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Synthesis and characterization of superparamagnetic iron nanocomposites by hydrazine reduction

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Abstract

Superparamagnetic iron nanocomposites were synthesized via a modified oxidation–reduction process. Magnetic iron nanoparticles were prepared first with a moderate reducing agent such as hydrazine. Then, iron nanoparticles obtained were modified by nickel ions in aqueous solution to form core–shell structure nanocomposites. The morphology and magnetic properties of iron nanocomposites were examined by transmission electron microscopy (TEM), VSM and SQUID magnetometer. Temperature dependent magnetization and susceptibility data indicate that the nanocomposites are superparamagnetic above 110 K. The diameter of the iron nanocomposites is determined to be about 6 nm from TEM, showing good agreement with the value acquired by Langevin function fit. X-ray diffraction (XRD) was used to investigate the crystal structure of the iron nanocomposites.

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1. Introduction

Superparamagnetic nanoparticles have been widely used in the fields of ferrofluid technology [1], magnetic catalyst supports [2], contrast enhancement of magnetic resonance imaging (MRI) [3] and magnetically guided site-specific drugs delivery [4] due to their special magnetic properties, i.e. the magnetization curve does not show hysteresis. Superparamagnetic iron nanoparticles are also important materials for their strong magnetism in comparison with any other magnetic particles, such as magnetite and ferrite. In the past decade, there have been quite a number of researches on the reduction of iron ions in aqueous solution to form iron nanoparticles by strong reducing agent such as KBH₄ [5], NaBH₄ [6,7] and LiAlH₄ [8]. However, as the reducing agents mentioned above are so strong that the nanoparticles produced are not uniform and their sizes are larger than their critical sizes. At the same time, the reduction of iron ions by KBH₄ in aqueous solution would rather produce various compounds like Fe₂B

than metallic iron [9], which will reduce their magnetism largely. Thus, the iron nanoparticles produced have no superparamagnetic characteristics and their applications are also limited.

To make full use of advantages of magnetic nanoparticles, magnetic nanoparticles with good physicochemical properties are necessary and desirable. The ideal magnetic nanoparticles are expected to be of high magnetic properties, small size with narrow size distribution, and superparamagnetic characteristics. However, the magnetic iron nanoparticles prepared by conventional methods were of wide size distribution and have no superparamagnetic characteristics [10]. In the present work, the synthesis of iron nanoparticles by reduction of ferrous ion using hydrazine as a reducing reagent in the presence of surfactant was successfully performed. The surface of iron nanoparticles coated by the solution containing nickel ions produced the stable iron composites of nanostructure, which shows superparamagnetic characteristics. The magnetism and structure of the products were characterized with VSM, SQUID magnetometer, transmission electron microscopy (TEM) and X-ray diffraction (XRD). The formation of iron nanocomposites was also discussed as well as the results obtained from magnetic susceptibility experiments.

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2. Experimental

2.1. Materials

Ferrous chloride tetrahydrate (FeCl₂·4H₂O), ammonium hydroxide, sodium dodecylbenzene sulfonate (SDS), nickel sulfate hexahydrate (NiSO₄·6H₂O), sodium acetate and hydrazine (N₂H₄·H₂O) were of reagent grade and were used without any further purification. Water was deionized and deoxygenated prior to use.

2.2. Preparation of iron nanoparticles

The preparation of iron nanoparticles was carried out as follows: $3.5 \text{ g FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.5 g SDS were dissolved in 100 ml deionized water under nitrogen gas with vigorous stirring at 70 °C, 50 ml N₂H₄·H₂O of 80% concentration was then added dropwise into the solution in 10 min. After several minutes, iron nanoparticles were obtained.

2.3. Surface modification of iron nanoparticles

Ammonium hydroxide (4 ml) was added into the 100 ml water solution containing 0.8 g NiSO₄·6H₂O and 0.02 g sodium acetate to form solution with pH 11–12, which was transferred into solution with iron nanoparticles prepared as given above to let the reaction proceed for 30 min. The magnetic particles obtained were then isolated from the liquid and solid mixture by magnetic decantation and washed with deionized water and ethanol for several times. The solid products were dried in vacuum at 60 °C for 12 h.

2.4. Characterization

Transmission electron microscopy (JEM100GX-II) was used to measure the morphology and size of samples obtained. The samples for TEM analyses were obtained by diluting the dispersed solution with ethanol and then placing a drop of the diluted solution onto a covered copper grid and evaporated in air at room temperature. Before the samples were withdrawn, the nanocomposites dispersed ethanol solutions were sonicated for 5 min to obtain the better particles dispersion on the copper grid. Vibrating sample magnetometer (VSM, EG & G Princeton Applied Research Vibration Sample Magnetometer, Model 155) was used to investigate the magnetic properties of nanocomposites by measuring the magnetization as a function of magnetic field intensity. The temperature dependence of magnetization for iron nanocomposites was investigated by a superconducting quantum interference device (SQUID) magnetometer (MPMS5, Quantum Design) at a temperature ranging from 5 to 300 K under different applied magnetic fields. Powder X-ray diffraction (MAC, MXP21VAHF, Cu Ka) was used to investigate the crystal structure of samples.

3. Results and discussion

3.1. Morphology of magnetic iron nanocomposites

The iron nanoparticles were prepared by the oxidationreduction reaction in ferrous ion solution with hydrazine as a moderate reducing agent. At the same time, the iron nanoparticles were also modified from nickel ions solution in the presence of accessory ingredient such as ammonium hydroxide to form iron nanocomposites. Nitrogen gas was injected into the solution to prevent the oxidation of iron nanoparticels in the aqueous solution and also to control the particle size. The surfactant, SDS, was added to make the iron nanocomposites disperse uniformly in the aqueous solution. Fig. 1 shows the TEM photograph of iron nanocomposites with average diameter of about 6 nm by statistical measurement of 500 particles from different regions of the TEM pictures. From the image, we found the produced nanocomposites were connected to each other through magnetostatic reaction and surface tension. Due to the equilibrium of self-repulsion and attracting, self-assembly and agglomeration were occurred when magnetic iron nanocomposites were dispersed on a carbon-coated copper grid.

3.2. Crystal structure of iron nanocomposites

Fig. 2 shows the X-ray diffraction patterns of iron nanocomposites. It was apparent from the X-ray diffraction data that the standard iron crystals with cubic structure have three diffraction peaks: $\{110\}$, $\{200\}$, $\{211\}$. Fig. 2 also shows that the cubic structure of nickel oxidized have five diffraction peaks: $\{111\}$, $\{200\}$, $\{220\}$, $\{420\}$, $\{422\}$. As the shape and positions were far away from those of Ni₂O₃ and metallic Ni, a conclusion can be drawn that the nickel oxide obtained was NiO. Because the metallic nickel deposited on the surface of iron nanoparticles was in contact with air, the metallic nickel was oxidized to the nickel oxide, which is probably NiO.

It is well known that the nanometer sized iron particles are very easy to be oxidized in air. However, from the XRD pattern (Fig. 2), except pure cubic iron, no other iron oxide (Fe₂O₃ or Fe₃O₄) phase was detected, which might be resulted from the protection of NiO on the surface of nanopar-



Fig. 1. TEM of magnetic iron nanocomposites.



Fig. 2. X-ray diffraction patterns of magnetic iron nanocomposites.

ticles. On the other hand, a thin oxide layer on the surface of iron particles might be useful to protect metals from further oxidation. Because no iron oxide was detected by XRD from the nanocomposites, only a very small fraction in crystalline form exists.

3.3. Magnetic properties of iron nanocomposites

The magnetic properties of iron nanocomposites were tested by VSM and SQUID magnetometer at temperature ranging from 5 to 300 K under different applied magnetic fields. Fig. 3 shows the magnetization versus field plots for the iron nanocomposites at temperature of 5 K (a) and 300 K (b). Fig. 3(b) shows that hysteresis disappeared with a little remanence and coercivity, indicating the absence of a long-range magnetic dipole–dipole interaction among the superparamagnetic iron nanocomposites. When the temperature is decreased to 5 K, the magnetization of the sample increases with a symmetric hysteresis loop as shown in Fig. 3(a), showing a transition from superparamagnetic to ferromagnetic behavior.

In magnetism, the temperature dependence of the magnetization for nano-sized magnetic particles reveals typical



Fig. 3. Magnetization curve of magnetic iron nanocomposites at (a) $5\,K$ and (b) $300\,K.$



Fig. 4. Temperature dependence of magnetization for iron nanocomposites at applied field of 800 Oe, the blocking temperature is about 110 K.

characteristics of superparamagnetism, showing the blocking temperature ($T_{\rm B}$) at which the magnetization curve with the zero-field-cooled (ZFC) exhibits a cusp [11]. Fig. 4 shows the temperature dependence of $M_{\rm ZFC}$ for the iron nanocomposites at an applied field of 800 Oe. While the temperature is below about 110 K, $M_{\rm ZFC}$ decreases rapidly with decreasing temperature revealing $T_{\rm B} = 110$ K.

In the theory of superparamagnetism, the magnetization of magnetic nanoparticles is free to be aligned to the applied field above the blocking temperature [12]. In consequence, magnetization curves versus applied fields should exhibit no hysteresis in superparamagnetic state. Then, the magnetization M is described by the standard Langevin function depending on the following relation:

$M = M_0[\operatorname{coth}(\mu H/k_{\rm B}T) - 1/(\mu H/k_{\rm B}T)]$

where $M_0 = N\mu$ (M_0 , saturation magnetization of the sample at a given temperature and N, total number of particles) [13]. The particle moment μ is given by the $M_s\langle V \rangle$ where M_s is the saturation magnetization of the bulk phase and $\langle V \rangle$ is the average volume of iron particles. Fig. 5 shows a good



Fig. 5. The plot of magnetization as a function of applied field with Langevin fit at 300 K.

agreement of experimental data with Langevin function fit for the iron nanocomposites in superparamagnetic state at 300 K. The magnetization data of the iron nanocomposites at 300 K reveals $M_0 = 87.2 \text{ emu g}^{-1}$. Using the saturation magnetization of the bulk iron (1707 emu/cm^3) [14], we can estimate the average volume $\langle V \rangle$ of Fe particles. The average volume is determined to be $8.2 \times 10^{-20} \text{ cm}^3$, which corresponds to a spherical Fe particle with a diameter of 5.4 nm. This is in good agreement with the diameter of about 6 nm determined by TEM micrographs of this sample. When the composite nanoparticle is assumed to have a core-shell structure (Fe-NiO) with a total diameter of 6 nm determined by TEM micrographs of the sample, the chemical composition obtained from calculation (Fe:NiO = 6:1 in molar ratio) corresponds to 5.6 nm Fe core diameter and 0.4 nm shell thickness of NiO. The values to be compared for examining the core-shell structure are now 5.4 and 5.6 nm, which may be regarded as a good agreement. The critical size of Fe particle is 18 nm [15], so it is also concluded that the iron nanocomposite is enough smaller than its critical size, and shows superparamagnetic characteristics.

Compared to the conventional methods [5–8], because hydrazine was a moderate reducing agent, the speed of the oxidation–reduction reaction might be controlled by adjusting the temperature during the reaction. The products prepared were metallic irons, and their sizes were very small and uniform, which were smaller than their critical sizes. At the same time, after the nickels on the surface of the iron nanoparticles were oxidized in air to nickel oxides, the iron nanoparticles will be coated more firmly to form core–shell structure iron nanocomposites.

3.4. Mechanism of reactions involved

According to the preliminary experiments, no iron particles were formed in aqueous solution by adding sufficient amount of hydrazine at 25 °C, even after 2 days. But it was found that the formation of iron nanoparticles might be completed within 15 min at 70 °C. Also, it was found that increasing the pH of solution was necessary for the formation of iron nanoparticles and an elevated reaction temperature was quite helpful in accelerating the reaction rate. Therefore, the reaction temperature was fixed at 70 °C and the pH of the solution was controlled at more than 10, in this work.

A reaction scheme, in the present study, could be expressed as the following equations:

$$2Fe^{2+} + N_2H_4 + 4OH^- \rightarrow 2Fe + N_2 + 4H_2O$$
 (1)

$$Ni^{2+} + 6NH_3 \cdot H_2O \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$
 (2)

$$2[Ni(NH_3)_6]^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni + N_2 + 12NH_3 + 4H_2O$$
(3)

During the course of the reaction, the pH of solution plays an important role in the formation of nanoparticles. The reduction of iron and nickel ions will be effectively achieved by N₂H₄, which is a reducing agent dependent on the pH of solution. This can be deduced from the standard electrode potentials in acidic and alkali solution, namely -0.23 and -1.16 V for the electrode reactions of N₂H₄ \Leftrightarrow N₂ + 4H⁺ + 4e and N₂H₄ + 4OH⁻ \Leftrightarrow N₂ + 4H₂O + 4e, respectively [16]. The latter is desirable for the reduction since the redox potential for Fe²⁺ and [Ni(NH₃)₆]²⁺ is -0.44 and -0.49 V, respectively. Therefore, in the case that the alkalinity of solution is enough, the iron and nickel ions will be reduced by N₂H₄ to metallic iron and nickel.

Based on the studies, results of the characterization and analysis given above, the formation of iron nanocomposites might be described by the model as shown in Fig. 6.

We assumed that the surface of iron nanoparticles (Fig. 6(a)) prepared were adsorbed uniformly by nickel ions (Fig. 6(b)), nickel ion will be reduced by reducing agent to the metallic nickel particles, which deposited uniformly on the surface of iron nanoparticles in the presence of accessory ingredient (Fig. 6(c)). Metallic nickel was oxidized under the air atmosphere to form core–shell structure (Fe–NiO) nanocomposites (Fig. 6(d)).

During the formation of nanocomposites, metallic nickel was not only from the in situ electrochemical reaction of iron with nickel ions but also from the oxidation–reduction of hydrazine with nickel ions, so the iron nanoparticles were coated firmly by the metallic nickel. When metallic nickel deposited on the surface of iron nanoparticles was oxidized first to nickel oxides in the air atmosphere, iron nanoparticles were coated more compactly by nickel oxides. Thus, it is very difficult for oxygen in the atmosphere to approach to the iron through the NiO thin coating to produce iron oxide between the outer layer of NiO and the inner Fe core. As a result, the iron nanocomposites were very stable and showed superparamagnetic characteristics with strong magnetism.



Fig. 6. Formation of iron nanocomposites.

4. Conclusions

The results of the present study show that iron nanoparticles could be synthesized with a moderate reducing agent such as hydrazine, and iron nanoparticles could be modified to form the nanocomposites structure, that is, the corona was NiO, and the core was metal iron. The iron nanocomposites were stable and showed superparamagnetic characteristics with its saturation magnetization of 87.2 emu g⁻¹. The iron nanocomposites were very useful for ferrofluid technology and magnetic catalyst supports. They can also be modified to form magnetic polymer microspheres for the immobilization of proteins and affinity ligands.

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