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SYNTHESIS OF MAGNETITE AND COBALT FERRITE NANOPARTICLES

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Fe_3O_4 and $CoFe_2O_4$ magnetic nanoparticles have been synthesized successfully in aqueous solution and coated with oleic acid. The solid and organic solution of the synthesized nanoparticles was obtained. Self-assembled monolayer films were formed using organic solution of these nanoparticles. Both of the two nanoparticles are spherical and have narrow size distributions. The crystal sizes determined by Debye-Scherre equation with XRD data were found close to the particle sizes calculated from TEM images, and this indicates that the synthesized nanoparticles are nanocrystalline. The superparamagnetic behavior of the nanoparticles was documented by the hysteresis loop measured at 300 K.

Keywords: cobalt ferrite nanoparticle; magnetite nanoparticles

INTRODUCTION

The majority of nanoparticle research has been focused upon II–VI semiconductors and noble metals. Comparatively little work has been conducted upon the fabrication of uniform oxide nanoparticles despite their many important technological applications [1,2]. The fabrication of patterned media arrays of discrete single domain magnetic nanoparticles is very important for their potential applications in multi-terabit/in^2 magnetic memory devices [3–6]. Such magnetic nanoparticles could also find applications in electromagnetic devices, pigments, ferrofluids, refrigeration systems, medical imaging, drug targeting, and catalysis. The syntheses of several uniform-sized magnetic metal nanoparticles have been reported [7–10]. However, relatively little work has been done on the fabrication of

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monodispersed and crystalline Fe_3O_4 and $CoFe_2O_4$ nanoparticles. In this paper, highly crystalline and monodispersed Fe_3O_4 and $CoFe_2O_4$ magnetic crystalline nanoparticle were obtained using chemical coprecipitation in aqueous solution. By self-assembly, monolayers of nanoparticle were prepared. Two kinds of nanoparticles were characterized by XRD, TEM, EDS, and VSM and their properties were compared.

EXPERIMENT

Preparation of Fe_3O_4 Nanoparticle by Chemical Coprecipitation in Aqueous Solution

All the chemicals, including $FeCl_2 \cdot 4H_2O$(99+%), $FeCl_3 \cdot 6H_2O$ (99+%), NaOH, sodium oleate (98%), $CHCl_3$ (HPLC grade) and CH_3COCH_3 (HPLC grade), were obtained from Aldrich Chemical Co. and used without further purification. Distilled water was passed through a six-cartridge Barnstead Nanopure II purification train consisting of Macropure pretreatment and deoxygenated by bubbling with N_2 gas for 1 h prior to the use, and the main synthetic steps were carried out under a N_2 gas atmosphere. Typically, 2.70 g of $FeCl_3 \cdot 6H_2O$ and 1.00 g of $FeCl_2 \cdot 4H_2O$ were dissolved into 50 ml of water. To this solution, 25 ml of 25% ammonia was added at 80°C under vigorous stirring. The stirring was continued for 30 min and the reacted mixture was cooled to room temperature. The precipitate was isolated in a magnetic field and washed with 20 ml of water. The precipitate was redispersed in 20 ml of water, 1 g of sodium oleate in 10 ml of water was added, and stirring for 1 h at room temperature. Then the suspension was slowly acidified with 1 M HCl until the pH = 4–5 and an oily black precipitate appeared. The precipitate was dissolved into 230 ml of chloroform, obtained a transparent solution. In order to remove the larger particle, 20 ml of acetone was added to the chloroform solution, and the solution became cloudy. Laying for 1 h, the larger particle sedimentated to the bottom and the solution became transparent again. The transparent solution was removed to another beaker and 230 ml of acetone was added to precipitate most of the particle, only the smaller particle existed still in the solution. The precipitate was dried in air naturally and could be soluble in chloroform readily.

Preparation of $CoFe_2O_4$ Nanoparticle in Aqueous Solution

A 10 ml water, dissolving 0.54 g $FeCl_3 \cdot 6H_2O$ and 0.238 g $CoCl_2 \cdot 6H_2O$, resulted in an aqueous solution. Dissolving 1.2 g NaOH in 10 ml water. Adding NaOH solution into the prepared solution under stirring at 80°C. The stirring was continued for 30 min and cooled to room temperature and the precipitate was isolated in a magnetic field, and washed with water

three times. Coating was carried out by adding aqueous solution of 0.2 g sodium oleate in 10 ml water and stirring for 1 h. The suspension was slowly acidified with 1 M HCl until the pH = 5, and an oily black precipitate appeared. The oily black precipitate was soluble in chloroform. The removal of bigger and smaller particles was carried out as the same procedure for Fe_3O_4 nanoparticle.

Characterization of Nanoparticles by XRD, TEM, EDS, and VSM

The structural properties of synthesized nanoparticles were analyzed by X-ray powder diffraction (XRD) with a Philips X'Pert-MPD System. The average diameter of the crystals was estimated using Scherrer's formula. TEM experiments was carried out on a JEOL JEM2010 transmission electron microscope operated at 200 kV, and EDS was performed with an EDAX X-ray energy-dispersive analysis system attached to the JEOL JEM2010 transmission electron microscope. TEM samples were prepared on the 400 mesh copper grid coated with carbon. A drop of the nanoparticle solution was carefully placed on the grid and dried in air. The size distributions of the particles were measured from enlarged photographs of the TEM images. The magnetization curves were characterized with Lake Shore 7300 VSM.

RESULTS AND DISCUSSION

Generally, XRD can be used to characterize the crystallinity of nanoparticle, and it gives an average diameters of all the nanoparticles. The XRD patterns of the Fe_3O_4 and $CoFe_2O_4$ nanoparticle samples are shown in Figure 1. The discernible peaks in Figure 1(a) can be indexed to (220), (311), (400), (333), and (440) planes of a cubic unit cell, which corresponds to that of magnetite structure (JCPDS card no. 79-0418), and the discernible peaks in Figure 1(b) can be indexed to (220), (311), (400), (511), and (440) planes of a cubic unit cell, which corresponds to cubic spinel structure of cobalt iron oxide (JCPDS card, no. 22-1086). The mean crystal sizes determined by Debye-Scherre equation with XRD data have been found 8.8 nm for Fe_3O_4 and 14.8 nm for $CoFe_2O_4$, which are close to the particle sizes calculated from TEM images (9.1 nm for Fe_3O_4 and 14.6 nm for $CoFe_2O_4$). This indicates that both of the Fe_3O_4 and $CoFe_2O_4$ are all nanocrystalline. Figure 2(a) is the TEM of Fe_3O_4 nanoparticle monolayer formed by self-assembly when a drop of the nanoparticle chloroform solution was carefully placed on the grid and dried in air. Most of the Fe_3O_4 particles are irregular spherical. A monolayer of nanoparticle is observed from the image with almost no any multilayer on it. The area of

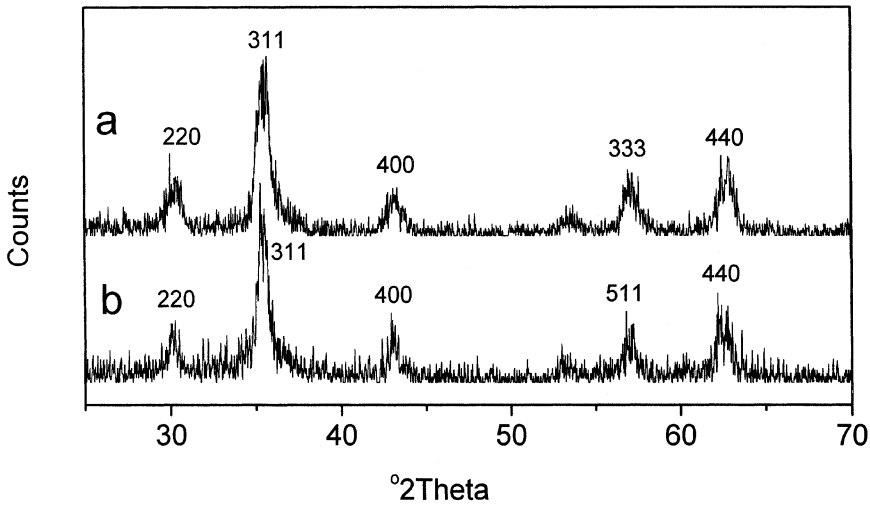

FIGURE 1 XRD patterns of (a) Fe_3O_4 nanoparticle and (b) $CoFe_2O_4$ nanoparticle.

single self-assembled monolayer was calculated of about 50 μm^2 from the TEM with lower magnification. Insertion in Figure 2(a) is the histogram of the size distribution of Fe_3O_4 nanoparticles obtained from enlarged image of Figure 2(a). The mean size of Fe_3O_4 nanoparticles is 9.1 nm with a standard deviation 2.3 nm. Figure 2(b) is the TEM image of $CoFe_2O_4$ nanoparticle monolayer formed by self-assembly. Most of the $CoFe_2O_4$ particles are also irregular spherical. The area of single self-assembled monolayer was filled the whole mesh of the copper grid observed from the

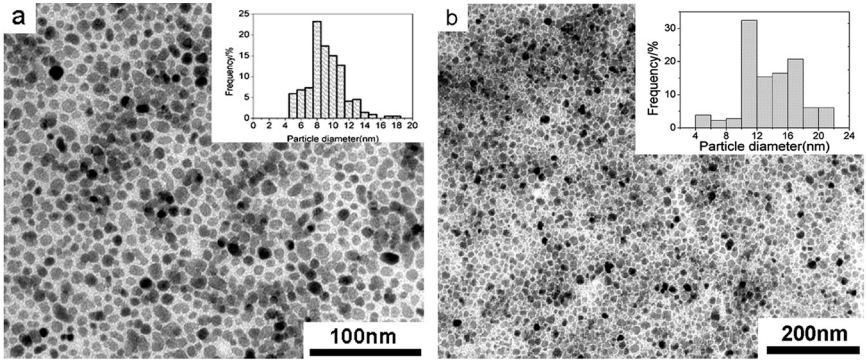

FIGURE 2 TEM of (a) Fe_3O_4 nanoparticle and (b) $CoFe_2O_4$ when a drop of the nanoparticle chloroform solution was placed on the Cu grid.

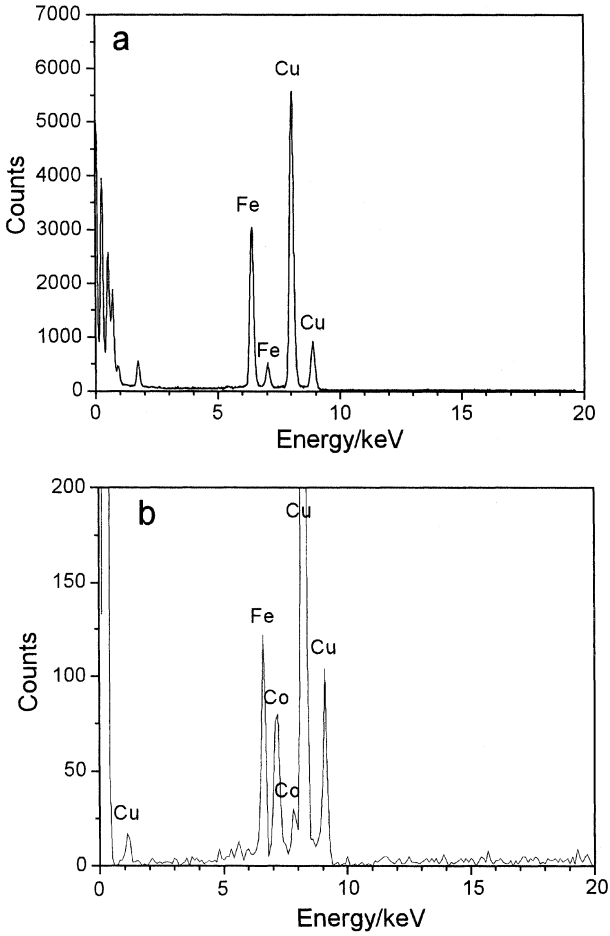

FIGURE 3 EDS patterns of (a) Fe_3O_4 and (b) Conanoparticle.

TEM with lower magnification. The histogram of the size distribution of $CoFe_2O_4$ nanoparticles obtained from enlarged image of Figure 2(b) is shown in the insertion in Figure 2(b). The mean size is 14.6 nm and the standard deviation is 2.8 nm. EDS results support the formation of nanoparticles. Figure 3(a) shows the EDS of the Fe_3O_4 nanoparticles, the particles contain Fe element and Figure 3(b) shows the EDS of the $CoFe_2O_4$ nanoparticles, the particles contain two elements of Fe and Co. The superparamagnetic behavior is documented by the hysteresis loop measured at 300 K as shown in Figure 4. There is almost immeasurable coercivity (0.814 Oe) for Fe_3O_4 at room temperature, this indicates that the

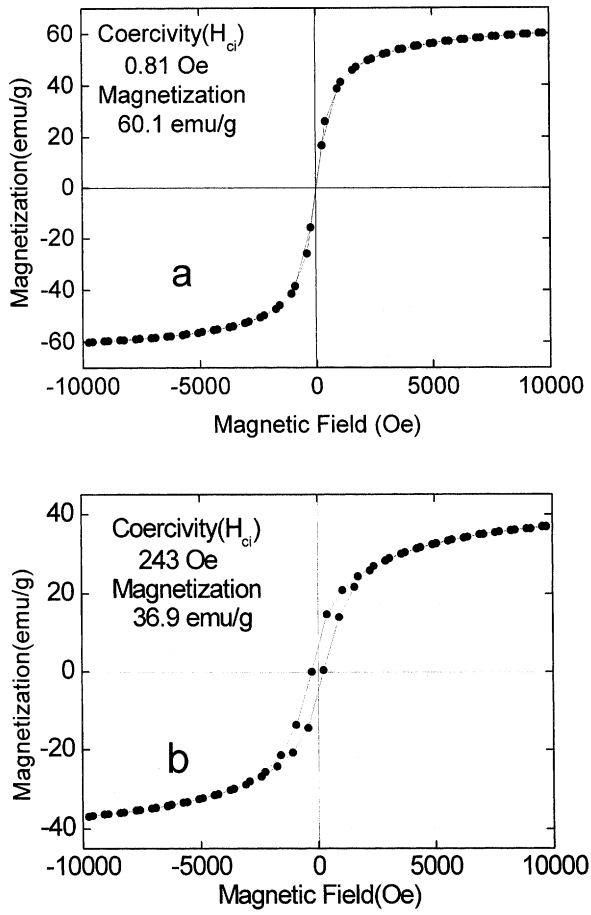

FIGURE 4 Magnetization versus applied field at 300 K for (a) Fe_3O_4 nanoparticle and (b) $CoFe_2O_4$ nanoparticle coated with oleic acid.

Fe_3O_4 particle are superparamagnetic and nanosized. The saturation magnetization, M_s, are 60.1 emu/g for Fe_3O_4, which are lower than that of bulk magnetite particles ($M_{bulk} = 92$ emu/g). The decrease in M_s is due to superparamagnetism of magnetite particles, which occur when the particle size decreases below 30 or 20 nm [11,12]. From the magnetization curves it can be seen that the magnetization does not saturate for Fe_3O_4, even at 10000 Oe. This phenomenon can be explained from the shape and size distributions observed by TEM. Comparing with Fe_3O_4 nanoparticle, $CoFe_2O_4$ nanoparticle has larger coercivity (243 Oe) at room temperature. This means that $CoFe_2O_4$ nanoparticle is a not very hard magnetic material.

CONCLUSIONS

Fe_3O_4 and $CoFe_2O_4$ nanoparticle has been synthesized successfully by chemical coprecipitation methods in aqueous solution and coated with oleic acid. These nanoparticles can be transferred to organic solution and the self-assembled monolayer films of these nanoparticles were formed using the organic solution. Both of the two nanoparticles are spherical and have narrow size distributions. The particles are magnetite structure and monocrystalline. The superparamagnetic behavior was documented by the hysteresis loop measured at 300 K, and it was found that Fe_3O_4 nanoparticle has good superparamagnetic and $CoFe_2O_4$ nanoparticle is a not very hard magnetic material.

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