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Biosynthesis and magnetic properties of mesoporous Fe_3O_4 composites

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ABSTRACT

Magnetic Fe_3O_4 materials with mesoporous structure are synthesized by co-precipitation method using yeast cells as a template. The X-ray diffraction (XRD) pattern indicates that the as-synthesized mesoporous hybrid Fe_3O_4 is well crystallized. The Barrett–Joyner–Halenda (BJH) models reveal the existence of mesostructure in the dried sample which has a specific surface area of 96.31 m^2/g and a pore size distribution of 8–14 nm. Transmission electron microscopy (TEM) measurements confirm the wormhole-like structure of the resulting samples. The composition and chemical bonds of the Fe_3O_4/cells composites are studied by Fourier transform infrared (FT-IR) spectroscopy. Preliminary magnetic properties of the mesoporous hybrid Fe_3O_4 are characterized by a vibrating sample magnetometer (VSM). The magnetic Fe_3O_4/cells composites with mesoporous structure have potential applications in biomedical areas, such as drug delivery.

1. Introduction

Since MCM-41 silica molecular sieve was first reported in 1992 [1,2], the research in the area of mesoporous materials has been intensively studied due to their promising applications involving catalysts, separation and host materials [3,4]. The Fe_3O_4 is an important magnetic material and has been widely used in different areas such as recording material, magnetically controlled transport of anticancer drugs and magnetic resonance imaging (MRI) [5–7]. The preparations of Fe_3O_4 with various morphologies (nanowires, nanorods, films and nanoparticles) by different methods were reported extensively [8–11]. To date, many approaches have been developed for the preparation of metal oxide with mesoporous structure [12,13], but using microbe cells as a template to synthesize mesoporous iron oxide has not been reported. Herein, we report a co-precipitation approach for the fabrication of organic–inorganic hybrid Fe_3O_4 with mesoporous structure using yeast cells as a template. The as-prepared mesoporous hybrid Fe_3O_4 materials have high surface area and relatively high saturation magnetization, which show potential applications in biological materials, such as drug delivery.

2. Experimental

2.1. Materials and methods

The starting materials used in this study included ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98.5%, Tianjin Bodi Chemical Co., Ltd), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 99.0%, Tianjin Bodi Chemical Co., Ltd), ammonia solution ($NH_3 \cdot H_2O$, 25.0%, Yantai Shuangshuang Chemical Co., Ltd) and yeast cells (Instant dry yeast, Angel Yeast Co., Ltd).

In a typical synthesis procedure, 0.8 g instant dry yeast were cultivated in 50 ml glucose aqueous solution at 36 °C for 2 h. A total of 4.04 g $Fe(NO_3)_3 \cdot 9H_2O$ and 2.78 g $FeSO_4 \cdot 7H_2O$ were dissolved in 30 ml deionized water, which was added to yeast cells culture solution and stirred for 1 h under N_2 atmosphere. A total of 4.7 ml 25% $NH_3 \cdot H_2O$ solution was added to the Fe^{3+}-Fe^{2+}-cells hybrid solution with stirring for 30 min under N_2 atmosphere. The black Fe_3O_4/cells precipitates were collected by centrifugation and washed with deionized water and ethanol for several times, and finally dried in a vacuum drying oven at 80 °C for 12 h. Some dried specimens were calcined at 300 °C for 2 h.

2.2. Characterization

The crystal structure of the hybrid Fe_3O_4 nanoparticles was obtained by an X-ray diffractometer with a Cu Kα ($\lambda = 0.15418$ nm) irradiation (X'Pert PRO, PANalytical X-ray Company, Holand). The Barrett–Joyner–Halenda (BJH) models and the nitrogen (N_2)

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adsorption–desorption isotherms (NADI) were carried out at 77 K using a computer-controlled sorption analyzer (Micromeritics, Gemini V2.0, America) operating in the continuous mode. The morphologies of the selected Fe_3O_4/cells powders were investigated with a transmission electron microscope (TEM) (JEM-100X, JEOL, Japan), using an accelerating voltage of 100 kV. Samples for TEM were prepared by air-drying a drop of sonicated ethanol suspension of powders onto a gelatin-coated copper mesh. The chemical bond linkages of samples were studied by Fourier transform infrared (FT-IR) spectroscopy (NEXUS 470, Nicolet, USA) by a KBr wafer technique. Magnetization measurements of the Fe_3O_4/cells composites were performed at room temperature using vibrating sample magnetometer (VSM) (JDWM-2000B, Changchun Yingpu Magnetoelectric Tech. Co., Ltd., China).

3. Results and discussion

The XRD pattern of the as-synthesized sample is shown in Fig. 1. All the reflection peaks in Fig. 1 are the same as the standard value of Fe_3O_4 crystal (JCPDS No. 79-0417). A very small amount of impurity whose peaks are almost negligible is detected in the XRD pattern. The mean particles size calculated from Fe_3O_4 diffraction peaks by the Scherrer equation is 17.4 nm, in good agreement with the result observed by TEM.

The NADI and the pore diameter distributions of the Fe_3O_4/cells composites (contain 0.8 g dry yeast) are shown in Fig. 2. The materials show type IV isotherms typical for mesoporous systems. The dried sample has a specific surface area of 96.31 m^2/g with a pore size distribution of 8–4 nm (Fig. 2a). After calcining at 300 °C, a higher surface area of 117.54 m^2/g can be obtained (Fig. 2b). The pore diameter of calcined sample increases slightly from 10 to 13 nm due to the carbonization of yeast cells. It can be inferred that the Fe_3O_4/cells composites have thermally stable mesostructure up to 300 °C.

TEM images of the mesoporous samples show the existence of wormhole-like structures. The disordered wormhole-like pore structure is formed from the agglomerates of hybrid Fe_3O_4 nanoparticles (Fig. 3a). It can be seen that the size of the nanoparticles is uniform with a diameter of about 16 nm. The wormhole-like mesostructure is retainable after calcining at 300 °C (Fig. 3b). In the samples heated at 300 °C, large agglomerates of the Fe_3O_4/carbon are observed. The accessible pores are connected at random, lacking discernible long-range order in the pore arrangement among the Fe_3O_4 nanoparticles.

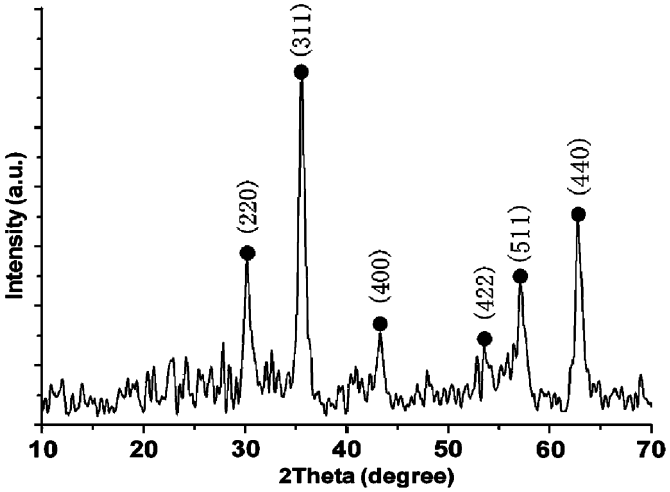

Fig. 1. XRD pattern of Fe_3O_4/cells composite with mesoporous structure.

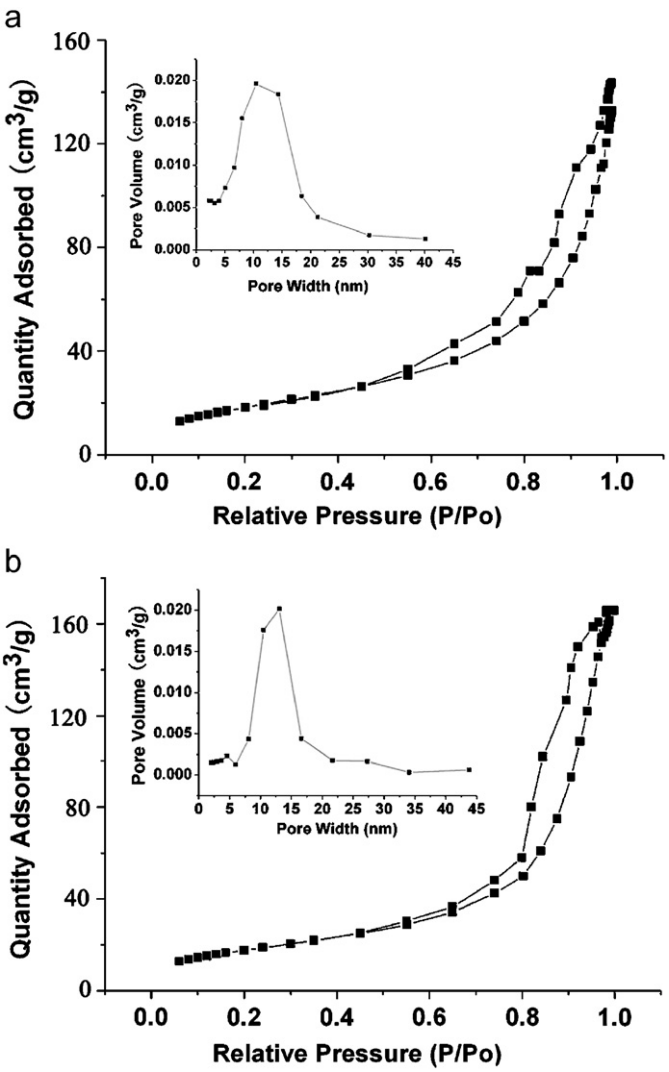

Fig. 2. NADI and pore size distributions for mesoporous Fe_3O_4/cells composites (a) dried at 80 °C and (b) calcined at 300 °C.

The mesoporosity is mainly due to the interparticle porosity rather than intraparticle porosity.

To realize the combination mechanism, the FT-IR spectra of Fe_3O_4/cells composites treated by different temperatures are shown in Fig. 4. The peak around 3376 cm^{-1} observed in curve *a*, *b* and *c* relates to the O–H group. The dominating absorption bands appeared at 1643 and 1538 cm^{-1} (curve *b*) are assigned to amide I and amide II, the characteristic IR absorption of protein which could be one of the significant components of yeast cells. After calcining at 300 °C, the characteristic peaks of the protein are weak due to the carbonization of yeast cells. The absorption band at 576 cm^{-1} is related to the vibrations of Fe–O functional group (trace b). In trace c, the two bands at 636 and 561 cm^{-1} are attributed to the high crystallinity of Fe_3O_4 nanoparticles. Comparing with the standard spectrum of naked Fe_3O_4 (Fe–O, 569 cm^{-1}) [14] and pure yeast cells (trace a, protein, 1656 and 1549 cm^{-1}), the characteristic peaks in the spectrum of Fe_3O_4/cells composites all shift slightly. The results indicate that yeast cells are chemically bonded to Fe_3O_4 nanoparticles by electrostatic interaction and chemical reaction.

The magnetic properties of Fe_3O_4/cells composites are evaluated by a VSM at room temperature as shown in Fig. 5. When yeast cells amount increases, the saturation magnetization of the