Simple synthesis and magnetic properties of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles

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**ABSTRACT**

In this paper, the magnetic properties of Fe$_3$O$_4$ nanoparticles at different temperatures were investigated. It was found that the magnetism of Fe$_3$O$_4$ nanoparticles vanished at 550 °C when exposed in the atmosphere for 2 h. X-ray diffractometer, Fourier transform infrared spectroscopy and scanning electron microscope were employed to explain the change of magnetism of Fe$_3$O$_4$ nanoparticles. The route of phase transitions from Fe$_3$O$_4$ to α-Fe$_2$O$_3$ along with the increasing temperature was brought out. In order to maintain the magnetism of Fe$_3$O$_4$ nanoparticles at a higher temperature, a simple method was introduced to deposit BaSO$_4$ shell on the Fe$_3$O$_4$ cores to prepare Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles. The magnetism of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles did not vanish till 750 °C. The change of magnetism of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles was proved to be related to the appearance of "holes" on the surfaces of BaSO$_4$ shells.

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1. Introduction

Magnetite (Fe$_3$O$_4$) is a common ferrite that has a cubic inverse spinel structure. The compound has exhibited unique electric and magnetic properties based on the transfer of electrons between Fe$^{2+}$ and Fe$^{3+}$ in the octahedral sites. As an important magnetic material, Fe$_3$O$_4$ nanoparticles have been widely used in mineral separation [1], heat transfer applications [2], protein separation [3], efficient hyperthermia for cancer therapy [4], biosensors [5], MR contrast agents [6–8], dynamic sealing [9], recovery of metal ions [10,11], and so on. Various methods have been reported in the literature for the preparation of ultrafine Fe$_3$O$_4$ nanoparticles, such as hydrothermal process [12], hydrolysis [13], thermal decomposition [14], microwave-synthesis [15], chemical precipitation from microemulsion [16], electron [17] and ultrasound irradiation [18].

It should be noted that magnetite (Fe$_3$O$_4$) is not thermodynamically stable under oxidizing conditions and pure magnetite will be oxidized to α-Fe$_2$O$_3$ when above 400 °C [19]. Thus, the application of Fe$_3$O$_4$ nanoparticles in many fields was restrained. For instance, magnetic fluid seals have been widely used for keeping vacuum or excluding a working space from dust in the atmosphere. In these applications the resisting pressure per stage of sealing gap is in first-order dependent on the strength of the magnetism of the magnetic fluid [9]. During the sealing process, the raise of temperature and contact with oxygen for magnetic fluid are inevitable, leading to short lifetime of the magnetic fluid seals. Therefore, there is a necessity to investigate the oxidation behavior of Fe$_3$O$_4$ nanoparticles at various temperatures or under different oxidizing conditions. Moreover, it is interesting to find a simple way to maintain the magnetism of Fe$_3$O$_4$ nanoparticles at a higher temperature.

Nejad and Jonsson [20] studied the oxidation behavior of Fe$_3$O$_4$ nanoparticles by H$_2$O$_2$, I$_2$C$^{-}$, MnO$_4$ and found that the oxidation kinetics of Fe$_3$O$_4$ nanoparticles was consistent with the second-order reaction. Sidhu et al. [21] have studied the oxidation mechanism of magnetite, Fe$_3$CoO$_4$, Fe$_2$NiO$_4$ and Fe$_2$ZnO$_4$ in the temperature range of 170–200 °C. They developed a theory on the basis of diffusion theory and concluded that during oxidation of magnetite the surface area of magnetite did not change and it was
the iron ion, which is diffusing out of the crystals of magnetite during the oxidation process. Jolivet and Tronc [22] showed that in acid media magnetite crystals were oxidized to γ-Fe2O3 by an adsorption reaction which traps mobile electrons from the bulk material and reduces the interfacial FeIII.

However, to the best of our knowledge there are few publications trying to maintain the magnetism of Fe3O4 nanoparticles at a higher temperature [23]. In order to make it, we have investigated the oxidation behavior of Fe3O4 nanoparticles at different temperatures in the atmosphere and synthesized Fe3O4/BaSO4 multi-core/shell particles by depositing BaSO4 shell onto the Fe3O4 cores. The results show that the thermodynamical stability of Fe3O4/BaSO4 multi-core/shell particles was improved obviously and their magnetism did not vanish till 750 °C.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used without further purification. Ferric chloride (FeCl3·6H2O), ferrous sulfate (FeSO4·7H2O), ammonium iron (II) sulfate hexahydrate ((NH4)2Fe(SO4)2), ammonia (NH3·H2O, 25% v/v aqueous), hydrazine hydrate (N2H4·H2O, 25% v/v aqueous), hydrazine hydrate solution (0.2 M), 10 ml of 50% hydrazine hydrate and 5 ml of ammonia were all purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC). Deionized water was used throughout experiments.

2.2. Synthesis of Fe3O4 nanoparticles

Fe3O4 nanoparticles were synthesized according to our previous report [24]. Simply, 136 ml of deionized water and 2 ml of N2H4·H2O were put into a three-neck, 250 ml round bottom flask equipped with a mechanical stirrer, and agitated for 30 min to eliminate the oxygen. Aqueous solutions of FeSO4 and FeCl3 were dropped into the flask with agitation. Immediately after the addition of the iron salts solution, 8 ml of NH4OH and 10 ml of deionized water were quickly syringed into the flask with vigorous stirring. The solution turned from grass-green to orange-yellow, and finally to black quickly, indicating the formation of magnetite. At the same time, turn on the microwave oven, circulate the cooling water, and modulate the heating power to gain an invariable temperature of 80 °C for 30 min. The precipitates were filtered and washed with deionized water and anhydrous ethanol for several times, and dried under vacuum for 24 h.

2.3. Synthesis of Fe3O4/BaSO4 multi-core/shell particles

A simple method was produced to synthesize Fe3O4/BaSO4 multi-core/shell particles. In a typical synthesis process, 50 ml of ammonium iron (II) sulfate hexahydrate solution (0.2 M), 10 ml of 50% hydrazine hydrate and 5 ml of ammonia were mixed together with vigorous stirring at 80 °C for 1 h. Elevate the temperature to 100 °C and then 40 ml of barium chloride solution (0.5 M) were slowly dropped into the mixture. After 1 h vigorous stirring, keep the system immovable for 1 h at 80 °C. Finally, the resultant were filtered with a magnet and washed with deionized water and anhydrous alcohol for several times, and dried under vacuum for 24 h.

2.4. Characterization

The obtained Fe3O4/BaSO4 multi-core/shell particles and pure Fe3O4 nanoparticles were calcined at different temperatures (150 °C, 250 °C, 350 °C, 450 °C, 550 °C, 650 °C, and 750 °C) for 2 h in the atmosphere. X-ray diffraction (XRD, X’Pert-Pro MPD, Holland) and Fourier transform infrared spectroscopy (FT-IR, Nicolet FT-IR Avatar 360, America) were employed to analyze the phase transitions of pure Fe3O4 nanoparticles after calcined at different temperatures. The qualitative analysis of the phase transitions of the calcined particles was performed on a Gouy magnetic balance (FDTX-FM-A, Nanjing University Plant, China). The calculated samples were dissolved in hydrochloric acid (HCl, 0.1 M) and potassium thiosulfate solution (KSCN, 0.1 g·mL−1) was added as a color-developing agent to form a red solution. U-2810 spectrophotometer (Hitachi, Japan) was used to measure the absorbency of the red solution that implying the concentration of FeII in each calcined particles. All the data are obtained through at least three times of experiments. Scanning electron microscope (SEM, Hitachi S-4700, Japan) was used to observe the morphology of Fe3O4/BaSO4 multi-core/shell particles.

3. Results and discussion

3.1. Magnetic properties analysis

The magnetic properties were characterized by a Gouy magnetic balance, in which magnetic weight is linear with the magnetism of the samples [15]. The magnetic weight of the two samples calcined at different temperatures was measured under different external magnetic field, due to the easier magnetization of pure Fe3O4 nanoparticles. The magnetic weight related to temperature is illustrated in Fig. 1. From Fig. 1, one can find that the magnetism of pure Fe3O4 nanoparticles reaches maximum when calcined at 250 °C for 2 h in the atmosphere and vanishes when calcined at 550 °C under the same conditions. In order to determine whether the magnetism vanishment is instantaneous or not, pure Fe3O4 nanoparticles were calcined at 550 °C for 20 min in the atmosphere and the magnetism vanishment happens again. Besides, pure Fe3O4 nanoparticles were calcined at 500 °C for 2 h in the atmosphere, and the particles still show magnetism. Thus, one can conclude that the magnetism vanishment of pure Fe3O4 nanoparticles is instantaneous when the temperature is equal to or above 550 °C.

However, for Fe3O4/BaSO4 multi-core/shell particles, there are two points of maximal magnetism, and one is at 250 °C and the other at 550 °C. The magnetism vanishment of the composite particles takes place at 750 °C for 2 h in the atmosphere. Experiments reveal that the magnetism vanishment of Fe3O4/BaSO4 multi-core/shell particles is also instantaneous when the temperature is equal to or above 750 °C.

3.2. XRD studies

To find the reason of magnetism vanishment of pure Fe3O4 nanoparticles, X-ray diffraction was performed using Cu Kα radiation. The XRD patterns of pure Fe3O4 nanoparticles calcined at different temperatures are shown in Fig. 2. From Fig. 2, one can find that there is almost no difference among the diffraction peaks of the particles calcined at 150 °C and 250 °C except the weakening in intensity of magnetite, especially for (3 1 1) peak. From 350 °C to 550 °C, the (3 1 1) peak keeps reduction, while (1 0 4) peak of hematite develops and becomes stronger and stronger. When at 550 °C, magnetite (Fe3O4) transforms to hematite (α-Fe2O3, [25]) completely [26].

Fig. 1. Relationship of magnetic weight of different samples and temperature.

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3.3. FT-IR studies

XRD cannot show the change of pure Fe₃O₄ nanoparticles after calcined at 150 °C and 250 °C. In order to reveal it, IR spectra (as shown in Fig. 3) of magnetite samples calcined at different temperatures were obtained using Fourier transform infrared spectroscopy (FT-IR). From Fig. 3, one can find the absorption peak of Fe–O in Fe₃O₄ at 571.1 cm⁻¹ [27]. After calcined at 150 °C for 2 h, the peak at 571.1 cm⁻¹ splits into two peaks at 632.9 cm⁻¹ and 563.4 cm⁻¹, respectively. The new arisen absorption peaks at 632.9 cm⁻¹ and 563.4 cm⁻¹ which are associated with Fe–O bond, are the characteristic peaks of γ-Fe₂O₃ [28]. XRD is not sensitive enough to differentiate between Fe₃O₄ and γ-Fe₂O₃, due to extreme similarity in crystal structure of the two phases. Provided that there is an intergradation, in which Fe₂O₃ and γ-Fe₂O₃ coexist at a certain proportion that owns the maximal magnetism. The intergradation appears when the pure Fe₂O₃ nanoparticles were calcined at 250 °C for 2 h in the atmosphere, leading to the maximal magnetism. Afterwards, the peak at 632.9 cm⁻¹ becomes weaker and weaker, and disappears at 550 °C. While, another new peak at 447.6 cm⁻¹ comes forth at 450 °C, and the peak becomes stronger and shifts to 463.1 cm⁻¹ when at 550 °C. According to Nasrazadani and Raman [29] the two absorption peaks at 532.5 cm⁻¹ and 463.1 cm⁻¹ can be assigned to the Fe–O absorption in hematite (α-Fe₂O₃). Therefore, one can get that 550 °C is the minimal temperature for the complete transformation from magnetite (Fe₂O₃) to hematite (α-Fe₂O₃), consistent with the results of XRD and magnetic properties analysis.

3.4. Fe³⁺ concentration analysis

It is well known that Fe₂O₃ is a mixed cubic oxide which contains 2/3 Fe³⁺ and 1/3 Fe²⁺ cations whereas α and γ-Fe₂O₃ contain only Fe³⁺ cations. In order to validate the gradual transformation from Fe₂O₃ to γ-Fe₂O₃ (550 °C for 2 h), Fe³⁺ concentration of the calcined samples was reflected via measuring the absorbency of the sample solution. Fig. 4 shows the results of the absorbency measurement. The inserted illustration demonstrates that the maximal absorbency of the sample solution occurs at 480 nm. Along with the increase of temperature from 150 °C to 550 °C, Fe³⁺ concentration of the calcined samples increases. After calcined at 550 °C for 2 h in the atmosphere, the Fe³⁺ concentration keeps the same, implying the complete transformation from Fe₂O₃ to α-Fe₂O₃.

3.5. SEM analysis

SEM images were obtained to observe the morphology of the Fe₂O₃/BaSO₄ multi-core/shell particles. Fig. 5(a) shows the image
of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles prior to calcination. One can find that there are some uncoated Fe$_3$O$_4$ nanoparticles depositing on the surfaces of BaSO$_4$ shells. When calcined at 250 °C for 2 h in the atmosphere, some of the uncoated Fe$_3$O$_4$ nanoparticles transformed to γ-Fe$_2$O$_3$, leading to the formation of an intergradation (discussed in Section 3.3). The samples show maximal magnetism at the intergradation. From the image, it can also be seen that the uncoated Fe$_3$O$_4$ nanoparticles are about 15 nm whereas the Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles are about 50–100 nm. Besides, some Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles were immersed in hydrochloric acid solution (HCl, 1.0 M) for 1 day and the magnetism of residual matters is almost the same with that of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles. Therefore, one can conclude that not only one Fe$_3$O$_4$ nanoparticle is coated by the BaSO$_4$ shell and Fe$_3$O$_4$ nanoparticles can be imagined to be inserted in the BaSO$_4$ particles as “sea-land” model. Fig. 5(b) shows the image of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles calcined at 750 °C for 2 h in the atmosphere. There are still some nanoparticles existed on the surfaces of BaSO$_4$ shells and the particle size is not altered [21]. Nevertheless, there are many “holes” emerged on the surfaces of BaSO$_4$ shells. The morphology of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles calcined at 650 °C and 700 °C were also observed (not show) and there is no hole emerged. Therefore, one can conclude that the magnetism vanishment of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles may be related to the appearance of “holes”, which provide a chance for Fe$_3$O$_4$ nanoparticles to contact with oxygen. According to Sidhu et al. [21], iron ion can diffuse out of the crystals of magnetite during the oxidation process in the temperature range of 170–200 °C. An assumption can be drawn as follows: in Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles, the BaSO$_4$ shells block the iron ion diffusing out of BaSO$_4$ shells when at about 200 °C. While the temperature rises to 550 °C, the iron ion breaches the hindrance and diffuses out of BaSO$_4$ shells, thus, leading to the formation of an intergradation again. The assumption can well explain the second maximal magnetism point of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles calcined at different temperatures. Besides, we guess that the number of “holes” may be related to the number of Fe$_3$O$_4$ nanoparticles enwrapped by BaSO$_4$ shells.

**4. Conclusions**

In summary, the magnetism of Fe$_3$O$_4$ nanoparticles has been investigated at different temperatures. The Fe$_3$O$_4$ nanoparticles are not stable and easy to be oxidized at high temperature. The phase transitions from Fe$_3$O$_4$ to α-Fe$_2$O$_3$ is completely accomplished when calcined at 550 °C for 2 h in the atmosphere. During the oxidation process, there exists an intergradation, in which the magnetic samples show maximal magnetism. A simple method has been introduced to deposit BaSO$_4$ shell on the Fe$_3$O$_4$ cores in order to maintain the magnetism at a higher temperature. The prepared Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles show two maximal magnetism points, and one is at 250 °C and the other at 550 °C. The first maximal point relates to the oxidation of uncoated Fe$_3$O$_4$ nanoparticles and the second maximal point is induced by the laggard diffusion of iron ion. After coated with BaSO$_4$ shells, the magnetism of Fe$_3$O$_4$ nanoparticles did not vanish till 750 °C. The structure of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles is confirmed to be “sea-land” structure. The magnetism vanishment of Fe$_3$O$_4$/BaSO$_4$ multi-core/shell particles at 750 °C may be related to the appearance of “holes”.

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