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Synthesis of Superparamagnetic Iron Oxide Nanoparticles in Carbon Reduction Method

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Abstract
The synthesis of mainly superparamagnetic iron oxide nanoparticles, The Fe_3O_4 nanoparticles (~500 nm) were synthesised by using carbon reduction method. The best parameters of synthesis of the nanoparticles are fixed through predictable by transmission electron microscope (TEM), X-ray diffraction and a vibrating illustration magnetometer of the Fe_3O_4 nanoparticles obtained under various experimental circumstances. The TEM characterisation results demonstration that the best ratio of the carbon and ferric chloride is 3:1 and the most suitable heating time is 3 h. The nanoparticles, which were obtained with furnace cooling under vacuum condition after 3 h heating, have the best magnetic properties and most stable crystal from. The characterisations of SiO_2 protected nanoparticles demonstrate that the component of the nanoparticles is Fe_3O_4. synthesising the superparamagnetic nanoparticles such as the micro latex method the hydrolytic method the sol–gel method and the common precipitation method. The UV–vis absorption spectrum of the Fe_3O_4 nanoparticles demonstrates wide-range light absorption of the Fe_3O_4 nanoparticles. Moreover, quantitative analysis of this new method is conducted to confirm repeatability. The actual qualities of the Fe_3O_4 nanoparticles are always consistent with the theoretical ones, which indicate that the repeatability of this method is excellent.

Introduction

Superparamagnetic iron oxide nanoparticles used in microchemical, catalysis, sensors, targeted drug transfer, cell separation applications. [[1]-[8]].hence , researches have been conducted synthesising the superparamagnetic nanoparticle, such as the micro latex method [[9], [10]], the hydrolytic

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method [[11], the sol–gel method and the common precipitation method The strict ratio of Fe^{2+} and Fe^{3+} must be controlled in all these methods to obtain Fe_3O_4 whereas the precursor of carbon reduction method is only Fe^{3+}, which leads to a simple process and no lead-in pollution agent. In addition, the Fe_3O_4 nanoparticles obtained by other methods. Mainly superparamagnetic iron oxide nanoparticles with comparatively best properties. The most suitable ratio of the reactants and heating time are confirmed through the transmission electron microscope (TEM) characterisation results. The nanoparticles which are obtained with furnace cooling under vacuum condition have the best magnetic properties and most stable crystal when compared with no furnace cooling, which are shown as the X-ray diffraction (XRD) and hysteresis cycles results. The UV–visible absorption spectrum of the Fe_3O_4 nanoparticles demonstrates wide-range light absorption of the Fe_3O_4 nanoparticles. To confirm the repeatability of this new method, quantitative analysis has been considered in this Letter. The results demonstrate that the carbon reduction method is repeatable. All the results show that mainly superparamagnetic Fe_3O_4 nanoparticles (~500 nm) are obtained in this Letter.

The advantages of this method lie in the simple process. No lead-in pollution agent and the products are mainly superparamagnetic. With no controlling of pH value, the solution concentration and reaction speed make the process of this method simple. All the reactants are carbon and ferric chloride so that no impurity exists in the product. The mainly superparamagnetic Fe_3O_4 nanoparticles (~500 nm) can fit the requirement of many applications because of their properties, such as high specific area.

Experimental

Ferric chloride (AR) was purchased from the Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Deionised water of 18.25 MΩ was purified through an ultra-pure (UPR) system which was purchased from Ultra-pure water visible Ltd.

Ferric chloride and carbon in the ratio of 1:2, 1:3 and 1:4 was used as reactants. Definite amounts of carbon were dispersed in 150 ml 35% ferric chloride solution. After immersing for several hours, the excessive solution was abandoned. The

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Fe_3O_4 superparamagnetic particles were obtained after heating the reactants at 400°C for 2, 3 and 4 h, under 0.2 Torr vacuum condition through a tube furnace (OTF-1200X-III) which is purchased from the KJ Group (Hefei, China). To illustrate that the properties of the particles obtained with furnace cooling under vacuum condition are even better, the particles were cooled in a furnace after heating. After the solid product was milled using an agate mortar, 500 nm Fe_3O_4 particles were obtained. In this reaction, a part of the Fe^{3+} of ferric chloride is reduced to Fe^{2+} by reducer carbon, and then Fe_3O_4 is generated under low oxygen conditions in this way. The carbon acts as reducer and plate, Fe^{3+} was reduced by carbon and Fe_3O_4 particles were generated on the carbon plate. The nanoparticles were protected by an SiO_2 layer in the sol–gel method.

The Fe_3O_4 particles obtained with different ratio of reactants were tested by TEM measurements (JEOL JEM-1200EX), which shows the amount of carbon in the product clearly. The shapes of the Fe_3O_4 particles obtained through different heating times are observed in the TEM images. The magnetic properties and the nano crystal stability obtained by furnace cooling under vacuum condition were measured by a Lake Shore 7307 vibrating sample magnetometer and the XRD Advanced XRD system (a Bruker D8) using Cu K radiation of wavelength 1.5406 Å.

Results and discussion

Confirmation of the experimental parameters

The ratio of the ferric chloride and carbon is the key to obtain nanoparticles with high dispersibility, because the carbon substrate might join the particles together. Fig. 1 shows the TEM images of superparamagnetic iron oxide nanoparticles obtained by different ratios reactants under 400°C for 4 h. Fe_3O_4 can be oxidised to Fe_2O_3 under more than 450°C, which is the reason why we heat the reactant under 400°C.

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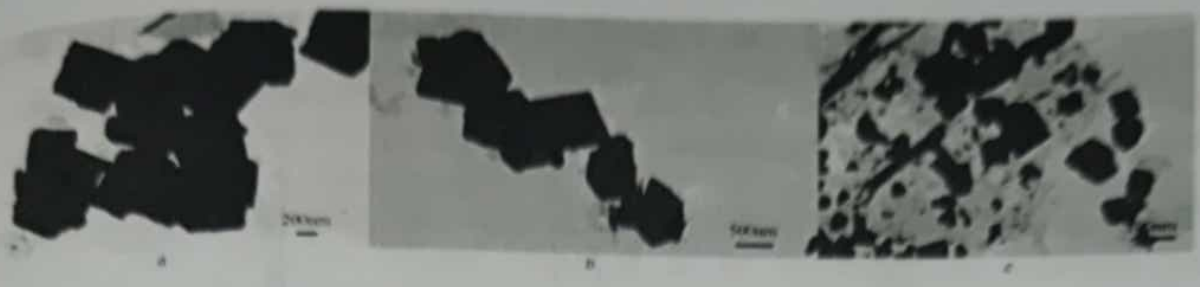

Figure 1
TEM images of superparamagnetic iron oxide nanoparticles obtained by where mole ratio of carbon and ferric chloride is 2:1, 3:1, and 4:1 under 400°C for 4 h

a 2:1

b 3:1

c 4:1

Uniformed 500 nm nanoparticles in square shape are observed in Figs. 1a and b while non-uniformed square particles embedding in carbon substrate are shown in Fig. 1c. It is obvious that the carbon is over-dosed when the ratio of the carbon and ferric chloride is 4:1 and the over-dosed carbon makes the particles aggregate together. Comparing Figs. 1a and b, the ratio of 3:1 is more suitable when considering the sufficiency of the reaction.

The TEM images of the Fe_3O_4 particles obtained after different heating times are shown in Fig. 2. The conditions of crystal formation can be represented by characterisation.

The unformed particles can be seen in Fig. 2a, while square formatted particles are observed in Figs. 2b and c. These results show that the Fe_3O_4 nanoparticles crystal formation time is at least 3 h. Considering the energy conservation, the most suitable heating time of this method is 3 h.

To research the effect of furnace cooling on the nanoparticles' magnetic properties, the magnetisation cycles have been characterised. The magnetisation behaviours are shown in Fig. 3. The saturation intensities of the particles are 31.1, 9.4

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and 34.9 emu/g, and the retentive magnetisms of the particles are 8.0, 2.1 and 4.9 emu/g, which are shown in Figs. 3a–c.

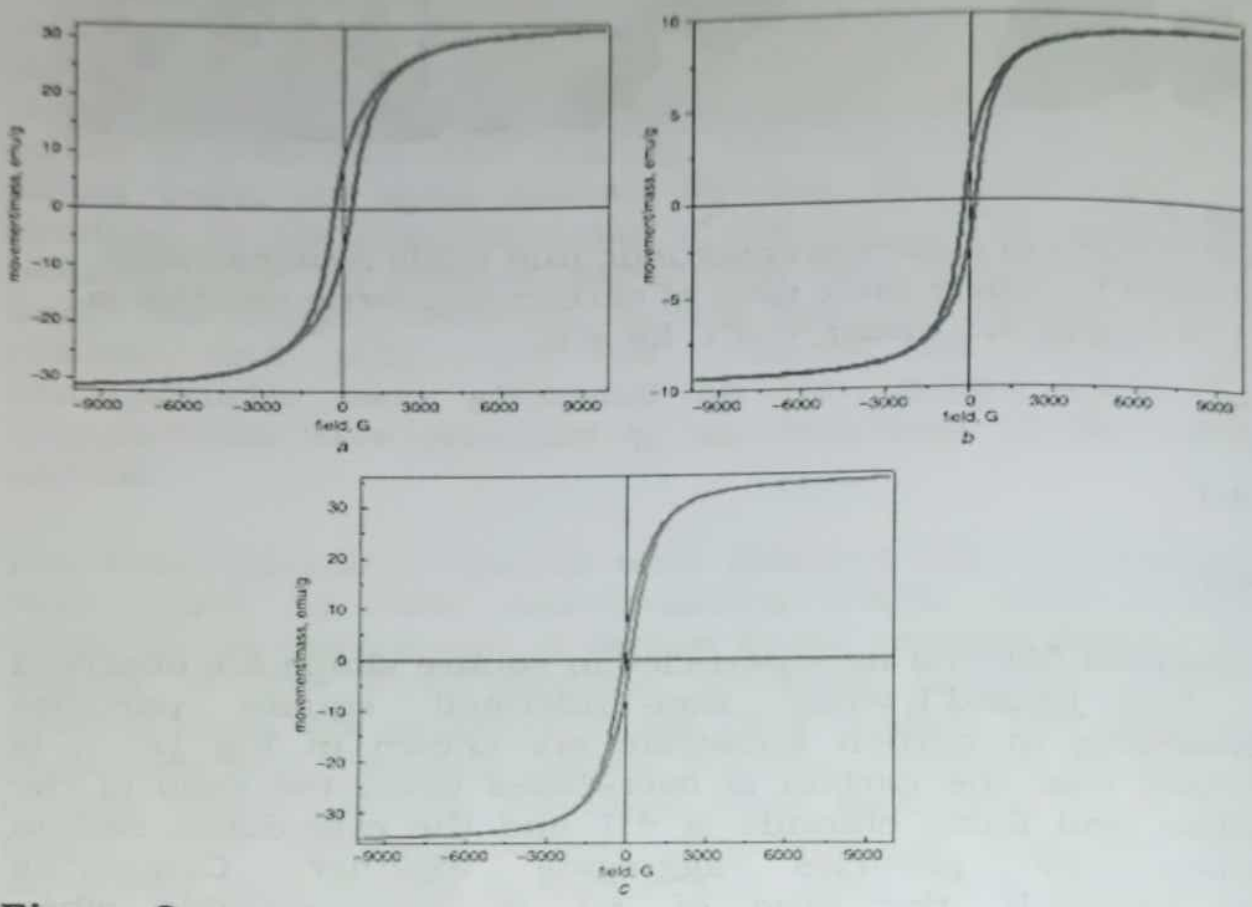

Figure 3
Hysteresis cycles of superparamagnetic iron oxide nanoparticles obtained by treating under 400°C for 4 h, 3 h, and 3 h with furnace cooling under vacuum condition

a 4 h

b 3 h

c 3 h with furnace cooling with vaccum condition

The result illustrates that the saturation intensity of the particles obtained with 3 h heating and furnace cooling under vacuum condition is the largest. What is more, the retentive magnetism of the particles obtained is smallest when compared with the saturation intensity. Thus it is concluded that furnace cooling leads to high magnetic intensities and small retentive magnetism, which leads to high dispersibility.

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To research the effect of furnace cooling on the nanoparticles' stability, the components have been characterised by XRD characterisation. The main components of the particles are all magnetite Fe_3O_4 under 400°C for 4, 3 and 3 h with furnace cooling under vacuum condition, which is demonstrated by Fig. 4. The results show that 3 h is enough to obtain the Fe_3O_4 nanoparticles, which is consistent with Fig. 2.

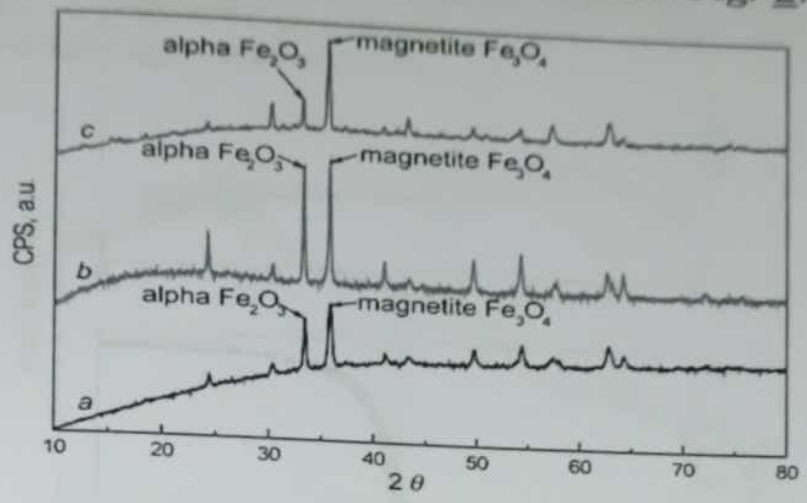

Figure 4
XRD spectra of iron oxide nanoparticles obtained by treating under 400°C for 4 h, 3 h, and 3 h with furnace cooling under vacuum condition
a 4 h
b 3 h
c 3 h with furnace cooling under vaccum condition

The solid Fe_3O_4 particles obtained in this work are in contact with air, so some of the particles were oxidised to Fe_2O_3. Therefore the nanoparticles can be well protected from being oxidised by some solvent, such as water or ethanol. Comparing spectra (a)–(c) in Fig. 4, the relative amount of Fe_2O_3 in the sample obtained with 3 h heating and furnace cooling under vacuum condition is the smallest. The result illustrates that the particles have higher stability after furnace cooling.

Above all, the experimental parameters are confirmed. The best ratio of the precursor is 3:1 when fabricating the particles with furnace cooling under vacuum condition after 3 h heating. The mainly superparamagnetic Fe_3O_4 nanoparticles (~500 nm) obtained through the carbon reduction method have high stability, magnetic intensity and dispersibility.

Confirmation of the nanoparticle's components
The iron oxide nanoparticles were protected by SiO_2 as soon as we took them out from the tube furnace. The nanoparticles can be well protected in this way. Fig. 5a shows that the component of the nanoparticles is only magnetite Fe_3O_4. The saturation intensity of the SiO_2 coated particles is 46.5 emu/g, which is shown in Fig. 5b.

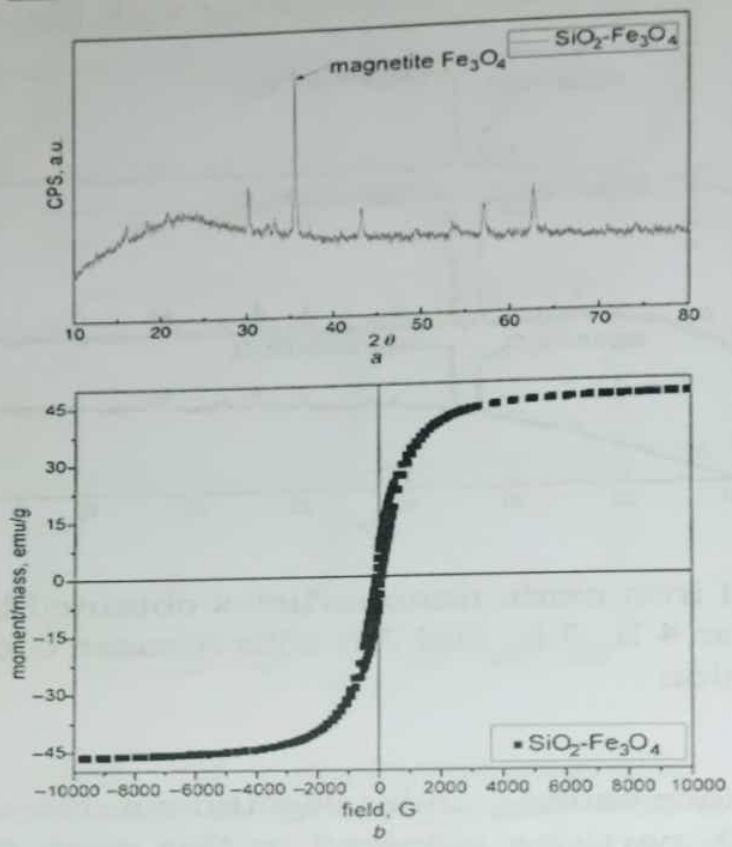

Figure-
XRD spectrum and hysteresis cycle of SiO_2-Fe_3O_4 nanoparticles

a XRD spectrum
b Hysteresis

There is no Fe_2O_3 characteristic peak in Fig. 5a, so the absence of Fe_2O_3 shows that the Fe_3O_4 has not been oxidised. The coated nanoparticles' saturation intensity should be less than that of the magetite Fe_3O_4 nanoparticles. The coating layer affects the magnetism of the magnetic core. Therefore, the magnetite Fe_3O_4 nanoparticles' saturation intensity should be more than 46.5 emu/g if the Fe_3O_4 nanoparticles are stable in air. The properties of the protected nanoparticles demonstrate

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that the component of the nanoparticles obtained is magnetite Fe_3O_4.

Optical properties of the iron oxide nanoparticles

The relatively wide-range light absorption of the Fe_3O_4 nanoparticles means that the nanoparticles can be applied more conveniently. Fig. 6 is the UV–vis absorption spectrum of superparamagnetic iron oxide nanoparticles. The result shows that the Fe_3O_4 nanoparticles obtained in this work have wide-range light absorption.

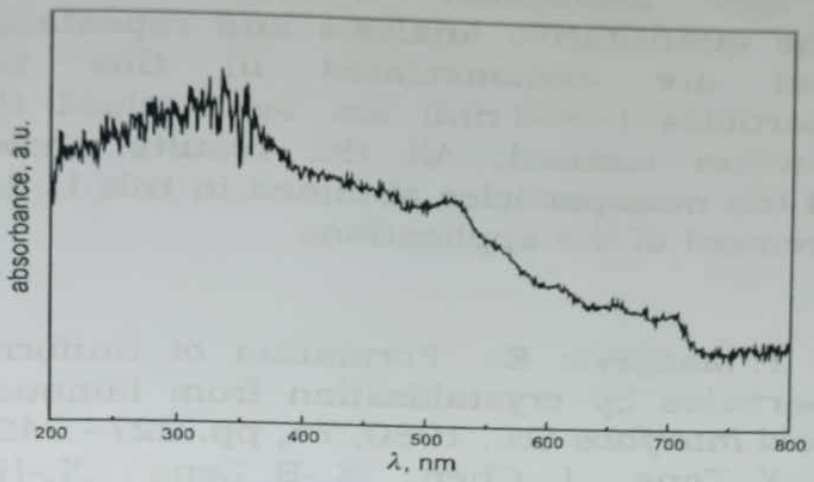

Figure 6
UV–vis absorption spectrum of superparamagnetic iron oxide nanoparticles

Repeatability calculation

The experiment has been repeated 4 times to confirm the repeatability of this method. The 0.6 mol carbon was immersed into the 150 ml 35% ferric chloride solution. The amounts of Fe^{3+} were 0.24, 0.22, 0.23 and 0.22 mol after the excessive solution was abandoned. Therefore the theoretical qualities are 18.2, 17.0, 17.8 and 17.0 g when the actual qualities are 18.7, 17.5, 18.5 and 18.3 g. The theoretical qualities are basically consistent with the actual ones. Owing to the excessive carbon coating around the Fe_3O_4 particles, the actual qualities are a little larger than the theoretical ones, which can be seen in the TEM images. The repeatability of this method is illustrated by the qualities calculation.

Conclusion

Based on the wide bio-applications of the superparamagnetic iron oxide nanoparticles, a new method of synthesising the

mainly superparamagnetic Fe_3O_4 nanoparticles is reported in this Letter. The best parameters of this method are fixed through TEM, XRD and VSM characterisation of the Fe_3O_4 nanoparticles synthesised under different experimental conditions. The results show that the best ratio of the precursor is 3:1 when fabricating the particles with furnace cooling under vacuum condition after 3 h heating. The characterisations of SiO_2 protected nanoparticles demonstrate that the component of the nanoparticles is Fe_3O_4. The UV–vis absorption spectrum of the Fe_3O_4 nanoparticles demonstrates wide-range light absorption of the Fe_3O_4 nanoparticles. Moreover, the quantitative analysis and repeatability of this new method are demonstrated in this Letter. The Fe_3O_4 nanoparticles (~500 nm) are synthesised through the carbon reduction method. All the results show that the properties of the nanoparticles obtained in this Letter can fully fit the requirement of the applications.

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