

Chemical Synthesis and Characterization of Magnetic Nanoparticles

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Abstract—This paper presents a method for the chemical synthesis and characterization of Fe₃O₄ magnetic nanoparticles (MNPs). In the work, MNPs were fabricated by chemical co-precipitation. The stoichiometric ratio of Fe²⁺/Fe³⁺ was 2:3, and polyethylene glycol 2000 (PEG-2000) was chosen as the dispersant. Isolated single MNPs were obtained from the diluted solution of MNPs dried on a clean silicon wafer surface. The X-ray diffractometer (XRD), scanning electron microscope (SEM) and magnetic force microscope (MFM) were used to characterize the Fe₃O₄ MNPs. The fabricated Fe₃O₄ MNPs were paramagnetic and able to be separated from the solution by a magnet. The experiment results have shown that this method can obtain the decentralized MNPs with the average diameter of 99.6 nm for different potential applications.

Keywords—Fe₃O₄ magnetic nanoparticles; chemical co-precipitation; characterization; magnetic force microscope

I. INTRODUCTION

Magnetic nanoparticles (MNPs) have been investigated in biotechnology and biomedicine in recent years due to their attractive properties such as the controllable size, superparamagnetic feature and biocompatibility, and their capabilities have been explored in the applications of disease therapy, magnetic resonance imaging (MRI), tissue engineering, cell labeling and drug delivery [1-4]. Vema et al. [5] evaluated the capability of quercetin loaded MNPs as drug delivery to therapeutics of lung cancer cells. Baraki et al. [6] labeled an acute soft tissue infection with superparamagnetic particles of iron oxide (SPIO) previously by MRI, and Silva et al. [7] used citrate-coated MNPs to label cells and monitor the fate of them by MRI. Hathaway et al. [8] incubated antibody-conjugated MNPs with cells to detect the breast tumor cells. On the other hand, the ratios of surface-to-volumes of MNPs are significantly increased, and the effects of quantum-sizes of MNPs are enhanced. Because of the features, MNPs also have an increasing interest in many applications. Yang et al. [9] successfully fabricated Fe₃O₄ nanoparticles using poly vinyl pyrrolidone (PVP) and ethylene glycol (EG). In the fabrication, the PVP and EG were used as the surface modification reagent and the dehydration, respectively. Gregorio et al. [10] reported the preparation of MNPs using the co-precipitation technique, coated with different concentrations of chitosan, and Zhang et al. [11] synthesized Fe₃O₄ MNPs with the diameters of about 10

nm and used them to remove phenol and aniline from an aqueous solution.

Recently, a number of clinical trials have been conducted to study potential applications of MNPs in biomedicine, and for this purpose, various methods such as electron beam lithography, oxidation method, gas-phase deposition, hydrothermal method and chemical co-precipitation [12-14] have been studied to obtain MNPs. Electron beam lithography is an approach that converts Fe particles into the Fe₃O₄ with electrons. With this method, however, it is difficult to monitor the sizes of particles and collect them. The oxidation method is a wet chemical preparation method. It is used for fabricating small-sized nanoparticles by crystallization, and it is easy to obtain uniform particles on the molecular level, but the whole reaction process takes a long time, and the material is expensive. Gas-phase deposition can produce one-dimensional iron oxide nanostructures. The method works as the chemical vapor deposition process assisted by catalyst, but the precise control of the synthesis conditions is difficult. The hydrothermal method synthesizes MNPs in an aqueous medium. It works at a temperature higher than 200°C and pressure higher than 13790 kPa [15]. In practice, it is difficult to meet such conditions and the equipment cost is high. Compared with other methods, chemical co-precipitation is simple and efficient to synthesize iron oxide nanoparticles under the condition of a proper temperature, PH and ionic strength.

In this work, the chemical co-precipitation method together with the dispersant of polyethylene glycol 2000 (PEG-2000) was used in the experiment to obtain well dispersed Fe₃O₄ MNPs. The stoichiometric ratio of Fe²⁺/Fe³⁺ was 2:3. The X-ray diffractometer (XRD), scanning electron microscope (SEM) and magnetic force microscope (MFM) were used to characterize the MNPs. SEM images were acquired with and without the use of PEG-2000 to compare the effect of the polymer on the dispersion of MNPs. The details are described in the following sections.

II. MATERIALS AND METHODS

A. Materials

The analytical reagent grade of ferrous chloride

(FeCl₂·4H₂O), ferric chloride (FeCl₃·6H₂O) and hydrochloric acid (HCl) were used for the synthesis of Fe₃O₄ MNPs. 0.5 mol/L aqueous ammonia (NH₃·H₂O) was used as the precipitant, and catalytic polyethylene glycol 2000 (PEG-2000) was used for dispersing the particles. High purity nitrogen (N₂) was used to protect the process in the experiment. Ultrapure water was prepared by the Millipore water purification system and magnetic stirrer (HJ-3) was used for the synthesis. The high-speed centrifugation (5430R, Eppendorf) was used to separate the MNPs.

B. Instruments used for characterization

Properties of Fe₃O₄ MNPs synthesized by chemical co-precipitation together with PEG-2000 were analyzed by a TongDa TD-3000 diffractometer using Cu-Kα (λ=0.154 nm). The sizes and structures of the particles were examined by SEM (FEI QUANT-250 FEG) at the 5 kv accelerated voltage, from which the samples were prepared by dispersing the particles in absolute ethyl alcohol and then depositing the MNPs on a clean silicon wafer surface and then dried in the air at the room temperature. An MFM (Benyuan CSPM-5500) was used to analyze the nanoscale magnetic properties of the Fe₃O₄ MNPs, and the two-pass scan method was used. The sample topography was acquired during the first scan. The probe was close to the sample surface. The magnetic force image was obtained during the second scan. The probe was kept at the constant distance of 15 nm higher than the first scan profile. The used magnetic probe was the BudgetSensors' Multi75M-G, and the resonant frequency was 75 kHz. The MFM images of Fe₃O₄ MNPs were acquired under the conditions of the clean room environment with the controlled room temperature, and the tapping-lift mode was used for imaging.

C. Synthesis of Fe₃O₄ nanoparticles

All chemicals in the experiment were used without further purification and the Fe₃O₄ MNPs were fabricated by chemical co-precipitation in liquid. First, 0.0795 g FeCl₂·4H₂O was diluted with ultrapure water to 50 ml, a few drops of concentrated hydrochloric acid was added into 0.1621 g FeCl₃·6H₂O to prevent the hydrolysis of Fe³⁺, and then ultrapure water was added to 50 ml. Second, the two solutions were mixed together in a conical flask after the dissociation of them with ultrasonic oscillation completely. 1 g PEG-2000 was then added as dispersant and mixed with the solution again by ultrasonic oscillation. The stoichiometric ratio of Fe²⁺/Fe³⁺ was 2:3 in the experiment. The constant temperature magnetic stirrer was set to work at the temperature of 70 °C to ensure the required synthesis temperature. The solution was continuously stirred for 10 minutes, and then 5 mol/L NH₃·H₂O was gradually added into the solution as the precipitant until the color of the mixture was changed from yellow to black. 45 minutes later, the synthesis was completed. The whole synthesis process was protected with N₂. After the reaction, the solution was naturally cooled down. At the room temperature, the MNPs were separated using a permanent magnet. Large particles and unreacted materials were then removed with the centrifugation (1000 rpm/min, 5 min), and the MNPs were washed with absolute ethyl alcohol until the washing liquid became neutral. The resultant MNPs were

dispersed in absolute ethyl alcohol.

The chemical co-precipitation of Fe₃O₄ formation is expressed by^[1]



where the stoichiometric ratio Fe²⁺/Fe³⁺ was 1:2. The ratio of 2:3 was used in the synthesis process in order to improve the yield of the reactants.

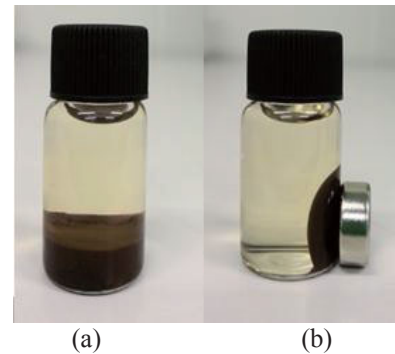
III. RESULTS AND DISCUSSIONS

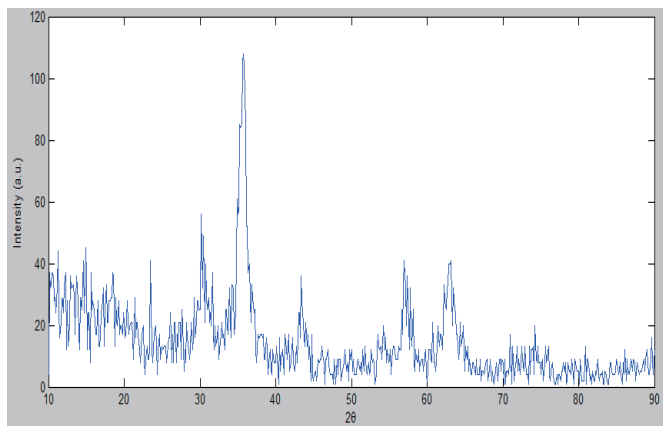
The morphology and magnetism of the synthesized MNPs were investigated by the XRD, SEM, AFM and MFM on the nanoscale^[16-18]. The XRD was used to examine the element presence. SEM and AFM were used to image 3D geometric parameters, and MFM to measure the magnetic properties of MNPs.

In this work, the Fe₃O₄ MNPs were fabricated by chemical co-precipitation method together with the dispersant of PEG-2000, and the obtained paramagnetic particles were observed using the XRD, SEM, AFM and MFM. It can be seen from the results that the average size of Fe₃O₄ MNPs is 99.6 nm in diameter. The particles were conveniently separated from the solution in external magnetic fields.

The Fe₃O₄ MNPs after reaction in bottles and its XRD pattern are shown in Fig. 1. Fig. 1(a) is the resultant solution after reaction for one hour and it has clearly been separated. Fig. 1(b) is the resultant solution in a magnetic field. It can be observed that when the reaction solution is placed adjacent to a permanent magnet, it becomes limpid in a few seconds. This indicates that the obtained MNPs have good magnetism. Fig. 1(c) shows the XRD pattern of Fe₃O₄ MNPs synthesized by the chemical co-precipitation method and it clearly shows the XRD signals. Comparing with the obtained results, all the diffraction peaks show the pure Fe₃O₄ structure. The broadened reflection peaks indicate the existence of nanoparticles.

It is evident from Fig. 1 that the precipitation reactions of the Fe²⁺, Fe³⁺ and ammonia solutions can obtain the magnetite and maghemite mixture. The differentiation between them cannot be identified using the X-ray data in Fig. 1(c). The color of result products is black showing the existence of magnetite.





(c)

Fig. 1. Fe_3O_4 MNPs after reaction and its XRD pattern. (a) The solution after reaction for one hour, (b) the solution in a magnetic field, and (c) the XRD pattern of Fe_3O_4 MNPs.

The SEM image of Fe_3O_4 MNPs with the information of size and dispersion is shown in Fig. 2. It can be seen that the Fe_3O_4 MNPs are quasi-spherical in shape and they are well dispersed. The average diameter of the particles is 99.6 nm, and the standard deviation is 6.8 nm. Some large Fe_3O_4 MNPs are also observed, as shown in Fig. 2, and this suggests that part of Fe_3O_4 MNPs could be agglomerated during the reaction process. For comparison, the SEM image of the agglomerated Fe_3O_4 MNPs synthesized without the use of PEG-2000 is shown in Fig. 3.

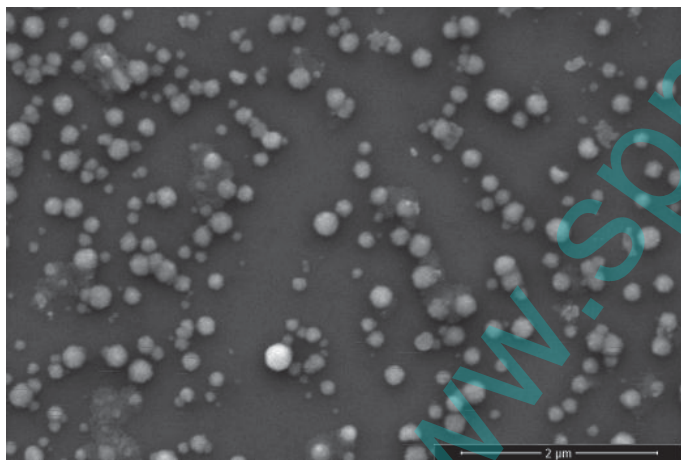


Fig. 2. SEM image of Fe_3O_4 MNPs.

All reactions have rendered the black color of the magnetic nano particles and there is no visual difference between the particles fabricated with and without the use of dispersants. According to the formation principle of Fe_3O_4 MNPs, PEG-2000 plays an important role in the process. The SEM image of Fe_3O_4 MNPs without the use of PEG-2000 is shown in Fig. 3. It is clear that the Fe_3O_4 particles are obtained without the use of the PEG-2000 aggregate with each other and the polymer affects the crystallinity of precipitated reaction products. To estimate the actual magnetic information of Fe_3O_4 MNPs, their magnetic characteristics were analyzed by

MFM, as shown in Fig. 4.

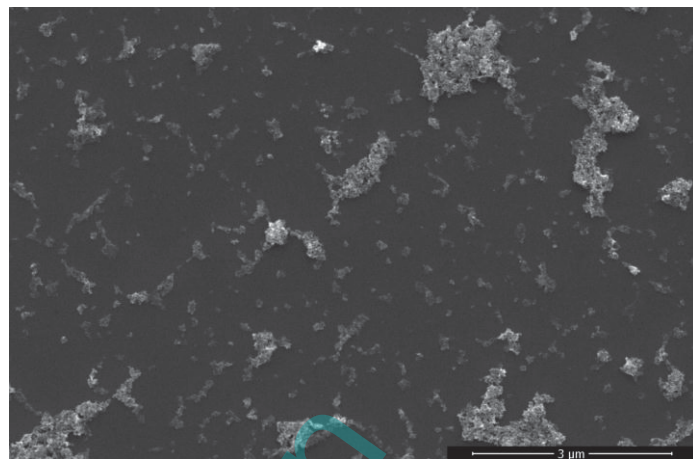
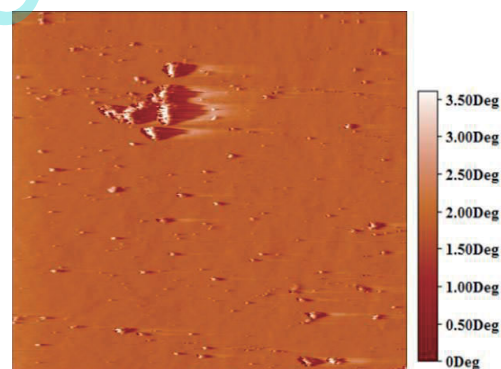
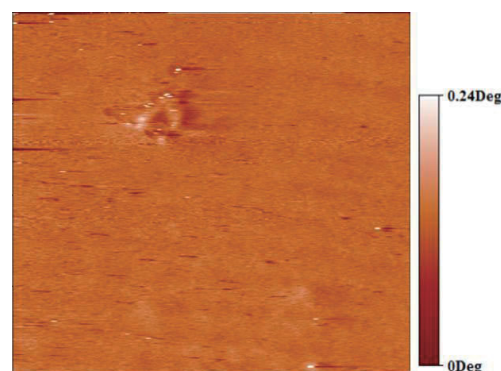


Fig. 3. SEM image of Fe_3O_4 MNPs without the use of PEG-2000.

Fig. 4 shows the MFM images of the synthesized Fe_3O_4 MNPs and they present the paramagnetic behaviors of the Fe_3O_4 particles in different scanning areas. In the experiment, MFM was used to analyze the nanoscale magnetic properties of Fe_3O_4 MNPs. In the images, the magnetic signals from the separated MNPs are obvious. Although the MNPs have small barriers of magnetic anisotropy and easily-changed magnetization with a magnet, they have their stable magnetic domains.



(a)



(b)

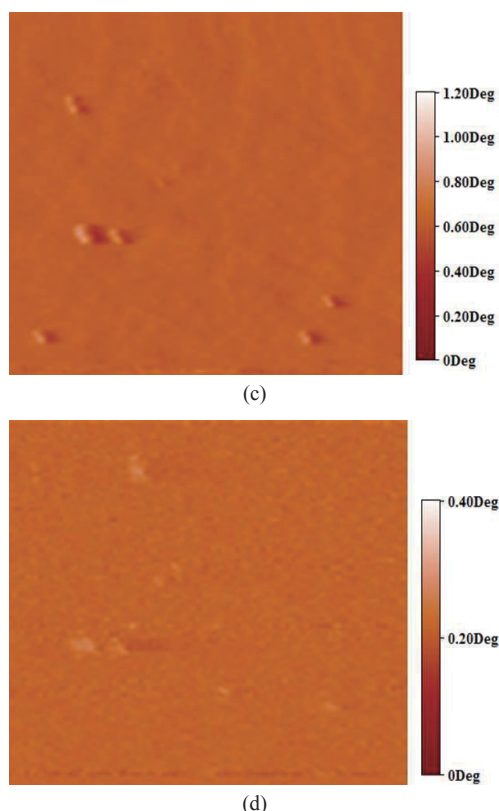


Fig. 4. MFM images of Fe_3O_4 MNPs in different scanning areas. (a) and (c) are the images corresponding to the magnetic force images of (b) and (d). The scanning area of (a) is $20 \times 20 \mu\text{m}^2$ and (c) is $5 \times 5 \mu\text{m}^2$. The image resolution is 1024×1024 .

IV. CONCLUSIONS

The method for chemical synthesis and characterization of Fe_3O_4 MNPs was presented in this work. The Fe_3O_4 MNPs with the average diameter of 99.6 nm were successfully obtained by the chemical co-precipitation method. In the experiment, PEG-2000 was used as the dispersant to prevent the particles from agglomeration. The XRD, SEM, AFM and MFM were used to characterize the properties of Fe_3O_4 MNPs. The fabricated Fe_3O_4 MNPs were paramagnetic and easily separated from the solution by an external magnetic field. The experiment results have shown that this method is able to obtain the decentralized MNPs with the average diameter of 99.6 nm for different potential applications.

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