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Synthesis and Characterization of Ultrafine and Porous Structure of Magnesium Ferrite Nanospheres

Research Article

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Abstract

Porous sphere-shaped magnesium ($MgFe_2O_4$) spinel ferrite particles were synthesized with high yields, crystallinity and purity through an easy, quick, reproducible and low-temperature hydrothermal synthesis route starting from an aqueous suspension of coprecipitated metal oxalates. The structural and morphological properties of the prepared materials were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, infrared spectroscopy and N_2 adsorption–desorption measurement. Results show that the obtained $MgFe_2O_4$ particles are nearly spherical in shape and about 100-250 nm in mean diameter. Every magnetic microsphere is made of many ultrafine $MgFe_2O_4$ nanoparticles and porous in structure. The obtained sphere-shaped products exhibited a saturation magnetization of 70.25 emu/g and a coercivity of 326.41 Oe at room temperature.

Keywords: $MgFe_2O_4$ Nanospheres; Hydrothermal method; Porous structure; Magnetic properties; Electron microscopy

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Introduction

Functional magnetic materials, such as transition metal oxides with spinel structure MFe_2O_4 (M=Mg, Mn, Fe, Co, Ni, Zn, etc.) are one family of the most important materials in advanced technology [1,2]. As an important part of nanomaterials, nanomagnetic materials have attracted considerable attention due to their utilizations in the magnetic field sensor, bio-sensors, magnetic-storage media, catalysis,optics, sensors and drug-delivery carriers, and so on [3-9]. However, the magnetic properties of nanoparticles strongly depend on the synthesis conditions, particle size, shape and composition. Therefore, the ability to manipulate the shape and size of nanomaterials is crucial to determine their magnetic properties and achieve the scientific and technological needs. Hence, it is desirable to develop strategies for morphology-controlled synthesis of nanosized spinel ferrites.

Currently, different morphologies of spinel ferrites have been reported, including nanospheres [9], nanorods [10,11], hollow tubes [12,13], spindle-shaped spinel [14] and nanowires [15,16]. There are few reports on porous sphere-shaped ferrites. Porous-structured ferrites should perform even more effectively in catalysis, adsorption and wave absorption because of their porous framework [17,18].

Among the family of ferrite materials, magnesium ferrite ($MgFe_2O_4$) is one of the most important ferrites. It has a cubic structure of normal spinel-type and is a soft magnetic n-type semiconducting material, which finds a number of applications in heterogeneous catalysis, adsorption, sensors, and in magnetic technologies [19]. To date, a variety of synthetic approaches, including solvothermal method [9], solid-state reaction [20,21] polymer calcination approach [22], pulsed laser deposition technique [23] and co-precipitation method [24] have been reported to prepare $MgFe_2O_4$ nanoparticles. However, these reports reveal that high temperature treatment, long time consuming, and complex procedures are generally required for effective synthesis of such functional materials. Therefore, developing simpler and environmentally benign methods is technically important and desired.

In this study, porous sphere-shaped $MgFe_2O_4$ particles were fabricated using low-temperature hydrothermal method. Ethylene glycol (EG) and poly-ethylene glycol (PEG) were used as the solvent and so template, respectively. Magnesium chloride ($MgCl_2.6H_2O$) and ferric chloride ($FeCl_3.6H_2O$) were used as cation sources in the reaction system. The as-prepared products exhibited good magnetic properties at room temperature.

Experimental

Materials and physical measurements

Magnesium chloride hexahydrate ($MgCl_2.6H_2O$, Merck ≥99%) ferric chloride hexahydrate ($FeCl_3.6H_2O$, Merck ≥99%) salts, sodium acetate trihydrate ($CH_3COONa.3H_2O$, ≥95%), Ethylene glycol (EG), PEG (Mn=4,000, Shanghai Chemical Regent Co., Ltd., China) and were used for the synthesis of $MgFe_2O_4$ nanoparticles. All chemicals were analytical grade and used as received without further purification. The X-ray diffraction (XRD) patterns of the $MgFe_2O_4$ particles were obtained using an X'Pert PRO X-ray diffractometer (Model D8 Discover, Bruker) with CuKα radiation (λ = 0.154 nm) in reflection mode and 2θ ranging from 10° to 80°. The morphological analysis of the samples is carried out using Scanning Electron Microscope (SEM, S-4700, Hitachi, Japan). The elemental composition of the samples is tested by energy-dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) images were obtained on a Philips EM280 transmission electron microscopy with an accelerating voltage of 150 kV. The magnetic properties of the samples were measured with a vibrating sample magnetometer (VSM). N_2 adsorption/ desorption isotherms were performed at 196°C, by a BELSORP mini-II surface area measurement equipment, after degassing the samples under vacuum at 100°C overnight. IR transmittance spectra of ferrite powder samples were measured on Bruker Equinox 55 infrared spectrophotometer (KBr pellets) in the range of 4000–400cm^{-1}.

Preparation of porous sphere-shaped $MgFe_2O_4$ particles

We synthesized porous magnesium ferrite ($MgFe_2O_4$) nanospheres exactly in the same manner as described in our previous work [25] but with a small modification. In a typical preparation, firstly 2g of surfactant PEG was dissolved in 40 mL ethylene glycol under vigorous stirring to form a clear solution, and then 3.6 g sodium acetate trihydrate, 2.5 mmol $MgCl_2{\cdot}6H_2O$ and 5 mmol $FeCl_3{\cdot}6H_2O$ were added to the above solution. This mixture was then vigorously stirred at 50°C for 30 min to form a homogeneous solution. Finally the mixture was transferred into a 100 mL Teflon-lined autoclave, which was heated at 180°C for 16 h. After being cooled to room temperature, the black powders were collected and washed several times with distilled water and ethanol to remove the impurities, and finally dried at 80°C in a vacuum oven for 8 h.

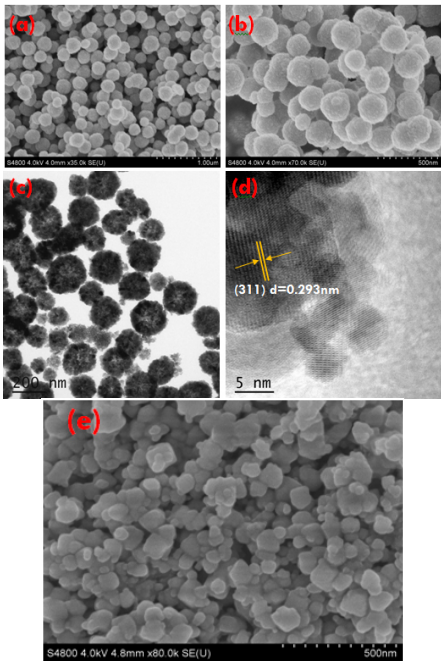
For comparison, $MgFe_2O_4$ nanoparticles were also prepared using the same method without the introduction of PEG.

Results and discussion

Morphology and pore structures of $MgFe_2O_4$ nanospheres

Scanning electron microscope (SEM) was used to study the size and morphology of the porous sphere-like $MgFe_2O_4$ particles and $MgFe_2O_4$ nanoparticles (prepared without PEG). As shown in Figure. 1 (a&b), the micrographs indicate that they are 100-250 nm spheres in dimension and composed of small primary particles. The particles are packed tightly as an outcome of the attractive magnetic force and instinctive nature to reduce surface energy by aggregation. [26] TEM and HRTEM were used to further examine the morphology, particle size and crystallinity of the self-assembled products. Figure. 1c show TEM image of sphere-shaped $MgFe_2O_4$ particles, it could be further observed that the products are formed by nanoparticles, which are consistent with the SEM images. As shown in Figure. 1c, sphere-shaped $MgFe_2O_4$ nanoparticles are assembled by the layers of nanoparticles and exhibit porous structures at the center. Further evidence of the microstructure for sphere-shaped $MgFe_2O_4$ particles is given in HR-TEM image. HRTEM images shown in Figure. 1d confirmed the single-crystalline nature of the primary nanospheres. As depicted in Figure. 1d, the atomic lattice fringes can be clearly observed, and the interplanar spacings were measured to be 0.293 nm, which were close to the {311} lattice plane of cubic $MgFe_2O_4$. Figure. 1e shows the SEM image of $MgFe_2O_4$ nanoparticles prepared without PEG for comparison. $MgFe_2O_4$ nanoparticles are about 10–85 nm in diameter.

Figure 1. SEM (a and b), TEM (c), HRTEM (d) images of $MgFe_2O_4$ nanospheres and SEM (e) image of $MgFe_2O_4$ nanoparticles



Further, the nitrogen sorption measurement was conducted to evaluate the porous structure and specific surface area for such magnetic nanoparticles. Figure. 2 shows the large hysteresis loops between the adsorption and desorption isotherms in the P/P0 ranging from 0.7 to 1, which confirms the formation of mesopore textural porosity and the slight pore size distribution towards smaller mesopores (see the inset of Figure. 2). The specific surface area was thus estimated, by Brunauer–Emmett–Teller (BET) equation [27], to be 53 m^2/g. In addition, the sorption exhibits type IV isotherm and the pore analysis has revealed that the pore sizes in the porous nanospheres mainly fall into 7.59 nm, which are in good agreement with the TEM analysis. The generation of porosity is because of the interspace between nanoparticles; therefore, the pore size distribution is very broad. Moreover, such nanospheres possess a higher specific surface area than $MgFe_2O_4$ nanoparticles.

Crystal structure of the porous sphere-like $MgFe_2O_4$ particles

Phase investigation of the crystallized products (porous sphere-like $MgFe_2O_4$ particles and $MgFe_2O_4$ nanoparticles) was performed by XRD and the diffraction pattern is presented in Figure. 3. All the XRD peaks can be indexed to the cubic spinel (JCPDS card no. 73-1960) structure with no extra lines corresponding to any other planes, which show that the prepared ferrites are single phase. The broadened nature of these diffraction peaks indicates that the grain size of the sample is on nano meter scale.

An additional quantitative analysis of the prepared porous $MgFe_2O_4$ nanospheres was provided by EDX. EDX measurement results comply with what is expected from the synthesis. In other words, mass ratios of chemical compositions are in agreement with the outcomes of the EDX (Figure. 4). The experimental mass percentage and atom percentage for the sample are given in the Table (See Figure.4 inset).

Magnetic properties of the porous sphere-like $MgFe_2O_4$ particles

Such porous oriented ferrite nanospheres have exhibited good magnetic property. The hysteresis loop of the $MgFe_2O_4$ spheres was recorded with VSM at the room temperature. The saturation magnetization (Ms), remanent magnetization (Mr) and coercivity (Hc) of the product were obtained based on the magnetic hysteresis loop. As shown in Figure. 5 and Table 1, the Ms, Mr and Hc of nanospheres are 70.25 emu/g, 19.60 emu/g and 326.41Oe respectively; for nanoparticles, they are 50.46 emu/g, 11.42 emu/g and 617.83 Oe. The saturation value of 70.25 emu/g obtained in the porous $MgFe_2O_4$ nanospheres is higher than the value of 68.9 emu/g for $MgFe_2O_4$ synthesized by a novel hydrothermal method [28] using acetates and aloe vera plant-extracted solution, 48.6 emu/g for $MgFe_2O_4$ nanostructures fabricated by electrospinning [29], 30.6 emu/g for sol–gel/combustion synthesized $MgFe_2O_4$ nano materials [30] and 14.09 emu/g for co-precipitation-synthesized $MgFe_2O_4$ nanoparticles [31]. Porous sphere-like $MgFe_2O_4$ nanospheres exhibit better magnetic properties than $MgFe_2O_4$ nanoparticles.

According to the literature, the Ms, Mr and Hc of the nanocrystals are merely determined by the size [32]. Moreover, the morphologies of $MgFe_2O_4$ have some influence on magnetic properties [33]. Combined with XRD and TEM results, we suggest that the good magnetic properties of sphere-shaped $MgFe_2O_4$ particles can be attributed to the high level of crystallinity and proper nanoparticle size, as well as the unique morphology.

FT-IR analysis was applied to investigate the presence of functional groups and impurity on the surface of the products. As can be seen in Figure. 6, The typical low frequency band at around 592 cm^{-1} refers to Fe–O vibration (Fe^{3+} bond) in octahedral and tetrahedral sites and the band at around 435 cm^{-1} refers to Fe–O vibration (Fe^{2+} bond) in octahedral sites [34]. In addition, the bands at 3411 and 1621 cm^{-1} are attributed to the surface hydroxyl and the adsorbed water molecules, respectively [35]. The peakat 1078 cm^{-1} may be attributed to the C-H bending frequencies of the remaining trace EG [36].

Conclusions

In summary, we have successfully demonstrated a simple hydrothermal route to prepare porous $MgFe_2O_4$ nanospheres. The most important advantage of this method is that it provides a one step, simple, general and inexpensive method for the preparation of ferrite nanoparticles at low synthesis temperature. The synthesized $MgFe_2O_4$ nanoparticles had a spherical structure with a mean diameter of about 200 nm, higher surface area and high magnetization of 70.25 emu/g. These porous $MgFe_2O_4$ nano

Figure 2. N_2 sorption isotherm of the porous $MgFe_2O_4$ nanospheres, with insets showing the BJH pore-size distributions for the corresponding samples

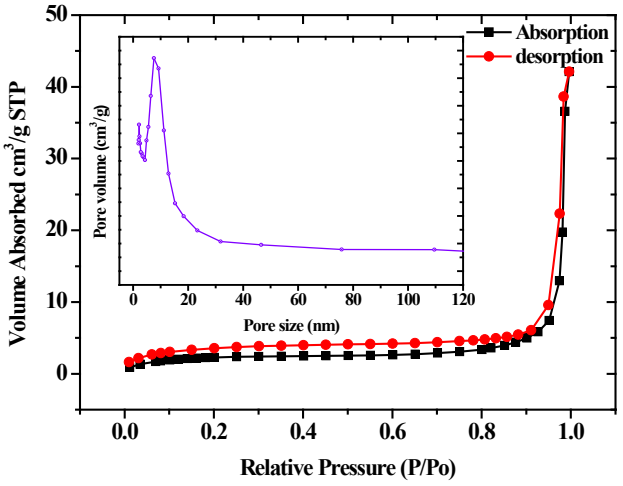


Figure 3. XRD patterns of the $MgFe_2O_4$ nanoparticles (a) and porous $MgFe_2O_4$ nanospheres (b)

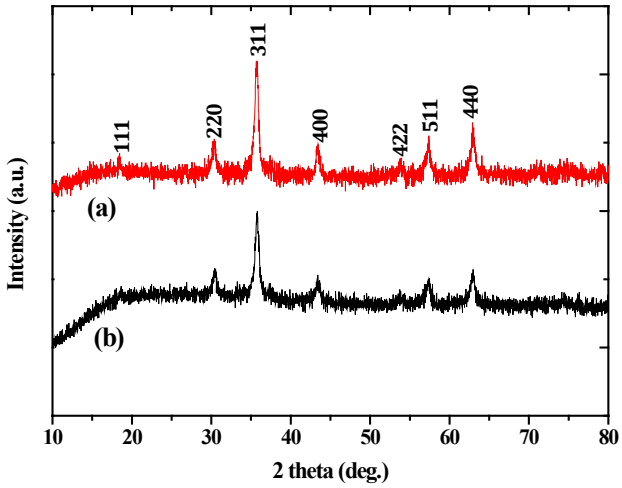


Figure. 4. EDS spectrum for the porous $MgFe_2O_4$ nanospheres

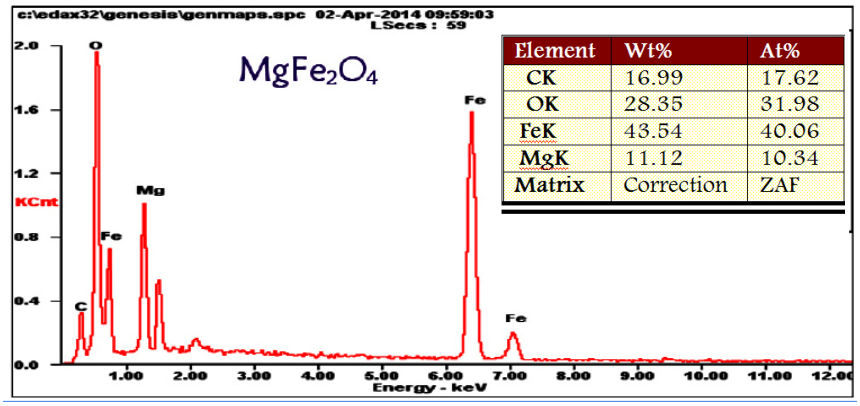


Table 1. Magnetic characteristic of the $MgFe_2O_4$ nanoparticles

Sample	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
$MgFe_2O_4$ spheres	70.25	19.6	326.41
$MgFe_2O_4$ particles	50.46	11.42	617.83

Figure 5. Magnetization hysteresis loop of the porous $MgFe_2O_4$ nanospheres. The downright inset is an expanded low-field curve

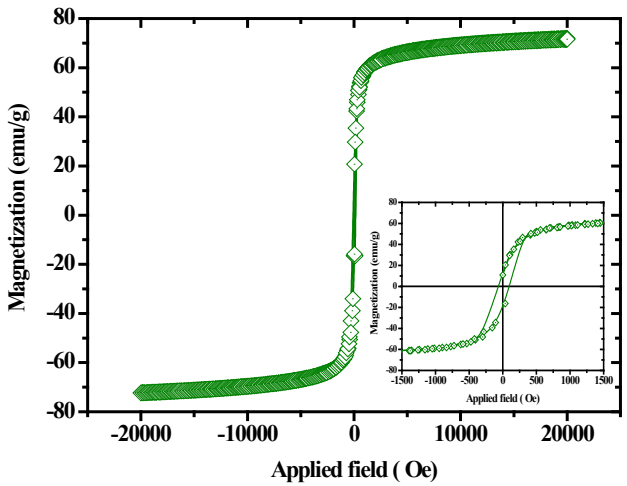
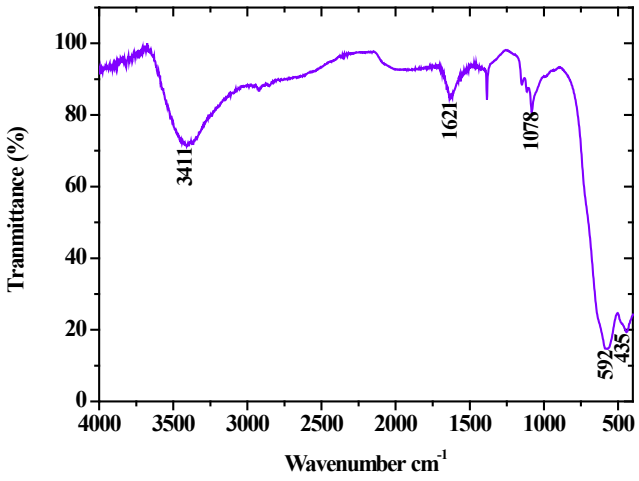


Figure 6. FTIR spectrum of the porous $MgFe_2O_4$ nanospheres



spheres have excellent magnetic properties than that of the $MgFe_2O_4$ nanoparticles. The developed magnetic nanomaterial is expected to find potential applications in separation, anodic material in lithium ion batteries, catalysts, and as electronic material for nanodevices and storage devices.

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