

## Synthesis and characterization of magnetic nanoparticles

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Magnetic nanoparticles with average diameter in the range of 6.4–8.3 nm have been synthesized by a chemical co-precipitation of Fe(II) and Fe(III) salts in 1.5 M  $\text{NH}_4\text{OH}$  solution. The size of the magnetic particles is dependent on both temperature and the ionic strength of the iron ion solutions. The magnetic particles formed at higher temperature or lower ionic strength were slightly larger than those formed at lower temperature or higher ionic strength respectively. In spite of the different reaction conditions, all the resultant nanoparticles are nearly spherical and have a similar crystalline structure. At 300 K, such prepared nanoparticles are superparamagnetic. The saturation magnetizations for 7.8 and 6.4 nm particles are 71 and 63 emu/g respectively, which are only ~20–30% less than the saturation magnetization (90 emu/g) of bulk  $\text{Fe}_3\text{O}_4$ . Our results indicated that a control of the reaction conditions could be used to tailor the size of magnetic nanoparticles in free precipitation.

**Keywords** Magnetic particle, magnetite, co-precipitation

### Introduction

Recently there is a growing interest in the synthesis and fabrication of magnetic nanoparticles for both theoretical and applied researches.<sup>1-6</sup> This is because magnetic nanoparticles are not only important in basic science, but also useful in practical applications.<sup>7</sup> Due to their extremely small size, magnetic nanoparticles have a number of novel properties that largely differ from their bulk counterparts.<sup>8</sup> Their unique magnetic, thermal and tribological properties make them become a new type of materials promising in various applications such as information storage,<sup>9</sup> magnetic resonance imaging,<sup>10</sup> bioprocessing,<sup>11</sup> and ferrofluids.<sup>12</sup>

Most of magnetic nanoparticles are made of iron oxides including magnetite,  $\text{Fe}_3\text{O}_4$  or maghemite,  $\gamma\text{-Fe}_2\text{O}_3$ , which can be synthesized by chemical co-precipitation.<sup>13</sup> Since the size and size distribution of the magnetic nanoparticles can directly affect their properties and performance. It is crucially important to control these parameters of such prepared magnetic nanoparticles. Various techniques such as microemulsions, vesicles, self-assemblies, and free precipitation have been exploited in order to have a better control of the size distribution of the magnetic nanoparticles.<sup>14-17</sup> Of these methods, free precipitation is of special interest because 1) the size distribution can be varied by the reaction conditions such as the concentration of reactants, the type of base used, pH and ionic strength of the precipitation media.<sup>18-20</sup> and 2) the resultant nanoparticles are free from organic impurities introduced in other techniques such as microemulsions and vesicles preparations.

However, owing to the complexity in the particle crystallization, it still remains a challenge in free precipitation to control the particle size distribution in required nanometer range. In this aspect, more work has to be done to explore the proper conditions for a better control of particle size and size distribution. In this study, we have synthesized several kinds of magnetite nanoparticles by varying ionic strength and temperature. Unlike many of the previous preparations, the co-precipitation was conducted by adding dilute alkaline solution into the solution of iron salts. The magnetic nanoparticles were characterized by various techniques including transmission electron microscopy (TEM), X-ray diffraction (XRD), and magnetometry.

Received December 6, 1999; accepted May 25, 2000.

Project supported by the National 973 Rare Earth Program of China and the Natural Science Foundation of Fujian Province.

## Experimental

### Synthesis of magnetic nanoparticles

The magnetic nanoparticles were prepared via a coprecipitation of ferric and ferrous chloride salts in 1.5 M ammonium hydroxide (NH<sub>4</sub>OH) solution. A stoichiometry of Fe<sup>3+</sup>/Fe<sup>2+</sup> = 2 was used to ensure a preferential crystallization of Fe<sub>3</sub>O<sub>4</sub>. The preparation was basically following Massart's procedure.<sup>13</sup> Briefly, 1.1 g of FeCl<sub>3</sub>·6H<sub>2</sub>O (4 mmol) and 0.4 g of FeCl<sub>2</sub>·4H<sub>2</sub>O (2 mmol) were dissolved in 100 mL of deoxygenated water or 100 mL of 1.0 M NaCl aqueous solution. Sodium chloride (NaCl) was used to adjust the ionic strength of the iron solutions. The above solutions were placed in a water-bath preheated to 25°C and 70°C to test the temperature effect on the crystallization of the nanoparticles. 1.5 M NH<sub>4</sub>OH solution was continuously added under vigorous magnetic stirring until pH reached 9. The dark precipitate generated was collected using a magnet and washed with deoxygenated water three times. Such purified product was re-dispersed in deoxygenated water for further characterization.

### Techniques

**Electron microscopy** Transmission electron micrographs were obtained using a Jeol 100CX spectrometer operated at 100 kV. Each sample was prepared by evaporating a corresponding very dilute nanoparticle suspension onto a carbon coated copper grid. Particle size and distribution was sampled over ~100 particles. The number average diameter ( $D_n$ ) is defined as  $\frac{1}{n} \sum n_i D_i$ , where  $n$  is the number of particles sampled; and  $n_i$  and  $D_i$  are the number and diameter of the nanoparticles in group  $i$ , respectively. The variance of the size distribution is defined as  $\frac{1}{n} \sum n_i [D_i - D_n]^2$ . The relative standard deviation ( $p$ ) is defined as  $[\text{Var}(D)]^{1/2}/D_n$ .<sup>18</sup>

**X-ray diffraction (XRD)** The measurements were performed on a Rigaku Rotaflex D/max-C X-ray powder diffractometer operated in the reflection mode with Cu K<sub>α</sub> ( $\lambda = 0.15406$  nm) radiation and equipped with a graphite back monochromator. The scanning rate is 6°/min.

**Magnetometry** The magnetization curves of

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were measured with a superconducting quantum interference device (SQUID) magnetometer. The sample was placed in a quasi cylindrical holder. The measurements were carried out at 300 K with an applied magnetic field up to 10 kOe.

## Results and discussion

### TEM images of magnetite particles

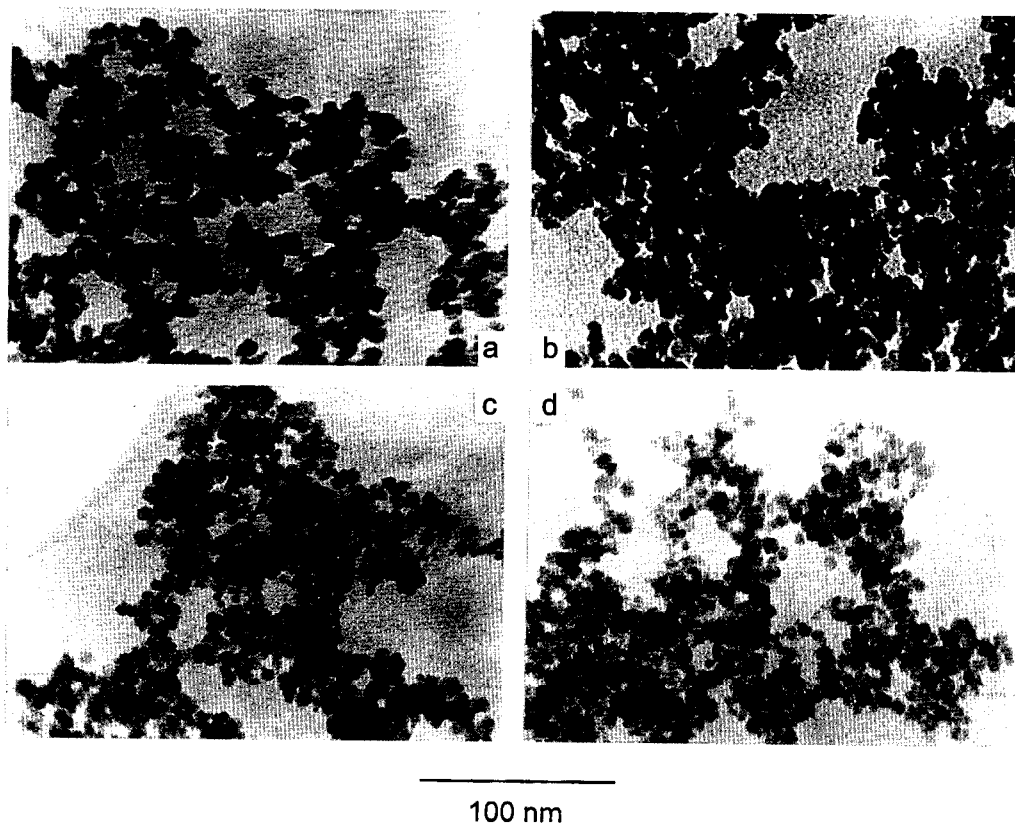
Fig. 1 shows the typical TEM images of four kinds of iron oxide nanoparticles formed in iron solutions with or without 1.0 M NaCl at 25°C and 70°C, respectively. It is observable that the particle size is dependent on the preparation conditions. The iron oxide particles formed in NaCl-free solutions are slightly smaller than those formed in 1.0 M NaCl solution. Irrespective of the different reaction conditions, all the particles exhibit spherical or nearly spherical shapes. Table 1 summarized the calculated number average particle size ( $D_n$ ) and the relative standard deviation ( $p$  (D)) of the magnetic nanoparticles formed at different temperatures and NaCl concentrations. For each given temperature, the particles formed in 1.0 M NaCl solutions were ~1.5 nm smaller than those formed in NaCl-free solutions. However, the influence of temperature on particle size is much less prominent than NaCl. When temperature increased from 25°C to 70°C, the particle size increased slightly (~0.5 nm). The enhancement of temperature on iron oxide particle size was also observed by Feltn *et al.*<sup>17</sup> High temperature favors the crystallization of such particles.

**Table 1** Number average particle size ( $D_n$ ) and relative standard deviation from TEM

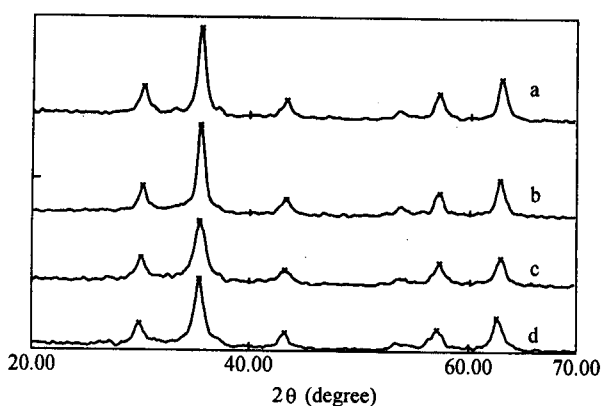
Synthesis conditions	$T$ (°C)	$D_n$ (nm)	$p$ (D)
NaCl-free iron solution	25°C	7.8	0.19
NaCl-free iron solution	50°C	7.9	0.18
NaCl free iron solution	70°C	8.3	0.20
1.0 M NaCl iron solution	25°C	6.4	0.17
1.0 M NaCl iron solution	50°C	6.5	0.18
1.0 M NaCl iron solution	70°C	6.8	0.18

### X-Ray powder diffraction

Fig. 2 shows the typical XRD patterns of the corresponding iron oxide nanoparticles depicted in Fig. 1. In



**Fig. 1** Transmission electron imagings of particles synthesized in conditions: (a) salt-free, 25°C; (b) salt-free, 70°C; (c) 1.0 M NaCl, 25°C; (d) 1.0 M NaCl, 70°C.



**Fig. 2** X-ray diffraction patterns of particles synthesized in conditions: (a) salt-free, 25°C; (b) salt-free, 70°C; (c) 1.0 M NaCl, 25°C; (d) 1.0 M NaCl, 70°C.

the angular ( $2\theta$ ) range 20–70°, six peaks can be clearly identified. The peak positions and relative intensities were consistent with the characteristic of magnetite.<sup>19</sup> Except for the aforementioned peaks, there are

no other peaks appearing in these XRD patterns, indicating that the nanoparticles are mainly composed of crystalline  $\text{Fe}_3\text{O}_4$ . The peaks of the nanoparticles formed in 1.0 M NaCl solutions are slightly broader than those formed in NaCl-free solutions, which is essentially attributed to the size effect since the nanoparticles formed in 1.0 M NaCl solutions are obviously smaller.<sup>21</sup> Nevertheless, the four samples have the same peak positions, implying that the variation of the ionic strength and temperature induces no significant structural change.

Fig. 3 shows the typical magnetization curves measured at 300 K for 6.4 nm and 7.8 nm  $\text{Fe}_3\text{O}_4$  nanoparticles respectively formed at 25°C from NaCl-free solution and 1.0 M NaCl solution. There is no hysteresis in the magnetization, *i. e.*, both remanence and coercivity are zero, suggesting that such prepared nanoparticles are superparamagnetic. The saturation magnetization ( $M_s$ ) is 71 and 63 emu/g respectively for 7.8 and 6.4 nm particles, which are ~20% and ~30% less than the saturation magnetization of bulk  $\text{Fe}_3\text{O}_4$  (90 emu/g), but close to that of bulk  $\gamma\text{-Fe}_2\text{O}_3$  (76 emu/g). The smaller

$M_s$  value of 6.4 nm particles is attributed to the size effect. In the nanometer range,  $M_s$  decreases with particle size owing to the quantum size effect. In this connection, it is worth noting that the  $M_s$  values of our nanoparticles are comparable to those obtained by Ziolo *et al.*<sup>1</sup> and Chu *et al.*<sup>6</sup>, but higher than those obtained by Cohen *et al.*<sup>22</sup> and Pileni *et al.*<sup>2</sup>

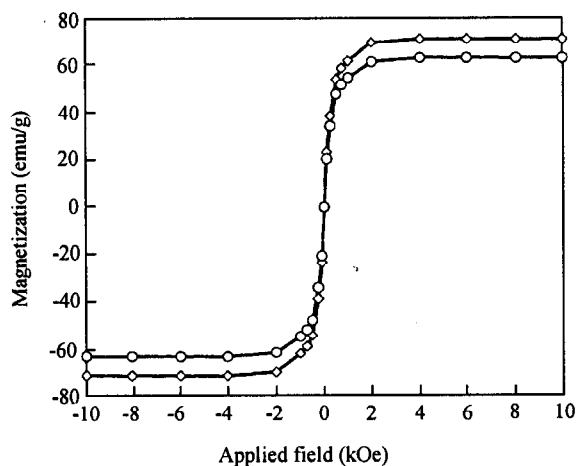


Fig. 3 Magnetization curves of 6.4 (○) and 7.8 nm (◇) magnetic nanoparticles at 300 K.

It has been known that iron oxide particles formed via microemulsion and self-assembly suffered with a disadvantage of low crystallization.<sup>15</sup> Accordingly, the resultant nanoparticles have a lower magnetization. As manifested by XRD patterns, the nanoparticles prepared in this study have no such a problem. Although the nanoparticles formed in the presence of 1.0 M NaCl have a lower  $M_s$  than the nanoparticles formed in the absence of NaCl due to the size effect, the nanoparticles obtained in this procedure have a higher  $M_s$  than the particles formed in organic structures with similar size.<sup>22</sup>

## Conclusion

Magnetic nanoparticles have been synthesized via a chemical co-precipitation of Fe(II) and Fe(III) salts in 1.5 M  $\text{NH}_4\text{OH}$  solution. Such formed particles have spherical or nearly spherical shapes. The size of the magnetic nanoparticles is in the range of 6.4 to 8.3 nm, depending on both temperature and the ionic strength of the iron ion solutions. At 300 K, the nanoparticles are superparamagnetic. The saturation

magnetizations of 7.8 and 6.4 nm particles are 71 emu/g and 63 emu/g respectively, which are only ~20%—30% less than the saturation magnetization of bulk  $\text{Fe}_3\text{O}_4$ .

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