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Facile route to γ-Fe_2O_3/SiO_2 nanocomposite used as a precursor of magnetic fluid

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Abstract

Maghemite (γ-Fe_2O_3) nanoparticles (NPs) homogeneously dispersed in silica matrix were obtained via a three-step chemical procedure at mild conditions. The acid-treated solids were obtained using silica NPs, $Fe(NO_3)_3{\cdot}9H_2O$ and acetic acid. The nanocomposites with various contents of maghemite were prepared by heating the acid-treated solids at 80 °C for 2 h and then at 400 °C for 1 h. The acid-treated solids were studied by means of Fourier Transform infrared spectroscopy (FT-IR) and thermogravimetry (TG). The morphology and particle size of the magnetic nanocrystallites were evaluated by the transmission electron microscopy (TEM) technique, while the nature of the obtained nanocomposites was studied using X-ray powder diffraction (XRD) and vibrating sample magnetometer (VSM), showing that the acid treatment played a critical role for the magnetic-phase formation and the maximum saturation magnetization (Ms) of the obtained nanocomposite was 37.78 emu g^{-1}. However, when $FeCl_3{\cdot}6H_2O$ was used as precursor instead of $Fe(NO_3)_3{\cdot}9H_2O$, pure hematite (α-Fe_2O_3) particles dispersed in silica matrix were obtained. Magnetic fluid (MF) was prepared using the maghemite/silica nanocomposites by high-energy ball milling and was characterized by UV–vis, Gouy magnetic balance and rotating rheometer.

Keywords: Composite materials; Iron oxide; Magnetic properties; Nanocrystallites

1. Introduction

The synthesis of magnetic nanomaterials is a subject of great interest due to the broad applications of these materials, including data storage [1], magnetic resonance contrast-enhancing media [2], gas sensors [3,4], magnetic fluids (MFs) [5], magnetic refrigeration [6], magneto-optics [7,8], bioprocessing [9,10], and so on. Among a variety of magnetic materials, maghemite powder (γ-Fe_2O_3, the cubic form of iron (III) oxide) has received much attention due to the excellent ferrimagnetic and anti-oxidation properties, and has been used widely for the production of magnetic materials and catalysts.

Various methods had been reported in literature for preparing iron oxide NPs, such as wet chemical synthesis [11], sol–gel processing [12], chemical vapor deposition [13], electrochemical preparation [14], pyrolysis techniques [15,16], and so on. Generally, these methods encountered difficulties in large-scale production of magnetic NPs with controllable particle size and single crystalline structure. The preparation of pure γ-Fe_2O_3 NPs also presents some difficulties partially arising from the different states of metal oxides, which can lead to the simultaneous presence of various oxides (FeO, Fe_2O_3, and Fe_3O_4) during the heating treatment. Moreover, Fe_2O_3, besides the maghemite phase, also exhibits amorphous or other crystalline phase, among which hematite (α-Fe_2O_3) is the one that is thermodynamically stable. γ-Fe_2O_3 transforms to α-Fe_2O_3 at a temperature above 380 °C. Moreover, the performance of the materials made of γ-Fe_2O_3 depends strongly on the particle size and particle size distribution (PSD). Magnetic NPs with a uniformity size distribution were difficult to be obtained using conventional methods. The aggregation of NPs induced the loss of some excellent performance of nanomaterials. One way to stabilize the magnetic NPs and also to prevent the magnetic NPs from aggregation is

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uniformly dispersing the iron oxide particles in some matrix, such as glass [17,18], silica matrix [8,19,20], ceramic [21], or polymer [7,22]. Consequently, pure iron oxide NPs homogeneously dispersed in some matrix could demonstrate satisfactory properties, though the dispersion process might be rather complicated.

Magnetic fluid (MF) is a colloidal suspension of magnetic NPs dispersed in a solvent (water or organic solvent) by some surfactants. The performance and stability of the MFs are controlled by the nature of the particle–particle interactions which in turn are dictated by the surfactant layers on the particles. Based on the abroad applications (such as in some loudspeakers and computer hard discs for dynamic sealing), research and development on the preparation and characterization of MFs have been very active since the inception of MFs. Laibinis and co-workers [23] successfully prepared stable and water-based MFs consisting of iron oxide NPs, stabilized by self-associated bilayers of two alkanoic acids. Sousa and co-workers [24] prepared biocompatible MFs based on γ-Fe_2O_3 NPs, which were successfully grafted by antibodies to transport the NPs into different human tissues.

In this paper, to prepare the maghemite NPs with high purity and narrow PSD, the precursor was mixed with silica NPs and treated with acetic acid first, and then followed with heating treatment. The γ-Fe_2O_3 NPs were homogeneously dispersed in the silica matrix. Stable MF was obtained using the nanocomposites by ball milling. The magnetic properties and rheological behavior of the MF were investigated.

2. Experimental

2.1. Materials

Silica NPs (M-5, Cabot GmbH, about 30 nm, 200 $m^2\,g^{-1}$) were obtained from Deutschland Cabot GmbH. Ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), ferric chloride ($FeCl_3{\cdot}6H_2O$), ethyl alcohol and acetic acid were all analytic grade, purchased from the commercial market, and used without further purification before utilization. Oleate sodium and polyethylene glycol 4000 (PEG-4000) were chemical grade. Deionized water was used throughout the experiments.

2.2. Preparation procedure

2.2.1. Particle preparation

The silica–maghemite composites with various maghemite contents were obtained as follows: 0.3 g of fumed silica (M-5) was dispersed in 10 ml of CH_3CH_2OH containing certain amount of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$). Then 10 ml of acetic acid was added, which could ensure that the acid was superfluous. The particulate mixtures were dispersed uniformity using a high-energy ball mill operating at 40 rpm for 3 h followed by rapid removal of the solvent at 50 °C using a rotary evaporator. The rotary evaporator was vacuumed simultaneously at the working time. The russety solids were further dried for 2 h at 80 °C under air atmosphere to remove any physically absorbed acetic acid, and then crushed into powder. The as-prepared reddish particles were calcined at 400 °C for 1 h under air atmosphere. The brownish particles of γ-Fe_2O_3/SiO_2 were obtained. This process was named as *Standard Procedure*. The reddish particles were also calcined at different temperatures and for different time under air atmosphere to find the best conditions to prepare the γ-Fe_2O_3/SiO_2 nanocomposites.

To study the influence of iron concentration on the particle size, silica NPs with the same weight (0.3 g) were dispersed in 10 ml of CH_3CH_2OH containing 300, 606 and 808 mg of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) to produce *Powder a*, *b* and *c*, respectively. The preparation procedure was the same as the *Standard Procedure*. The magnetic products, *Powder a*, *b* and *c* were finally obtained.

To investigate the role of acetic acid during the formation of magnetic phase, some samples were prepared similarly as the *Standard Procedure*, just distinguishing from which the acetic acid was not added. The yellowish solids were obtained after heating treatment at 80 °C. After calcining at 400 °C for 1 h, the brownish particles were obtained.

To investigate the influence of precursor on the products, some samples were prepared similarly as the *Standard Procedure*, just distinguishing from which the precursor was changed to ferric chloride ($FeCl_3{\cdot}6H_2O$). The obtained yellowish solids after heating treatment at 80 °C were calcined at 400 °C for 1 h. The purplish particles were obtained.

2.2.2. Preparation of MF

The MF was prepared according to the procedures of the published article [25] by ball milling with some modifications. In a typical run, 2.1 g of γ-Fe_2O_3/SiO_2 (*Powder c*) was added to a mill pot, then the solution was added, in which 3 g of PEG-4000 powder was dissolved in 10 ml of water. The mill pot and small balls were made of carnelian. The volume of the pot was 50 ml. The milling operation was carried out with a QM-1SP4 planetary ball mill (Scientific Instrument Factory of Nanjing Univ., China) at room temperature for 3 h. The milling speed was set at 40 rpm. Thereafter, 3 g of oleate sodium dissolved in 5 ml of water was added. The milling operation was continued for additional 1 h. The obtained mixture was centrifuged at 4000 rpm to eliminate the foams. Then the MF was obtained.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were obtained using Nicolet FT-IR Avatar 360 with KBr method. The crystalline phases were identified by X-ray powder diffraction (XRD) measurements with a D/Max-III C, using Cu Kα radiation. The particle sizes were determined from transmission electron microscopy (TEM) images obtained using Libra 120 Energy Filtering TEM (EF-TEM) made by Carl Zeiss (Germany). The size could also be obtained by analyzing the broadened major peak of XRD spectra using the Scherrer's equation. The thermal behavior of the as-prepared solids was measured by thermogravimetry (TG) (Perkin-Elmer TGA7). The magnetic property of nanocomposites was measured using a BHV-55 vibrating sample magnetometer (VSM).

The stability of the MF was estimated by UV–vis measurements before and after sedimentation under gravitational field. The UV–vis spectra were obtained using a HITACHI U-2810 spectrophotometer. The rheological property measurements of the MFs were carried out using a Brookfield LVDV-III+ rotating rheometer, in some cases a magnetic field (17 mT) was applied to the samples. The magnetic property of the MF was measured by a Gouy magnetic balance (FD-TX-FM-A).

3. Results and discussion

3.1. FT-IR spectra

The IR spectra of the solids prepared with different procedures were displayed in Figs. 1–3. In these figures, the absorptions around 1100, 810 and 470 cm^{-1} are the characteristic absorption of the silica, and the peaks around 3380 cm^{-1} is the characteristic absorption of hydroxyl groups existed on the particle surface. Fig. 1 shows the IR spectra of the solids before calcination but after heating treatment at 80 °C for 2 h using ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) as precursor, in which Fig. 1a is the spectrum of the sample without treatment of acetic acid and Fig. 1b is that treated by acetic acid during the preparing process. The absorption peaks at 1381.5 cm^{-1} in Fig. 1a and 1389.2 cm^{-1} in Fig. 1b belong to the asymmetric stretching vibrations of NO_3^- group, revealing that nitrate in the as-prepared solids does not decompose at 80 °C yet. It is consistent to the result of the TG which shows that the NO_3^- group decomposed at