

Synthesis, characterization and self-assemblies of magnetite nanoparticles

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Monodisperse Fe₃O₄ nanoparticles (NPs) with a narrow size distribution were synthesized by a high-temperature solution-phase method. The diameter of magnetic NPs was tuned from 2 to 13 nm by varying the reaction conditions, and the monolayer and multilayer self-assemblies of the NPs were obtained. A few kinds of the assemblies are presented and the reasons that drive the particles to form the superlattices are discussed. The physical-property-measurement system (PPMS) results showed that the as-synthesized NPs are ferrimagnetic at low temperatures (5 K) while they are superparamagnetic at room temperature (300 K). In addition, the particles were transformed into hydrophilic ones by an exchange reaction. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: nanoparticles; self-assembly; magnetic properties

INTRODUCTION

On the nanometer scale, properties of materials are dramatically different from their bulk counterparts. The unique properties of nanomaterials (NPs) arise from the large fraction of atoms that reside on the surface of these particles and the finite number of atoms in each crystalline core.¹ Magnetic NPs that have important technological applications in, for example, magnetic recording media, ferrofluids, and catalysts² have been attracting a lot of attention for many years. Especially, due to the increased need for ultra-high density data storage, these magnetic materials have been investigated extensively. What is more, superparamagnetic iron oxide nanoparticles (SPION) with suitable biocompatible coatings have been used in biomedicine, particularly in magnetic resonance imaging (MRI), tissue engineering, and drug delivery applications.^{3,4} Additionally, the study on NPs can provide us with more knowledge of nature.^{5,6} Therefore, a lot of work has been done on magnetic NPs in the past decades.^{7,8} However, synthesizing NPs with a narrow size distribution presents a major challenge and so does the formation of the superlattice of the NPs.

Here, we present our work on magnetite nanoparticles. A high-temperature solution-phase method was employed. Magnetic NPs with a narrow size distribution have been obtained and their sizes can be controlled. We have also investigated the magnetic properties of the NPs.

EXPERIMENTAL

By the high-temperature solution-phase reaction⁹ method, we obtained the magnetite grains. Fe(acac)₃, 1,2-dodecanediol, oleic acid, and oleylamine (the stoichiometric ratio is 2:5:3:3 in mol) were mixed in phenyl ether (20 ml) under nitrogen. The mixture was heated to 200 °C and maintained at that temperature for about 30 min, and then heated to about 270 °C. After the experimental conditions were kept for about 1 h the mixture was cooled to room temperature naturally and a large excess of ethanol was added under ambient condition. After centrifugation and purification, the black product was dissolved into heptane. The presence of oleic acid and oleylamine in the organic solvent is not necessary. The particles are stable in heptane for at least 2 months. They can also be stable and redispersed into organic solvents in the solid state for a few weeks after being dried in an ambient condition. By choosing different times at 200 or 270 °C or by varying the concentration of the precursor, we obtained different particle sizes even exceeding 13 nm. The size distributions are narrow without a size selection procedure. Using 1,2-dodecanediol instead of 1,2-hexadecanediol to synthesize NPs and producing larger particles by varying the experimental conditions are the differences between another method⁹ and ours. And the fact that NPs can be stable in organic solvents without the presence of oleic acid and oleylamine suggests that the 1,2-dodecanediol is more compatible, which may be caused by the difference in the length of the carbon chain.

A heptane dispersion of the as-synthesized NPs was mixed with (3-mercaptopropyl) trimethoxydilane in dichloromethane under ambient conditions. Then the mixture was stirred at room temperature for 8 h. After

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centrifugation and purification, the hydrophilic NPs were obtained.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the hydrophobic NPs is shown in Fig. 1. All the XRD peak positions and relative intensities of the sample match well with the XRD patterns of Fe_3O_4 NPs in the literature,^{9,10} indicating a highly crystalline cubic spinel structure of the sample. The average size of the nanoparticles deduced from Sherrer's equation based on Fig. 1 is about 8 nm, which is in agreement with the one measured from the TEM images. So, we can draw the conclusion that the particles are nearly single crystals.

An X-ray photoelectron spectrum (Fig. 2) was used to analyze the elemental components and their states. The peaks of the C_{1s} , O_{2p} , N_{1s} and Fe_{2p} shown in Fig. 2(a) indicate the organic coating on the surface of the Fe_3O_4 particles. The positions of the $\text{Fe}(2p_{3/2})$ and $\text{Fe}(2p_{1/2})$ peaks (Fig. 2(b)) are 708.2 and 710.4 eV, respectively, which are in good agreement with the values reported for Fe_3O_4 in the handbook.¹¹

Figure 3(a) and (b) shows the self-assembly of the as-synthesized hydrophobic Fe_3O_4 NPs. The magnetite nanocrystal arrays were formed by evaporating the solvent from a dispersion on a substrate at room temperature (20 °C). To prepare the samples, the solution was dropped into the Formvar-coated copper TEM grid in a drip. When the dilute dispersion was used, monolayer self-assemblies were obtained as shown in Fig. 3(a). It has also been found that a high concentration of the solution leads to multilayer self-assemblies. As shown in Fig. 3(b), a well-organized 3D superlattice structure was obtained. The arrangement of the nanocrystal superlattice formation is believed to be driven by surface tension, attractive van der Waals forces, and magnetic interaction among these superparamagnetic particles.¹ The TEM image (Fig. 3(a)) shows that monodisperse NPs of 3.5-nm diameter were arranged in a 2-dimensional hexagonal closed packed way, demonstrating the uniformity of the particles size. The 2D fast Fourier transform (FFT) power

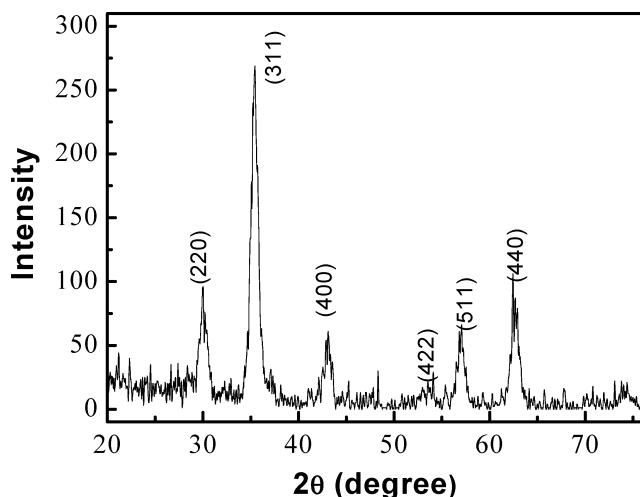


Figure 1. The XRD pattern of 8 nm Fe_3O_4 NPs, which shows the cubic inverse spinel structure of the samples.

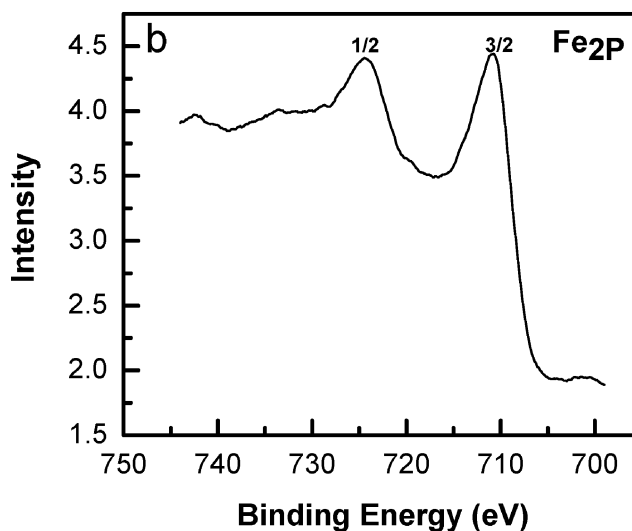
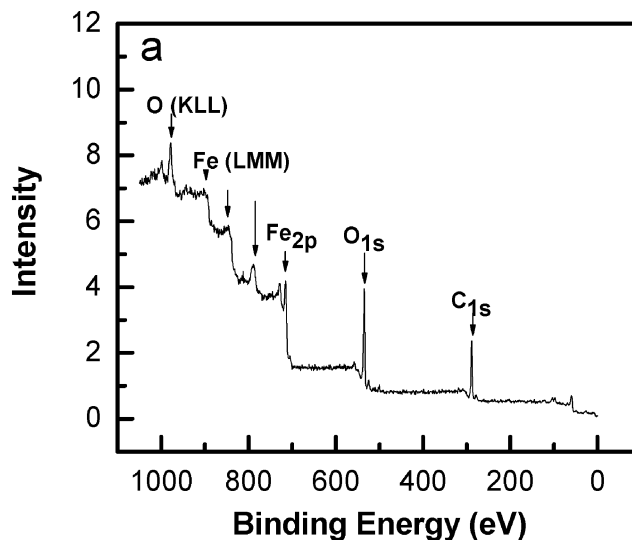


Figure 2. (a) XPS of the as-synthesized magnetite NPs, evidence for the existence of the organic coating can be found; (b) the details of the iron $\text{Fe}_{2p_{1/2}}$ and $\text{Fe}_{2p_{3/2}}$ peaks, which match well with the standard data from the handbook¹¹.

spectrum of the monolayer in the inset of Fig. 3(a) shows the hexagonal symmetry, and the one in Fig. 3(b) gives the superlattice symmetry of the multilayer self-assemblies. Figure 4(a) shows the boundary between two domains, which have the same structure symmetry but different orientations. From the FFT in Fig. 4(b)–(d), the symmetry of the structure can be determined. This twin structure will be useful to investigate the interaction among the domains. Furthermore, if the solvent concentration and the volatilization speed are compatible, we can get some interesting structures, for instance, band and cave, as shown in Fig. 4(e) and (f). The well-organized self-assemblies have a promising future in application such as high area density data storage.

To investigate the kinetics of superlattice formation, we mixed solutions of NPs of different sizes. The mixture was shaken and dispersed by ultrasonication to make sure that the

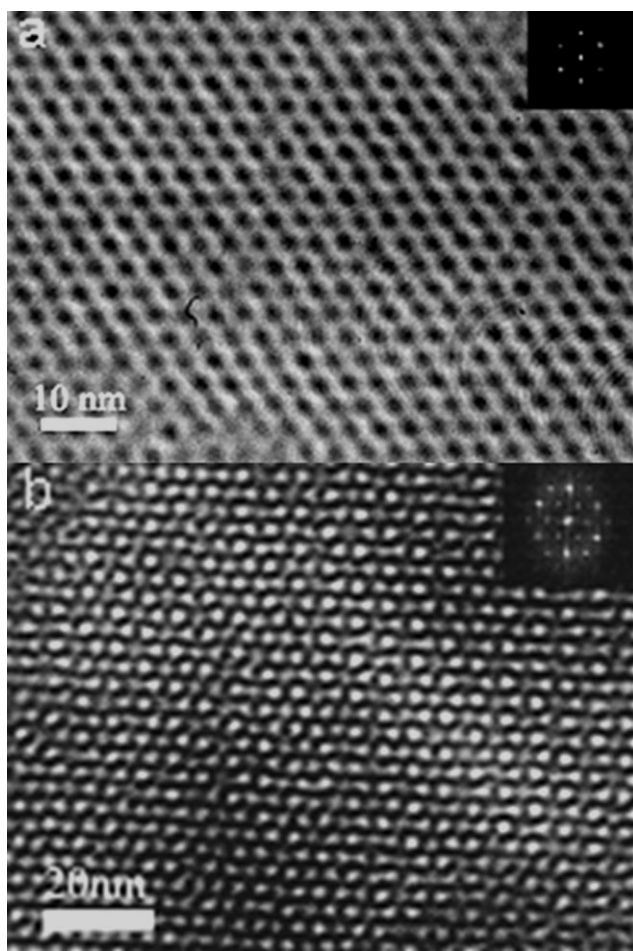


Figure 3. (a) TEM image of magnetite NPs monolayer self-assembly. The well-organized self-assembly demonstrates the uniformity of the NPs' size and shape. The inset is the FFT which shows the structure of the monolayer. (b) TEM image of multilayer self-assembly of Fe_3O_4 NPs, which was obtained by dropping the solvent with a higher concentration onto a TEM grid, and the inset is the FFT illustrating the structure symmetry of the superlattice.

NPs with different diameters mixed homogeneously, in other words, rule out any initial agglomeration of the particles from the different size groups locally retained. When the number of large particles is equal to that of small ones, the particles with the same size will get together preferentially (Fig. 5(a)); on the other hand when the small particles are much more than the big ones, the latter will be environed with the smaller (Fig. 5(b)). It is unreasonable that the surface tension of the solvent or the attractive van der Waals forces can separate the particles according to their sizes. These results indicate that magnetic interaction plays the most important role.¹² In the case of the hydrophilic ones, if the temperature of volatilization is high enough we get the TEM images of monodisperse NPs which show no difference compared to the hydrophobic ones, but when the solvent volatilizes at room temperature we can get some interesting patterns (Fig. 5(c) and (d)). The NPs were packed and formed into big particles because of the relatively large surface tension of water compared with the organic solvents, such as, heptane. Then the big ones self-assembled into lines or circles. In our

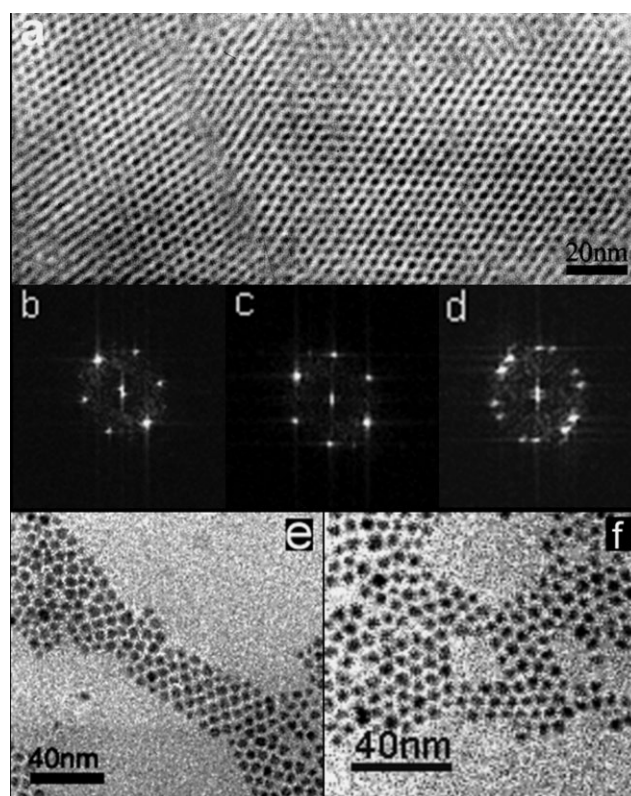


Figure 4. (a) TEM image of two domains having a common boundary; (b) FFT from the left domain; (c) FFT from the right domain; (d) FFT taken from the common boundary's region; (e) the image shows that the NPs form a band; (f) a square hole formed by the NPs.

opinion, the secondary important factor is the surface tension of the solvent. These two points together with another's opinion¹ may give an apt explanation for the formation of the self-assemblies.

The magnetic properties were investigated by a physical-property-measurement system. The ZFC/FC curves taken from the NPs with a diameter of about 8 nm in the powder state are shown in Fig. 6(a). Above the blocking temperature (T_B) of about 40 K, the FC and ZFC exhibit similar behavior. The curve declines nearly linearly and the slope is about 0.04 emu/gK. In this case, the particles are free to align with the applied field during the measuring time and this state is called *superparamagnetic*. Below T_B , the ZFC shows a steep increase of the magnetization up to around 40 K suggesting a relatively quick rotation of the magnetization of blocked magnetic particles toward the outer field. At 40 K, the magnetization reaches its maximum value. While at low temperatures below T_B , the FC curve decreases slightly and plateaus at last. The reason might be that the magnetization cannot relax during the time of measurement below T_B . From the well-known equation:

$$K = \frac{28k_B T_B}{V} \quad (1)$$

where K is the anisotropy constant, V is the particle's volume and k_B is Boltzmann's constant, respectively, we obtained the K value which is 0.3×10^4 erg/cm³, and it is smaller than that of bulk Fe_3O_4 which is about 2.5×10^5 erg/cm³.

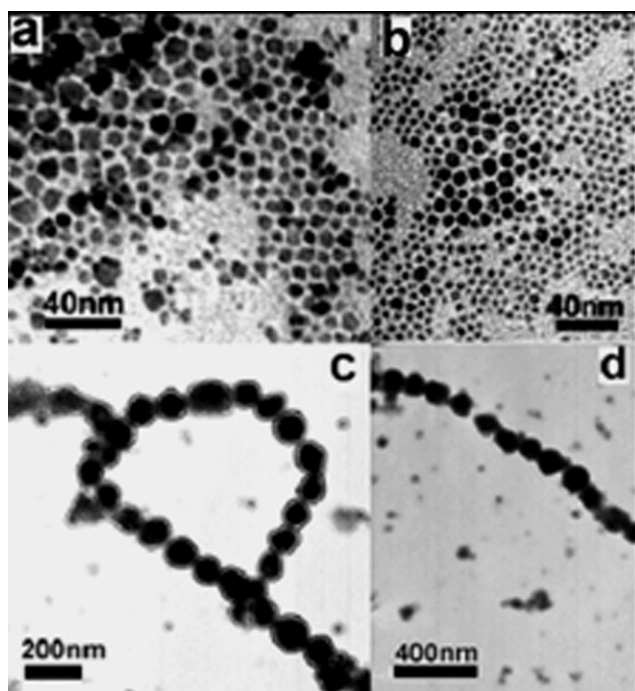


Figure 5. TEM image from the samples which contain big and small particles. (a) The NPs with the same size will get together when the number ratio of big NPs to small NPs is about 1 : 1; (b) the small NPs surround the big ones when the ratio is about 1 : 5; (c) the hydrophilic NPs were packed into large 'particles' and the large ones formed a circle; (d) the large 'particles' formed a line.

The hysteresis loop (Fig. 6(b)) at room temperature of the dried powder showed the expected behavior. The magnetite NPs did not display magnetic remanence and the initial slopes of the magnetization curves were steep. These facts are related to finite size and surface effects. According to those results, the particles are considered to be superparamagnetic. The steep initial slopes show the promising applications in magnetic devices on the nanometer scale. The M-H curve at 10 K (Fig. 6(c)) showed ferrimagnetic-like properties. The bulk-like behavior was observed. The σ_s (saturation magnetization) at 10 K is about 57.4 emu/g. The value of the saturation magnetization obtained at 10 K is almost the same as that of the bulk, indicating that free rotation driven by the thermal fluctuation may be frozen in this case. In other words, the finite size and the surface effects do not play a dominant role here. The coercive field is 106.2 Oe and the remanent magnetization is 12.7 emu/g. It is in agreement with the data from the literature.⁹ The difference may come from the dipolar interactions among the NPs, the different particles size and the spacing among the particles, while the σ_s at 300 K is 44.68 emu/g, which is smaller than the one at 10 K. In our opinion, the difference is caused by two reasons: (i) the thermal fluctuations at 300 K are stronger than those at 10 K; (ii) the particles' size will change along with the temperature.¹²

CONCLUSIONS

Magnetite NPs with a narrow size distribution have been obtained by a high-temperature solution-phase method and

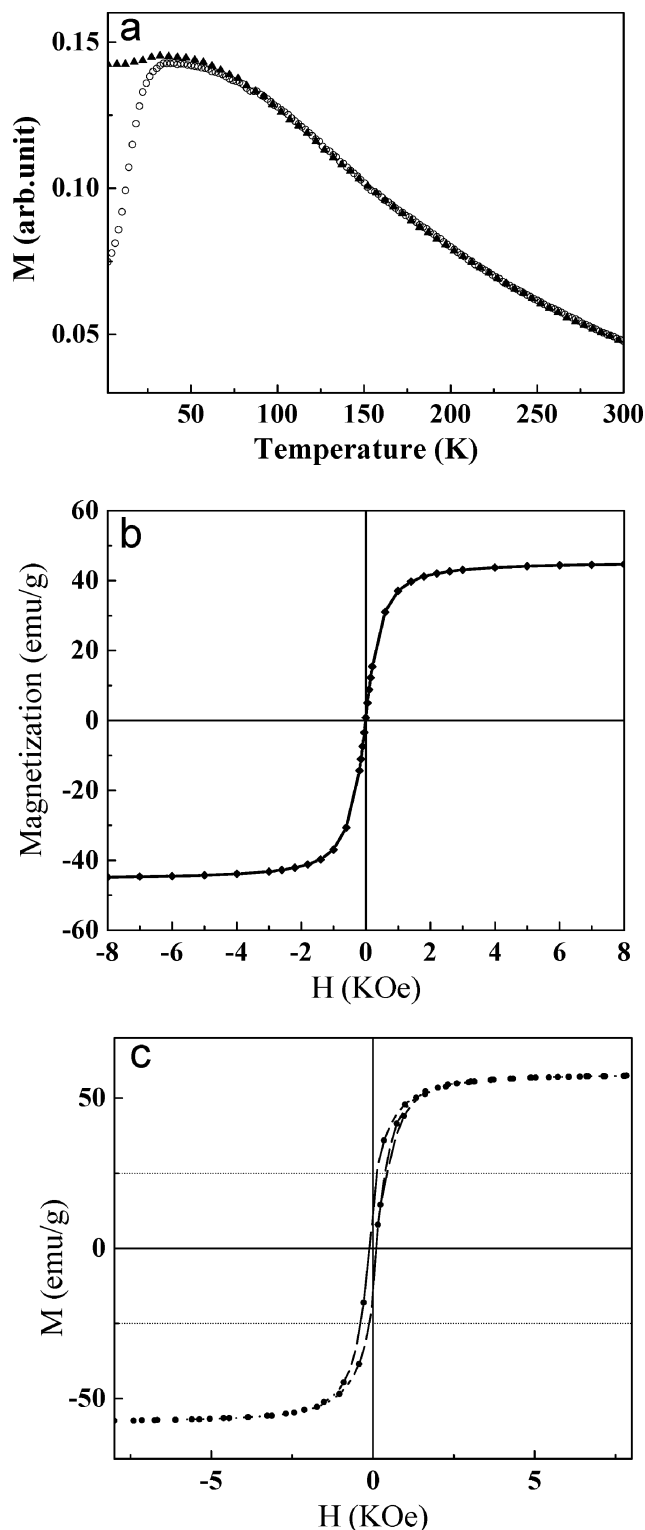


Figure 6. (a) Magnetization as a function of temperature, measured in FC (field-cooled) case and in ZFC (zero-field-cooled) case, respectively. The solid triangles constitute the FC curve and the circles constitute the ZFC curve. The T_B is about 40 K. (b) Hysteresis loop measured at 300 K for 8-nm NPs. It shows the superparamagnetic behavior; (c) magnetic hysteresis loop measured at 10 K for 8-nm magnetite NPs. Bulk-like behavior was observed.

the size can be controlled by varying the experimental parameters. The NPs were transformed into hydrophilic ones

by a new method. Highly-ordered monolayer and multilayer self-assemblies of the Fe₃O₄ NPs were obtained and the factors underlying the formation were discussed. The NPs were found to be superparamagnetic at room temperature while ferrimagnetic at 10 K. The unique properties caused by surface and finite-size effects suggest a promising application of the NPs in the future.

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