron microscope (FE-SEM, FEI Quanta 200F), and a transmission electron microscope (TEM, JEOL JEM-2100) with an accelerating voltage of 200 kV.

Magnetic properties of the sample were measured on a vibrating sample magnetometer (VSM, Lakeshore 7410) with an applied magnetic field of 20 kOe at room temperature. The electromagnetic parameters of the composites containing Fe_3O_4 microplates as fillers and paraffin as a matrix were measured on a vector network analyzer (VNA, Agilent N5230A) using a transmission/reflection mode in the 2–16 GHz band. Fe_3O_4 microplates (15 vol%) and paraffin (85 vol%) were mixed thoroughly and then pressed into a mold to fabricate coaxial toroidal specimens, with outer diameter of 7 mm, inner diameter of 3.04 mm, and thicknesses of 3–3.5 mm.

3. Results and discussion

3.1. Characterization of Fe_3O_4 microplates

The phase and purity of the as-synthesized product are determined by XRD, and the diffraction pattern is displayed in Fig. 1.

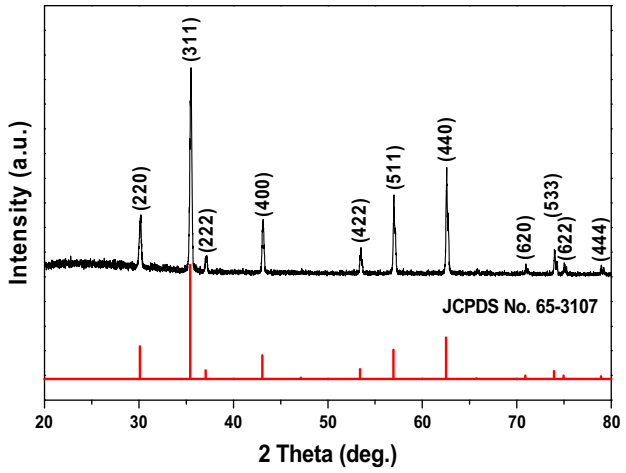

Fig. 1. XRD pattern of the as-obtained product. The lower panel shows standard diffraction patterns of Fe_3O_4 (JCPDS no. 65-3107).

All diffraction peaks can be perfectly indexed to the magnetite with an inverse spinel structure (JCPDS no. 65-3107) and lattice constants of $a=b=c=0.8391$ nm. The strong and sharp diffraction peaks indicate the high crystallinity of the as-obtained product.

Fig. 2a shows a low-magnification SEM image of the hydrothermally synthesized products. Plate-like characteristic can be easily distinguished for almost all the particles. The obtained Fe_3O_4 microplates have well-defined shapes, namely, hexagonal plates with side lengths of ~5.5 μm. The thickness of Fe_3O_4 microplates, estimated from high-magnification SEM image shown in Fig. 2b, is about 500 nm. The aspect ratio is thus determined to be ~20, comparable to that of Fe_3O_4 nanoplates reported elsewhere [31–33,36], but lower than that of noble metal nanoplates [37,38]. The obtained Fe_3O_4 microplates are further characterized by the TEM and selected-area electron diffraction (SAED) technique. Fig. 2c shows a typical TEM image of an individual Fe_3O_4 microplate with edge length of 4.5 μm, and its corresponding SAED pattern is shown in Fig. 2d. It is obvious that the hexagonal microplate is single-crystalline in nature, and the six-fold diffraction spots can be indexed to the equivalent {220} reflections of an *fcc* structure with zone axis of $[\bar{1}11]$. The top and bottom facets of Fe_3O_4 microplates correspond to the {111} crystallographic planes, of which the surface energy is the lowest for *fcc* crystal. Under an ideal condition, the hexagonal microplates grow uniformly along six $<110>$ directions. However, in a realistic experiment system, the breakdown of growth symmetry along $<110>$ directions, originated from the asymmetry of magnetite (space group: *Fd*-3*m*), may lead to the formation of irregular-shaped hexagons and triangular plates, as shown in Fig. S1 (see Supplementary file).

In general, nanocrystals with isotropic crystal structures usually have polyhedral shapes even when they are prepared in the presence of capping ligands [39,40]. Recent studies have demonstrated that the growth toward anisotropic morphologies can be facilitated by breaking the isotropic symmetry with the formation of twin planes during the nucleation stage [41,42]. The most representative case is the formation of nanoplates of noble metals, of which the stacking fault energy is lower than that of other metals, decreasing the energy required to form a twin plane [22,43]. The probability of twin plane formation has been examined in a case study of the nucleation of tabular silver halide (AgX) microcrystals [44]. Although the emergence of twinning in Fe_3O_4 has rarely been reported [45,46], we did find the evidence of twin planes in Fe_3O_4 microplates by careful SEM observations. A few microplates have obviously concave and convex edge facets, and those edges share a twinning plane between the top face and the bottom face, as shown in Fig. 3a and b. The twinning plane is easily identified to be the {111} planes of Fe_3O_4, as shown in Fig. 3c. The strongly alkaline and reductive conditions during the hydrothermal synthesis should be responsible for the formation of twin planes, the premise for the formation of anisotropic microplates. At low $N_2H_4 \cdot H_2O$ concentrations (5 and 7.5 ml), Fe_3O_4 octahedrons with sizes of 5–10 μm are also formed together with the Fe_3O_4 microplates (Fig. S2 in Supplementary file), consistent with the previous study [47,49]. The aspect ratio of Fe_3O_4 microplates is determined by the growth competition between $<110>$ and $<111>$ directions. Time-dependent experiments show the increase of both edge length and thickness of the microplates with the elongation of reaction duration, namely, a mean edge length of about 4 μm and an average thickness around 300 nm for the product obtained at a short duration of 1 h, and length of 8 μm and thickness of about 1 μm at a long duration of 12 h (Fig. S3 in Supplementary file). Further precise control of the size and uniformity of the microplates is needed for understanding the growth behavior as determined by surface energy.