The Formation of Magnetite Nanoparticle in Ordered System of the Soybean Lecithin

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A method of preparation of magnetite nanoparticles in ordered systems, as in vesicle and microemulsion, consisting of soybean lecithin and water has been introduced. The size of magnetite grain was controlled by the content of soybean lecithin and size of liposomes in the systems. It was found by experiment that magnetite nanoparticles were formed inside the double layer vesicles. The magnetite nanoparticles were separated by magnetic separation and centrifugation and the dispersion of the magnetite nanoparticles prepared at 10% (w/w) soybean lecithin was particularly stable. The formation of pure magnetite nanoparticles was confirmed by analyses of XRD and electron diffraction pattern.

Key Words : Nanoparticles, Soybean lecithin, The ordered systems, Magnetite

Introduction

Nanoparticles in the size range of nanometer have attracted great attention researchers at overseas in recent years. They exhibit unusual physical and chemical properties significantly different from those of the bulk materials due to their extremely small size and large specific surface.[1-4] Magnetic nanoparticles of spinel ferrites are of great interest in fundamental science, especially for contrast enhancement in magnetic resonance imaging (MRI).[5-11] By using aqueous intravesicular precipitation to prepare nanoparticles such as Al_2O_3 has been attempted[12] and also was reported to prepare magnetite in the Poly (vinyl alcohol) (PVA),[13] but there is no reported to prepare magnetite nanoparticles with soybean lecithin in ordered systems. Because the ordered systems composed of soybean lecithin with water have nanometer space, we use them as nanoreactors to prepare magnetite nanoparticles and to observe as well as to study the size and structure of the magnetite, which is very important to apply them to such as medicine, chemistry, and information technology.

In the present work, we used the soybean lecithin as the nanoreactors, which was not only as a stabilizer but also a protective agent in the preparation of magnetite nanoparticles by the co-precipitation and the final product were also studied.

Materials and Methods

Materials and Instruments. Soybean lecithin (Grade Injection) is purposed from Fat Plant of Shanghai of China. Water was doubly distilled and pure nitrogen gas was bubbled through it for more than 2 hrs just before use to remove the dissolved oxygen. Nitrogen was purified from traces of carbon dioxide and oxygen by passing the gas through a basic pyrogallol solution. The other reagents are analyzed reagents.

In order to observe morphology and particle size, we used a JEM-2000EXII field emission gun transmission electron microscope operated at 200 kV and with the vacuum better than 2×10^{-6} Pa and the typical electron diffraction pattern was taken.

The size distribution of particles in a supernatant fluid was also determined by photon correlation spectroscopy method (PCS) (Zetasizer 3000, Malvern Instruments, GB).

X-ray diffraction (XRD) was conducted on a Rigaku D/max-2500PC X-ray diffractometer using $CuK\alpha$ radiation to determine the crystal structure.

Adsorption of the soybean lecithin on the surface of Fe_3O_4 powders was examined by infrared spectroscopy (Hitachi model IR-440 infrared spectrometer).

Thermogravimetric analysis (TGA) was done in the nitrogen gas with a heating rate of 10 ºC min^{-1} up to 480 ºC on the Perkin-Elmer instruments.

Preparation of Magnetite Nanoparticles. A mixed solution of ferrous and ferric ions in the molar ratio 1 : 2 was prepared by dissolving 0.10 mol $FeCl_2 \cdot 6H_2O$ and 0.20 mol $FeCl_3 \cdot 4H_2O$ in a 10% (w/w) 100 mL aqueous solution of soybean lecithin at 25 ºC by sonication with ultrasonic homogenizer under nitrogen. Magnetite was precipitated by adding 50 mL of the above mentioned mixed solution to 100 mL aqueous solution of 2 mol·L^{-1} NH_3 (aq) at 35 ºC while stirring at 1000 rpm using an impeller and the reaction mixture was kept at pH 8-9. The mixture was subsequently aged at 35 ºC for 30 min and cooled to room temperature. After the end of magnetite precipitation, pH decreased to 5.0. Precipitates and supernatant fluid were separated by magnetic separation and centrifugation. The precipitates were washed with deionized water under ultrasonication for 30 min and then separated by centrifugation at 10000 rpm for 60 min. The source magnetite sol of ultrafine particle was

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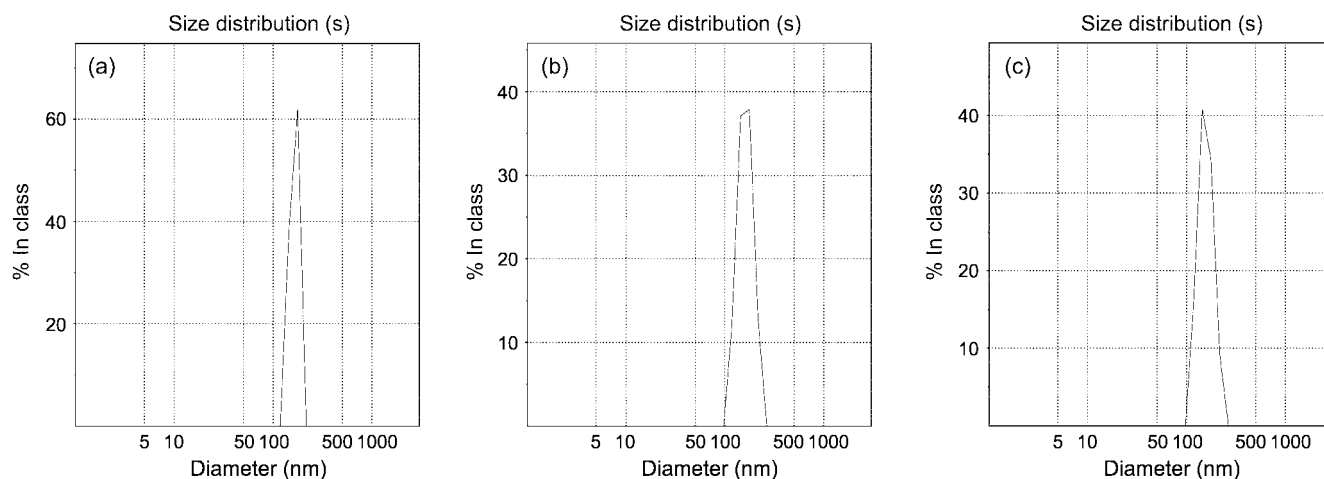
dialyzed through a cellophane film against running water until pH 6-7 and subsequently dried under vacuum at 35 °C before characterization.

Results and Discussion

Morphology and Particle Size. Figure 1 shows the morphology of the samples, the value for Fe_3O_4 coated soybean lecithin is about 7 nm by TEM. Figure 2 shows the mean size of particles in a supernatant fluid by PCS. The average size of particles is 164.8 nm analyses by intensity, 163.1 nm by volume and 158.3 nm by number respectively. We can see clearly from Figure 1 and Figure 2 that the nanoparticles were well dispersed by the lecithin. The result
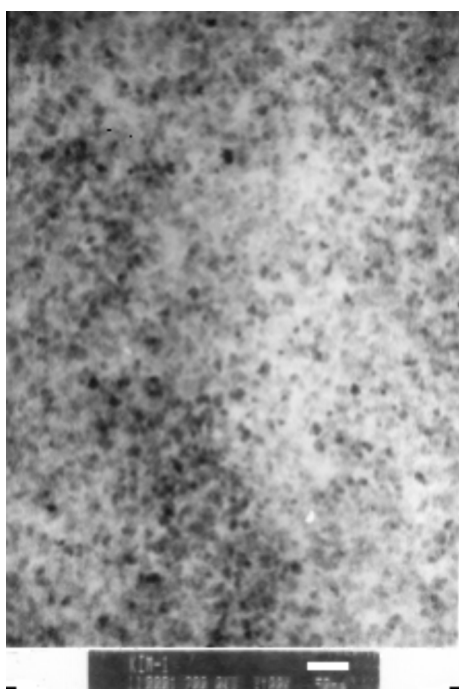
shows that such a fine particle size could be attributed to the inhibition effect of lecithin and also shows that the lecithin used as the stabilizer and the protective agent in the precipitation of Fe_3O_4 nanoparticles is also effective.

The result shows that the particle size of nanoparticle maybe attribute to the inhibition effect of soybean lecithin and also shows that soybean lecithin use as stabilizer and a protective agent in the precipitation of Fe_3O_4 nanoparticles is also effective. It was found by experiment that the size of Fe_3O_4 has increasing with the decrease of the concentration of soybean lecithin. The reason is probably that soybean lecithin is an amphipathic molecule, having a hydrophilic headgroup and two long hydropholic hydrocarbon chains. When their concentration exceed critical micelle concentration (CMC $\cong 1.6 \times 10$ mol·L^{-1}, double layer liposomes of the ordered systems are formed, which limited the particle size of the Fe_3O_4 particles. Magnetite was formed in the double layer liposomes of the ordered systems as Figure 3, one part magnetite was encapsulated within the double layer liposomes, and another part was formed in the extravesicular, the whole solution was divided numberless micro compartment. Since the vesicle wall is permeable to the hydroxyl ions, they diffuse down their chemical potential gradient into the intravesicular space and react with the available ferrous and ferric ions to form an intravesicular product. The typical electron diffraction pattern was shown in Figure 4.

Coverage and Adsorption by Soybean Lecithin. Figure

Figure 1. TEM photomicrograph of Fe_3O_4 nanoparticles (Bar = 50 nm).

Figure 3. Formation of Fe_3O_4 nanoparticles in the double layer liposomes of the ordered systems.
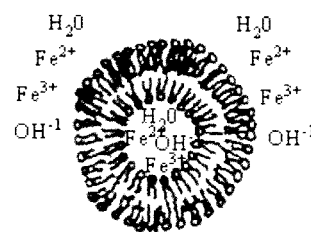

Figure 2. Particle size distribution of the Fe_3O_4 nanoparticles (a) size distribution by intensity, (b) size distribution by volume, (c) size distribution by number.

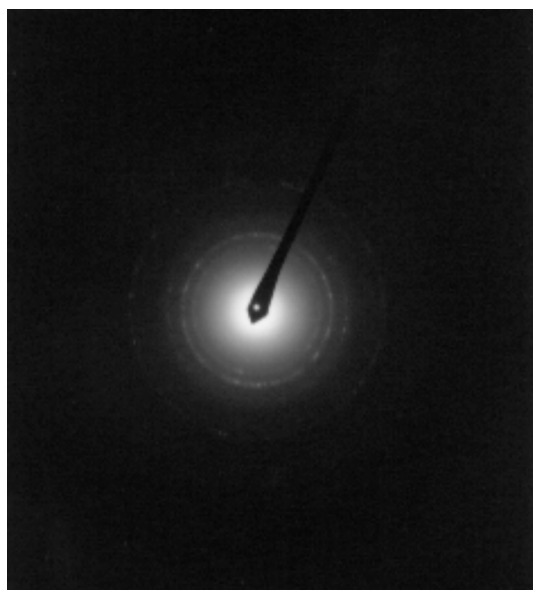**Figure 4**. Electron diffraction pattern of Fe_3O_4 nanoparticles.

5 shows IR spectra of the magnetite nanoparticles. As shown in Figure 5, the characteristic peak of Fe_3O_4 is 570.8 cm^{-1} and 3400 cm^{-1} is the hydroxy characteristic peak of water absorbed in the surface. Several absorption bands were observed in the figure, such as at 3423.0 cm^{-1} is the hydroxy stretching vibration characteristic peak, 2925 cm^{-1} is stretching vibration characteristic peak of carbon hydrogen and 1015 cm^{-1} is stretching vibration of carbon oxygen, 1436 cm^{-1} is bending vibration peak of hydroxy group. The intensity of the band from the Fe_3O_4 at decreased relative to the bands of soybean lecithin with increasing soybean

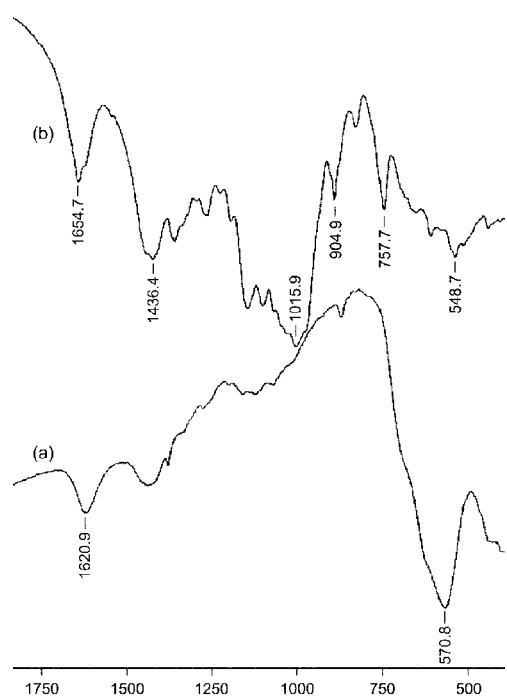**Figure 5**. Infrared spectra of the Fe_3O_4 nanoparticles (a) coated with the soybean lecithin (b) Fe_3O_4.

lecithin concentration, these results indicate that soybean lecithin irreversibly adsorbed on the surface of Fe_3O_4 particles even after carefully washing.

Soybean lecithin coverage[11,14]. The Thermogravimetric analysis was used to measure soybean lecithin coverage (Γ expressed in μmol m^{-2}). The adsorbed amount of on the magnetite particles was determined by TGA (PerkinElmer TGA-7) scanning from room temperature to 480 at 10 °C min^{-1}. The chemisorption of the soybean lecithin on magnetite is shown in Figure 6 where the soybean lecithin coverage is plotted against equilibrium concentration, at low total soybean lecithin concentration (less than $\approx$ 11 μmol/l), soybean lecithin is mostly adsorbed. At higher soybean lecithin concentration, the saturation level of 0.16 μmol·m^{-2} is reached. The isotherms are Langmurian in nature (Fig. 7), The Langmuir analysis of the soybean lecithin coating was performed with the help of equation:

$C_{eq}/\Gamma_L = 1/\Gamma_L^0 (C_{eq} + 1/K_L)$. Γ_L^0 is the value at saturation, K_L is the association constant. K_L value was calculated to be 3.01 mM^{-1} (Fig. 6).

Crystallographic and Magnetic Properties. Figure 8 shows the change in the X-ray diffraction patterns. The XRD peaks correspond to the spinel structure in all the samples. These peaks did not shift but became broader. The broadening of XRD peaks was observed in 2θ: 30.00, 35.82, 43.34, 54.34, 57.32, 62.84 etc. The broadening of XRD peaks is therefore predominantly attributed to the small size of crystallite, which is directly related to the decrease in the particle size. We attribute the broadening of XRD peaks to soybean lecithin, which is not removed, which reflect that space distance of the ordered systems formed is molecular distance. Because the change of the nanoparticles size brings about change of XRD diffraction patterns, we can use Scherrer formula to estimate the particle size. The volume average relative particle size of the crystal, D, was calculated with the Scherrer formula.[15]

$$D = K\lambda / \beta\cos(\theta)$$
$$\beta = B-b$$

Wherein: D: is the mean crystal size, λ: is the X-ray wavelength (nm), θ: is the Bragg angle, β: is the excess line broadening (radian), B is the linewidth (radian) and b is an instrument line broadening (radians), K: is the constant
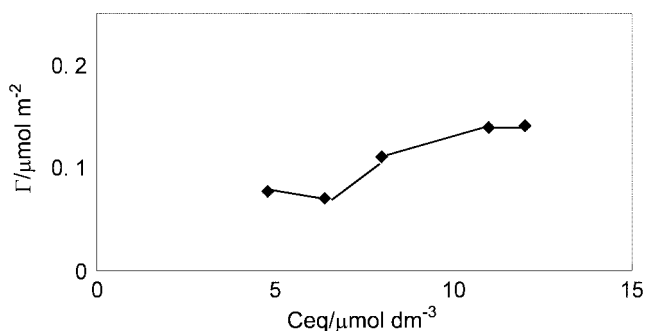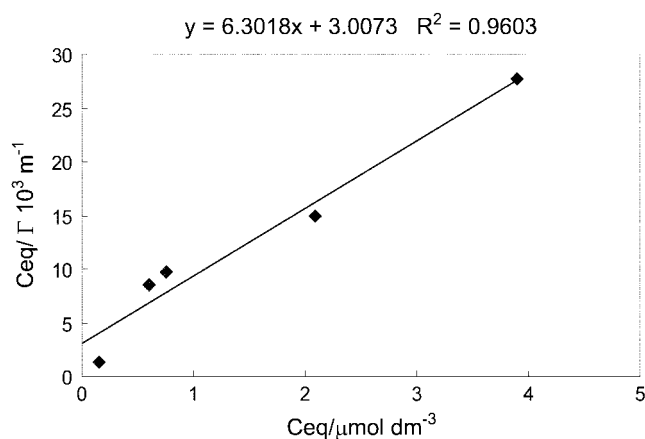

Figure 6. Evolution of the adsorbed amount as a function of total soybean lecithin concentration.

Figure 7. Langmuir plot of soybean lecithin adsorption (equilibrium free soybean lecithin/adsorbed soybean lecithin as a function of equilibrium free soybean lecithin) at micromolar concentration. Upper equation correspond to the Langmuir regression $C_{eq}/\Gamma_L = 1/\Gamma_L^0 (C_{eq} + 1/K_L)$. Γ_L^0 is the value at saturation, K_L is the association constant.
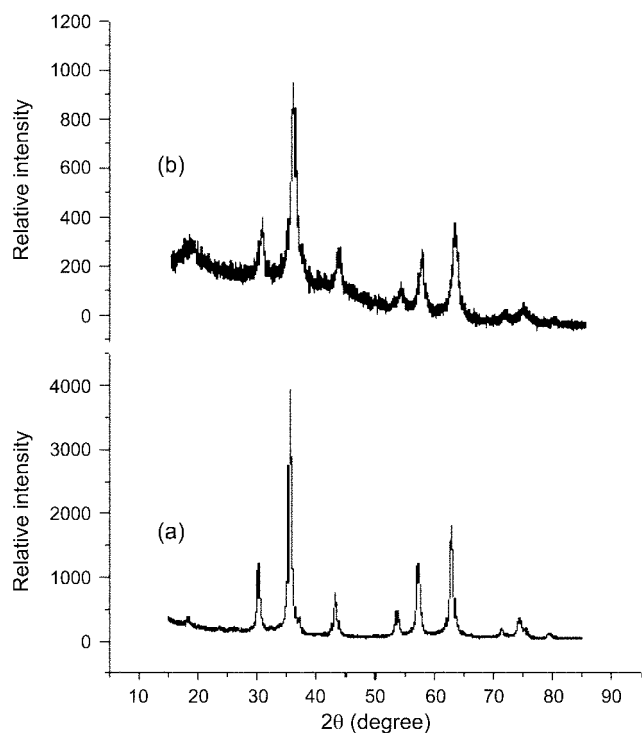
Figure 8. X-ray diffraction pattern of the Fe_3O_4 nanoparticles. (a) Fe_3O_4, (b) coated with soybean lecithin.

which is approximately equal to unity and is related both to the crystallite shape and to the way in which β and D is define. According to Scherrer formula, the diameter of particle size is about 7 nm, the result is corresponding with TEM. This shows that the soybean lecithin was added to limit the particle size and to form the core of fine particle Fe_3O_4.

Conclusion

Stable magnetite colloidal dispersions with average particle size about 7 nm has been successfully prepared by co-precipitation in a soybean lecithin aqueous solution. Each particle was covered with a soybean lecithin layer. From the measurements by TEM, The diameter of the Fe_3O_4 nano-particle is about 7 nm. The investigation of the Infrared spectra and TGA of Fe_3O_4 nanoparticle showed that the surfaces were protected by the soybean lecithin. Phase analysis of the final product by XRD confirmed the formation pure Fe_3O_4 nanoparticle.

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