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Uniform hollow magnetite spheres: Facile synthesis, growth mechanism, and their magnetic properties

Xing Zhou [a,b,*], Guizhe Zhao [b], Yaqing Liu [b,**]

[a] School of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215009, China
[b] Research Center for Engineering Technology of Polymeric Composites of Shanxi Province, North University of China, Taiyuan 030051, China

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ABSTRACT

Hierarchical porous Fe_3O_4 hollow spheres with high saturation magnetization were synthesized through a simple solvothermal process in ethylene glycol (EG) in the presence of Tetrabutylammonium chloride (TBAC) and urea. By investigating the effect of reaction temperature, time, the amount of urea, and concentration of iron ion on the formation of hollow spheres, it was proposed that the main formation mechanism of hollow spheres is Ostwald ripening process combined with assembly-then-inside-out evacuation process. Additionally, it is found that the morphology of Fe_3O_4 with nanoparticles, hollow, and irregular structures could be adjusted by changing the above factors. The resulting products were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX), and vibrating sample magnetometer (VSM). The hierarchical porous Fe_3O_4 hollow spheres exhibited enhanced saturation magnetization as compared with Fe_3O_4 nanoparticles.

1. Introduction

Magnetic materials, especially magnetite (Fe_3O_4), as one of the most basic and important magnetic materials, have attracted extensive attentions in recent years because of its potential applications in catalysis, superparamagnetism, high-density data storage, rheology, ferrofluids, biomaterials diagnostics, magnetic resonance imaging, and drug delivery [1–3]. In the past decade, various structural and morphological forms of Fe_3O_4 nano- and micro- materials were synthesized, for example, microspheres [4], nanoparticles [5,6], nanowires [7], nanotubes [8], nanocubes [9], octahedral particles [10], microrings [11], hollow core/shell hierarchical nanostructures [12], nanoroses [13], hollow spheres [14–16], and so on. Above all, more and more attention has been focused on hollow magnetic nano- or micro- spheres due to their excellent properties, such as magnetic condensation, higher specific surface, lower density, larger surface permeability without much sacrifice of mechanical/thermal stability and so on.

Recently, the magnetic materials with hierarchical structures are envisaged to serve as hosts for encapsulating guest molecules and sensitive materials such as drugs, proteins, cosmetics, and catalysts, and they can be manipulated by an external magnetic field [17–19]. Several methods for generating magnetic materials with hierarchical structures have been developed by employing novel mechanisms, including hard template [20], gas-bubble-assisted Ostwald ripening process [21], nanoscale Kirkendall effect [18], oriented assembly [22], and corrosion-based inside-out evacuation [23]. Although these methods do works, however, their shortcomings are obvious. First, many of them require hard template or an external magnetic field [17]. Second, some methods are complex or post-treatment process is required. Third, some formation mechanisms were cross-section nature and cannot yet explain some new phenomenon. Thus, the controlled assembly of hollow or hierarchical magnetite in the absence of hard template or an external magnetic field is still considerably difficult and the formation mechanism is still unclear. Therefore, it is still desirable to find an efficient route to synthesize well uniform magnetite hollow spheres, and it is necessary to discuss the self-assembly mechanism of hollow structures as well as structure and property relationships of magnetite for both fundamental studies and practical applications.

In this contribution, we report a new phenomenon for preparation of magnetite which converts solid Fe_3O_4 nanospheres

* Corresponding author at: School of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, Kerui road 1#, Suzhou 215009, China. Tel.: +86 512 68056461; fax: +86 512 68056461.
** Corresponding author.
E-mail addresses: xzhou@mail.usts.edu.cn (X. Zhou), zfflyq98@163.com (Y. Liu).

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to well dispersed and size-controlled magnetite hollow spheres, based on a solvothermal reaction. A possible formation mechanism for the magnetite hollow spheres was proposed based on a series of control experiments. In this formation process, solid Fe_3O_4 nanoparticles were first obtained, and then transformed to hollow structures. In addition, the magnetic properties of the Fe_3O_4 hollow spheres were also reported. The influence of the hollow structure on magnetic properties was investigated by means of a comparison between the hollow spheres and nanoparticles which were their building blocks.

2. Experimental

2.1. Preparation of Fe_3O_4 crystals

All the reagents were of analytical grade, and used without further purification. In a typical experiment, 1.2 g Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 4.5 mmol), 0.834 g Tetrabutylammonium chloride (TBAC, 3 mmol), and 3.6 g urea were mixed in a beaker, followed by the addition of 30 mL ethylene glycol (EG). After stirring vigorously for 30 min, the homogeneous solution was transferred to a Teflon-lined stainless steel autoclave with 50 mL capacity. Subsequently, the autoclave was maintained at 200 °C for 36 h, and then it was cooled to room temperature. The obtained black products were washed three times with deionized water and ethanol, and then vacuum-dried at 60 °C for 12 h. To investigate the formation mechanism of the hollow magnetite nano-spheres, we carried out a series of experiments, varying the amount of urea, Ferric chloride hexahydrate, reaction temperature and time.

2.2. Characterization

The morphology and structure of the samples were investigated by scanning electron microscopy (SEM, Hitachi, SU-1500) and transmission electron microscopy (TEM, JEOL, JEM-2100). The crystal structure of the samples were recorded with X-ray powder diffraction (XRD, Kigokn, D/MX RB, Cu-Kα radiation, λ = 0.154178 nm). Magnetic properties of the as-prepared samples were recorded using a vibrating sample magnetometer (VSM, Lake Shore 7407) at room temperature. High resolution transmission electron microscopy (HRTEM) images and the corresponding selected area electron diffraction (SAED) pattern were obtained using a JEM-2100 high resolution transmission electron microscope. The energy dispersive X-ray spectroscopy (EDX) analyses were obtained using a Sirion 200 FEG microscope, and the as-synthesized products were dispersed on the Si substrate.

3. Results and discussion

3.1. Characterization of magnetite hollow spheres

The phase and purity of the magnetite hollow spheres were characterized by XRD measurements. As shown in Fig. 1a, all peaks could be indexed as the standard XRD patterns of face-centered cubic lattice Fe_3O_4 (JCPDS card No. 19-0629). No peak of any other phase was detected, indicating that pure magnetite had been prepared in this process [16]. Based on the calculation of Scherrer's formula, the average diameter of particle is about 44.7 nm. The as-prepared product was also determined by EDX analysis under N_2 atmosphere. The EDX result shown in Fig. 1b demonstrates that the as-prepared sample contains Fe and O with the Fe/O atomic ratio of ~3:4, which agrees well with the expected stoichiometry and the XRD result.

The morphologies and sizes of the typical samples were investigated by SEM and TEM. The SEM image (Fig. 2a) shows that the product consists of a larger quantity of well-dispersed sphere like shapes and the size distribution of the spheres is narrow. From the TEM images as shown in Fig. 2b, we can observed that each of the spheres has a pale center region in contrast to a dark edge, suggesting that all spheres are hollow structures with ~357 nm in diameter and ~81 nm in shell thickness, respectively. The high-magnification TEM image of select area A is shown in the up-right of Fig. 2b. It can be observed that one Fe_3O_4 nanospheres was broken, which clearly shows the hollow nature of the Fe_3O_4 crystals. To obtain more detailed information of the crystal structure of the obtained hollow spheres Fe_3O_4, HRTEM image together with SAED pattern of the sample are recorded. Fig. 2c shows the HRTEM image of the Fe_3O_4 crystals which obtained from the areas marked with white pane B as shown in Fig. 2b. The lattice spacing was measured to be 0.254 nm, corresponding to the (3 1 1) planes of typical face-centered cubic lattice Fe_3O_4 structures.

The SAED pattern of the Fe_3O_4 crystals exhibited a remarkable single-crystal feature as shown in Fig. 2d, in which the spots were assigned to (1 3 1), (2 2 0), and (3 1 1) of face-centered cubic lattice Fe_3O_4, respectively. The HRTEM and SEAD results strongly suggest that highly ordered Fe_3O_4 hollow spheres are formed by oriented assembly of the primary nanoparticles.

3.2. Reaction temperature

To understand the formation mechanism of hierarchical Fe_3O_4 hollow spheres, temperature-dependent experiments were carried at 36 h for various reaction temperatures of 180, 190, 200, 210,

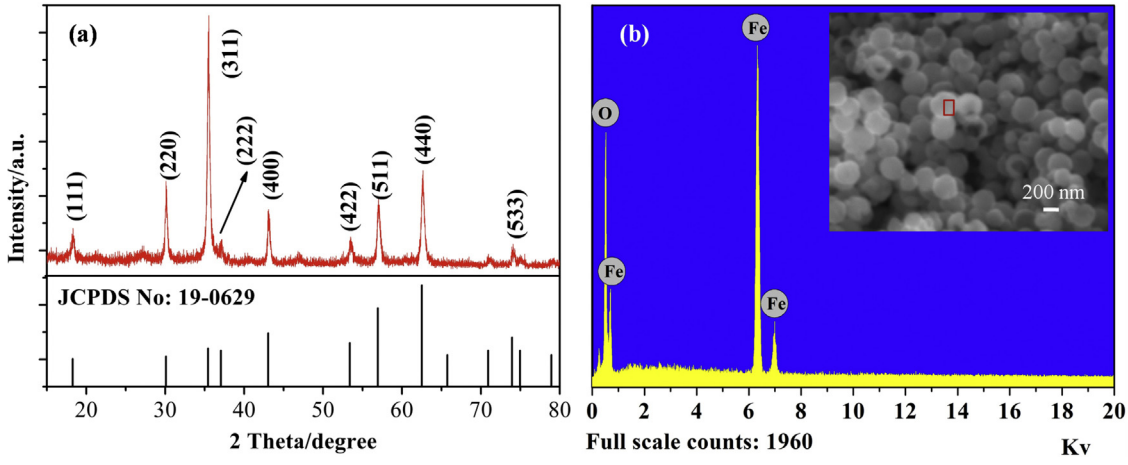

Fig. 1. (a) XRD pattern of the produced hollow magnetite nanospheres, (b) EDX spectrum of the sample. The inset of (b) is the corresponding SEM image.