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One-pot hydrothermal synthesis of highly monodisperse water-dispersible hollow magnetic microspheres and construction of photonic crystals

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HIGHLIGHTS

- Monodisperse water dispersible hollow Fe_3O_4 microspheres were synthesized.
- The products had high saturation magnetization value and big specific surface area.
- A gas-bubble-assisted Ostwald ripening process was possibly responsible.
- The products could be used to fabricate photonic crystals.

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ABSTRACT

Water-dispersible monodisperse hollow Fe_3O_4 microspheres were prepared via a one-pot hydrothermal process based on $FeCl_3{\cdot}6H_2O$, sodium citrate, urea and sodium polyacrylate (PAAS). Different alkali sources and $FeCl_3{\cdot}6H_2O$ amounts were added to investigate the formation mechanism, and a gas-bubble-assisted Ostwald ripening process was possibly responsible for the formation of hollow structure. In the process, the particle size and morphology could be effectively controlled by the slight change of $FeCl_3{\cdot}6H_2O$ addition amount. Meanwhile, monodisperse solid microspheres were obtained when sodium acetate was added to offer alkaline environment. The microspheres exhibited superparamagnetic properties with high saturation magnetization value about 76.7 emu g^{-1} at room temperature, and the BET surface area of the sample was 50.04 m^2 g^{-1}. Besides, it was found that the particles could be used for constructing photonic crystals. Such monodisperse hollow Fe_3O_4 microspheres have a great application potential in biomedicine, MRI agents and color display areas.

1. Introduction

Magnetite has been widely used in the field of biomedicine, magnetic resonance image (MRI), water treatment, drug delivery, enzyme immobilization and functional materials [1–6]. However, solid magnetite particles have some drawbacks such as high density to sink and relatively low specific surface area, which restrict its application in biomedicine and wave-absorbing material [7,8]. Recently, hollow microspheres have received increasing attention because of their special structure and novel properties, including low density, high specific surface area and distinct optical performance [9,10]. Therefore, hollow Fe_3O_4 microspheres have been synthesized to meet the demands of many scientific applications [11,12]. Template-assisted method is a facile way to synthesize hollow structure, while polystyrene latex sphere [13], silica spheres [14] and emulsions [15] have been used as templates to direct the formation of hollow structure. The process usually involves the deposition of shell materials and removal of the templates under harsh conditions. In particular, removal conditions such as high temperature [16] or acid-etching [17] may result in the collapse of hollow structure. Moreover, the saturation magnetization value of deposited Fe_3O_4 particles is relatively low due to the restriction of synthesis process. To overcome the disadvantages of the template-assisted method, solvothermal route relying on Kirkendall effect [18], Ostwald ripening mechanism [19] or self-supported mechanism [20] has been widely adopted for the preparation of hollow Fe_3O_4 microspheres. Among them, Ostwald ripening mechanism is more widely accepted to fabricate hollow materials. For example, Hu et al [21] prepared monodisperse hollow Fe_3O_4 with the addition of NH_4Ac as the structure-directing

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agent. They found that the gas bubbles, produced by the decomposition of NH_4Ac, played a crucial role in the formation of hollow structure. Thus, a gas-bubble-assisted mechanism was proposed to explain the process. Subsequently, different alkali sources such as sodium didecylbenzenesulfonate [22], NH_4HCO_3 [23] and NaOH [24], were used as the structure-directing agents. Chen et al. [25] reported the synthesis of porous hollow Fe_3O_4 microspheres with the addition of dodecylamide and NaOH. The big hollow interior made the Fe_3O_4 microspheres good anode materials. However, the reaction required about 4 days to obtain the hollow structure. Sodium formate (HCOONa) was also used as the structure-directing agent to prepare hollow microspheres [26]. Unfortunately, small nanoparticles could be unavoidably produced in the system. To our knowledge, products synthesized in EG system always showed poor water dispersibility which was of special importance in biomedicine application [5,27]. Besides, EG was not an environmental-friendly solvent. Recently, hollow Fe_3O_4 microspheres have been successfully synthesized using deionized water as solvent. Tang et al. [28] first reported the fabrication of water-dispersible hollow Fe_3O_4 microspheres using sodium citrate as reducing agent and polyacrylamide (PAM) as stabilizer. However, the control of particle size was not mentioned. Subsequently, many researchers have synthesized microspheres with similar approach [29–31]. Among them, Zou et al [32] prepared hollow Fe_3O_4 microspheres with particle size of 200–340 nm and PAAS was added for stabilization, but the formation mechanism was not explained clearly and the particle size was poorly controlled.

In the present work, monodisperse water-dispersible hollow Fe_3O_4 microspheres were successfully prepared via a facile hydrothermal reduction method by modifying the system as reported previously [28,32]. Different alkali sources and Fe^{3+} amounts were chosen to study the formation mechanism of porous hollow structure. The as-synthesized products exhibited highly water-dispersibility and superparamagnetic properties with high saturation magnetization, which were important in biomedicine. Finally, it was found that the synthesized porous hollow Fe_3O_4 could be used to fabricate photonic crystals.

2. Experimental section

2.1. Experimental procedure

All reagents are analytically pure and used as-received without further purification. The products were synthesized as reported [28,32] with some modification. In a typical experiment, 5 mmol $FeCl_3{\cdot}6H_2O$, 10 mmol sodium citrate were dissolved in 80 ml distilled water to form yellow transparent solution. Then 1 g urea was added in above solution, followed by the addition of 0.6 g PAAS. After 30 min vigorously magnetic stirring, the viscous transparent mixture was transferred to a 100 ml Teflon-lined stainless-steel autoclave and maintained at 200 °C for 12 h. The product was collected with a magnet and washed with distilled water and ethanol for several times. Finally, the sample was dried in a vacuum oven at 45 °C for 12 h.

The fabrication of photonic crystals was carried out as follows, a vial containing 5 mL Fe_3O_4 solution with a concentration of 5 mg mL^{-1} was placed before a magnet with a strength about 500 G. The magnet was moved from left to right to change the magnetic field intensity and magnetic direction.

2.2. Characterization

The crystalline structure of the sample was characterized by X-ray diffraction (Shimadzu XRD-7000, Cu Kα radiation, λ = 1.5406 Å) and the morphology was obtained by Transmission electron microscopy (TEM, JEM-3010, 75 kV). Thermal properties were determined through thermogravimetric analysis (TGA Q50, TA instruments) at a heating rate of 10 °C/min. The magnetic properties were assessed with a vibrating sample magnetometer (VSM, Lakeshore 7307). N_2 adsorption–desorption isotherms were obtained on a TriStar II 20 apparatus. The pore size distribution was calculated from the absorption branch of the N_2 adsorption–desorption isotherm. Fourier Transform Infrared (FTIR) spectra were acquired on a TENSOR27 FTIR spectrometer (Bruker). The particle size was measured by a Beckman Coulter Delsa Nano C (Beckman, US, measuring range: 0.6 nm–7 μm, temperature: 25 °C) and deionized water was used as testing medium.

3. Results and discussion

3.1. Structures and properties of the hollow Fe_3O_4 microspheres

Fig. 1 shows XRD pattern of the sample synthesized with a typical experiment. Eight characteristic peaks located at (111), (220), (311), (222), (400), (422), (511), (440) correspond well to the standard reflections for Fe_3O_4 microspheres (JCPDS 79-0419). No obvious peak attributed to the hematite or other impurities can be found, indicating that pure magnetite microspheres have been successfully synthesized. Calculation with Scherrer's formula for the strongest peak (311) reveals that the crystallite size is about 11.78 nm. The morphology and structure were investigated by TEM as shown in Fig. 2. The average size of the sample is about 380 nm with narrow size distribution. The microspheres have pale center region while the edge is relatively dark, confirming the formation of hollow structure. The selected-area electron diffraction (SAED) recorded on the edge of a magnetite microsphere (inset in Fig. 2a) shows obvious diffraction rings, indicating that the magnetic hollow spheres are polycrystalline. Meanwhile, the low magnification TEM exhibits uniform size as shown in Fig. 2b, also confirming the narrow distribution of the sample. In addition, as depicted in Fig. 2c, it can be clearly observed that the microsphere is loosely composed of many primary nanoparticles with the size of approximately 12 nm (corresponding well to the XRD result), which indicates it is highly porous.

The functional groups of hollow spheres were measured by FT-IR spectroscopy as shown in Fig. 3a. The peaks at 576 cm^{-1} and 3424 cm^{-1} belong to the Fe–O bond and surface hydroxyl of Fe_3O_4 microspheres. The absorption bands located at 1626 cm^{-1} and 1404 cm^{-1} can be identified as COO^- anti-symmetrical

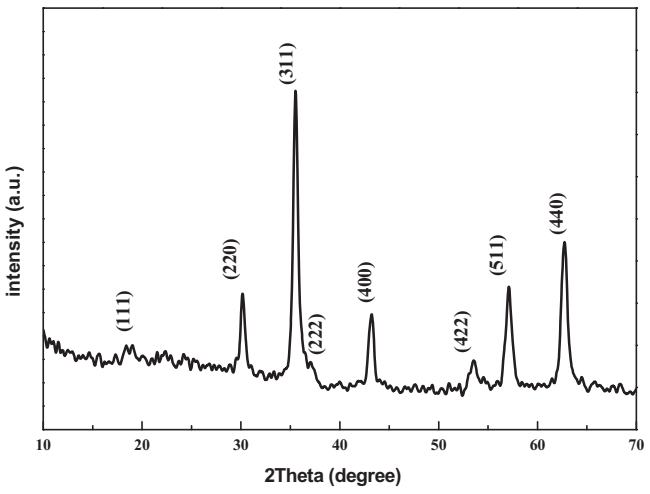

Fig. 1. XRD pattern of the typical products synthesized at 200 °C, 12 h.