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Microwave synthesis of magnetic Fe_3O_4 nanoparticles used as a precursor of nanocomposites and ferrofluids

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Abstract

Methods to synthesize magnetic Fe_3O_4 nanoparticles and to modify the surface of particles are presented in the present investigation. Fe_3O_4 magnetic nanoparticles were prepared by the co-precipitation of Fe^{3+} and Fe^{2+}, $NH_3 \cdot H_2O$ was used as the precipitating agent to adjust the pH value, and the aging of Fe_3O_4 magnetic nanoparticles was accelerated by microwave (MW) irradiation. The obtained Fe_3O_4 magnetic nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and vibrating sample magnetometer (VSM). The average size of Fe_3O_4 crystallites was found to be around 8–9 nm. Thereafter, the surface of Fe_3O_4 magnetic nanoparticles was modified by stearic acid. The resultant sample was characterized by FT-IR, scanning electron microscopy (SEM), XRD, lipophilic degree (LD) and sedimentation test. The FT-IR results indicated that a covalent bond was formed by chemical reaction between the hydroxyl groups on the surface of Fe_3O_4 nanoparticles and carboxyl groups of stearic acid, which changed the polarity of Fe_3O_4 nanoparticles. The dispersion of Fe_3O_4 in organic solvent was greatly improved. Effects of reaction time, reaction temperature and concentration of stearic acid on particle surface modification were investigated. In addition, Fe_3O_4/polystyrene (PS) nanocomposite was synthesized by adding surface modified Fe_3O_4 magnetic nanoparticles into styrene monomer, followed by the radical polymerization. The obtained nanocomposite was tested by thermogravimetry (TG), differential scanning calorimetry (DSC) and XRD. Results revealed that the thermal stability of PS was not significantly changed after adding Fe_3O_4 nanoparticles. The Fe_3O_4 magnetic fluid was characterized using UV–vis spectrophotometer, Gouy magnetic balance and laser particle-size analyzer. The testing results showed that the magnetic fluid had excellent stability, and had susceptibility of 4.46×10^{-8} and saturated magnetization of 6.56 emu/g. In addition, the mean size d (0.99) of magnetic Fe_3O_4 nanoparticles in the fluid was 36.19 nm.

Keywords: Fe_3O_4 nanoparticles; Stearic acid; Surface modification; Lipophilic degree; Magnetic fluid

1. Introduction

Nanosized Fe_3O_4 (magnetite), an important member of spinel type ferrite, is widely used for recording material, pigments, electrophotographic developer [1], mineral separation [2], efficient heat transfer applications [3], cancer therapy [4], and so on. A variety of methods have been reported in the literature to synthesize Fe_3O_4 nanoparticles, including the reduction of hematite by CO/CO_2 [5], γ-ray radiation [6], co-precipitation from the solution of ferrous/ferric-salt mixture in alkaline medium [7], hydrolysis [8], sol–gel technique [9] and oxidation of $Fe(OH)_2$ by H_2O_2 [10]. However, due to large specific surface area, high surface energy and magnetization, Fe_3O_4 nanoparticles are prone to aggregate. In order to improve the dispersion of nanoparticles and the compatibility of nanoparticles with organic solvents, surface treatment for Fe_3O_4 nanoparticles is a necessity.

Our previous studies [11] have shown that co-precipitation from the solution of Fe^{2+}/Fe^{3+} with aqueous ammonia followed by aging at room temperature for

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7 days and heating at 70 °C for 30 min under Ar protection was an optimal way to obtain Fe_3O_4 nanoparticles with high saturation magnetization. However, the aging period is not favorable. Microwave (MW) irradiation might be a promising method in processing materials due to its thermal and non-thermal effects. Compared with the conventional methods, MW synthesis has the advantages of short reaction time, small particle size and narrow size distribution.

In the present investigation, magnetic Fe_3O_4 nanoparticles were prepared by the co-precipitation of Fe^{3+}/Fe^{2+} using $NH_3 \cdot H_2O$ as the precipitating agent to adjust the pH value. Then, the magnetic nanoparticles were aged under MW irradiation. Afterwards, the surface of the Fe_3O_4 magnetic nanoparticles was modified by stearic acid.

2. Experimental

2.1. Materials

Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), aqueous ammonia, ethyl alcohol absolute, methyl alcohol, acetone and toluene were all analytic grade. Stearic acid and paraffin liquid were chemical grade. Deionized water was used throughout experiments.

2.2. Synthesis of magnetite nanoparticles

To synthesize Fe_3O_4 nanoparticles, a solution of mixture of $FeCl_3$ (0.5 M) and $FeSO_4$ (0.5 M) with a molar ratio of 1.75 : 1 was prepared under Ar protection. 10 ml of ammonia aqueous solution was then quickly charged into the solution with vigorously stirring, followed by more ammonia aqueous solution being dropped into the mixture slowly with stirring until the pH value of the solution reached 9. Thereafter, the solution was kept stirring for additional 30 min under Ar protection. The resulted black mixture was aged under MW irradiation with the frequency of 2.45 GHz in a water bath for 2 h. The flask was against the middle of filter whose pore size was 7.0×5.5 cm. Finally, the precipitate was collected by filtration and washed three times with deionized water and ethyl alcohol, respectively, and then dried under vacuum for 12 h.

2.3. Modification

Surface modification of Fe_3O_4 nanoparticles was carried out by the reaction of nanoparticles with stearic acid. The typical procedure was as follows: stearic acid of different amount, Fe_3O_4 of 1 g and toluene solution of 50 ml were mixed together in a flask with a reflux condenser. The reaction mixture was stirred for 1 h at a temperature of 100 °C under Ar protection. Then, the magnetite particles were separated by high-speed centrifugation and purged with acetone for 48 h using a Soxhlet extractor to remove the remnant stearic acid and toluene on the surface. The retrieved particles were dried under vacuum for 12 h.

2.4. Determination of lipophilic degree

The measurement of lipophilic degree (LD) was performed by the titration for the pretreated particles with methyl alcohol. Typically, 0.4 g of Fe_3O_4 pretreated with stearic acid, was put into 40 ml of H_2O and titrated with methyl alcohol under stirring until all particles were wetted. The LD was calculated according to the following expression [12]:

$$\mathrm{LD} = \frac{V}{V + 40} \times 100\%, \tag{1}$$

where V was the volume of methyl alcohol used in the experiments.

2.5. Preparation of nanocomposite

Fe_3O_4/polystyrene (PS) nanocomposite was synthesized as follows. About 110 mg of surface-modified Fe_3O_4 magnetic nanoparticles and 10 ml of styrene monomer were under ultrasonic oscillation for 30 min. Thereafter, 36 mg of azobisisobutyronitrile (AIBN) was added into the mixture, followed by the radical polymerization at a temperature of 90 °C for 4 h. After that, the obtained products were charged into tetrahydrofuran (THF) under stirring until dissolved. The resulted suspension was poured into 200 ml of methyl alcohol under vigorous stirring. Finally, the precipitation was collected by filtration and dried under vacuum for 12 h.

2.6. Preparation of magnetic fluid

To prepare Fe_3O_4 magnetic fluid, 1 g of Fe_3O_4 and 50 ml of toluene solution of stearic acid were mixed together in a flask with a reflux condenser. The mixture was stirred for 1 h at a temperature of 75 °C under Ar protection, then 50 ml paraffin liquid was poured into the solution, afterwards, the mixture was kept at 50 °C under stirring and Ar protection for 1 h. Finally, the obtained solution was stirred at room temperature for 8 h.

2.7. Characterization

Fourier transform infrared (FT-IR) spectra were obtained using Nicolet FT-IR Avatar 360 with KBr method. The nanoparticles sizes were determined by Hitachi H-600-II transmission electron microscope (TEM). X-ray diffraction (XRD) measurements were carried out with D/Max-IIIC, using Cu-Kα radiation. The magnetic properties of nanoparticles were measured on a BHV-55 vibrating sample magnetometer (VSM). The modification effects were revealed by scanning electron microscopy (SEM) (HITACHI S570) and sedimentation test. The thermal stability of nanocomposites was measured by