Chem. Mater. **1996,** *8,* 2209−2211

Synthesis and Characterization of Nanometer-Size Fe_3O_4 and γ-Fe_2O_3 Particles

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Received February 23, 1996

Much attention has been focused on magnetic recording media materials, due to the increased need for high area density, in particular the conventional magnetic materials for information storage systems such as the oxides of iron, nickel, and cobalt.[1−3] Incorporating these materials into thin films, recording media can be fabricated by using a recording head which can flip the magnetic spin of metal oxides by either a magnetic or an electric field. Conventional magnetic recording media have been made by using mixtures of polymeric surfactants and micrometer-size iron oxide particles.[2] Recently there has been considerable interest in magnetooptic devices which combine magnetic and optical phenomena. Optical recording media can be made by depositing or arresting the growth of nanometer-size, magnetic particles of metal oxides inside optically transparent materials. When the particles are below 10 nm, they are optically transparent and candidates for incorporation into ultrathin films of polymers. A variety of techniques for the formation of ultrathin films are available and include spin-coating, self-assembly, sputtering, plasma polymerization, and Langmuir−Blodgett film deposition. The nanoparticles exhibit superparamagnetic behavior because of the infinitely small coercivity arising from the negligible energy barrier in the hysteresis of the magnetization loop of the particles as predicted by Bloch and Neel.[2]

Synthesis of iron oxide nanoparticles (Fe_3O_4) larger than 10 nm diameter has been carried out in bulk aqueous solution and surfactant systems.[4−12] The formation of iron oxide vesicles was reported by Mann.[4] Fendler's research group published a procedure for synthesizing Fe_3O_4 nanoparticles in bulk aqueous solution without the use of surfactant vesicles.[5−7] This procedure has an advantage in that no surfactant needs to be removed from the nanoparticles before incorporation into an ultrathin film. Subsequently other research groups reported procedures for synthesizing iron oxide nanoparticles in either molecular assemblies such as vesicles or Langmuir monolayers.[8−12]

In this work, we report the synthesis of magnetite (Fe_3O_4) nanoparticles in aqueous solutions without any surfactants. The Fe_3O_4 particles have an average diameter less than 10 nm and a narrow size distribution. This particle size is smaller than heretofore reported. The colloidal suspensions of the magnetite can be then directly oxidized by aeration to form colloidal suspensions of γ-Fe_2O_3. The procedure that we report for the synthesis of Fe_3O_4 and γ-Fe_2O_3 nanoparticles in an aqueous solutions, while similar to previous protocols reported in the literature, contains significant new synthesis modifications. The reaction steps in our process are as follows:

$$\mathrm{FeCl_2}\ (1\ \mathrm{mol}) + \mathrm{FeCl_3}\ (2\ \mathrm{mol}) \rightarrow \mathrm{Fe_3O_4} \xrightarrow{\text{oxidation}} \gamma\text{-}\mathrm{Fe_2O_3}$$

To prepare Fe_3O_4 nanoparticles, homogeneous in size and composition, it is important to perform the above reaction in an aqueous solution with a molar ratio of Fe(II)/Fe(III) = 0.5 and a pH = 11−12. Volumes of 0.85 mL of 12.1 N HCl and 25 mL of purified, deoxygenated water (resistance of 17.8 MΩ, by nitrogen gas bubbling for 30 min) were combined, and 5.2 g of $FeCl_3$ and 2.0 g of $FeCl_2$ were successively dissolved in the solution with stirring. The resulting solution was added dropwise into 250 mL of 1.5 M NaOH solution under vigorous stirring. The last step generated an instant black precipitate. The paramagneticity was checked in situ by placing a magnet near the black precipitate of Fe_3O_4. The precipitate was isolated in the magnetic field, and the supernatant was removed from the precipitate by decantation. Purified deoxygenated water was added to the precipitate and the solution decanted after centrifugation at 4000 rpm. After repeating the last procedure three times, 500 mL of 0.01 M HCl solution was added to the precipitate (with stirring) to neutralize the anionic charges on the nanoparticles. The cationic colloidal nanoparticles were again separated by centrifugation (4000 rpm) and peptized by adding water. The result was a clear, transparent cationic colloid (hydrosol).

Samples for transmission electron microscopy (TEM) samples were prepared on 400 mesh copper grids coated with Formvar film. A drop of Fe_3O_4 nanoparticle sol was carefully placed on the copper grid surface and dried. TEM experiments were carried out on a Hitachi-600 transmission electron microscope. Figure 1 shows a TEM image of Fe_3O_4 nanoparticles. The nanoparticles are nearly spherical and have an average diameter of 8.5 ± 1.3 nm. This size is considerably smaller than

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S0897-4756(96)00157-3 CCC: $12.00

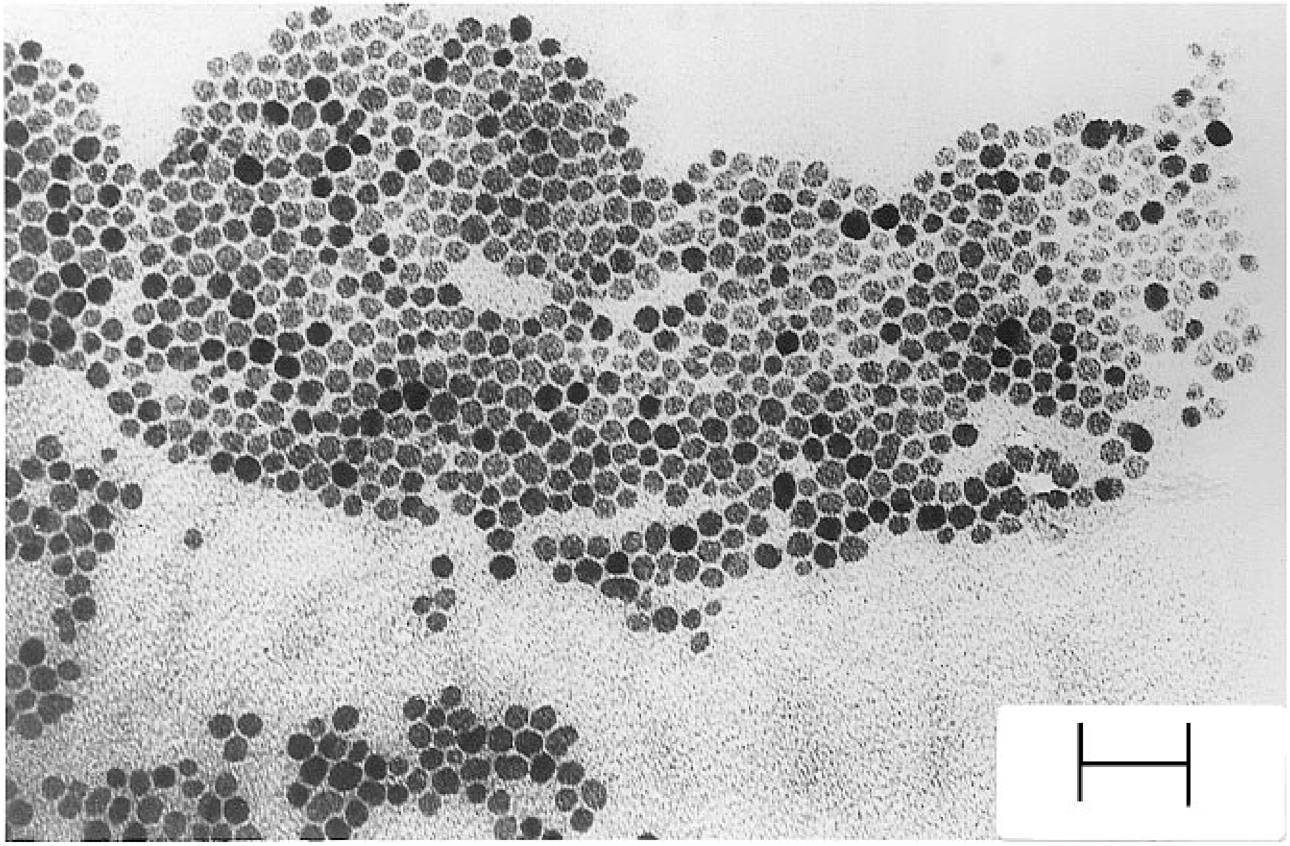

Figure 1. Scanning electron micrograph of Fe_3O_4 particles. Bar length is 30 nm.

others reported in the literature. Selected area electron diffraction (SAED) was performed on isolated crystals of the Fe_3O_4. The lattice parameters obtained were consistent for that of single crystals of Fe_3O_4.

Since the hydrosol of Fe_3O_4 nanoparticles contains no surfactants, it can be used as a source for direct incorporation of the nanoparticles into ultrathin films without additional purification to remove the surfactant. The stability of Fe_3O_4 particles with respect to oxidation is one of critical problems in its use in a magnetic recording material. On the other hand, γ-Fe_2O_3 is stable to further oxidation and several techniques have been reported to synthesize γ-Fe_2O_3 particles. Recently Ziolo et al. reported the synthesis of γ-Fe_2O_3 nanoparticles in a polymer matrix-mediated system.[13] The resulting nanocomposite with appreciable optical transmission in the visible region at room temperature was isolated as a γ-Fe_2O_3/polymer nanocomposite. The nanocomposite was synthesized in an ion-exchange resin. The material showed a magnetic susceptibility of 46 emu/g and superparamagnetism with a particle size about 10 nm. Further, Diaz et al. reported the synthesis of magnetic nanoparticles in a polypyrrole powder.[14] The composite was prepared in a polymerized polypyrrole dissolved in an aqueous solution containing a dispersion of metal oxide nanoparticles. Tailor-dressed magnetic particles in a polypyrrole matrix ferrofluid were reported by Bidan et al.[15] They reported a novel method of including nanometer-sized magnetic particles into polypyrrole based on the use of magnetic fluids or ferrofluids in which a magnetic core of γ-Fe_2O_3 is surrounded by an anionic complexing shell. For these nanocomposites of iron oxides in polymer matrixes, the micropores and microvoids of the polymer matrix enable the synthesis of the nanometer particles of iron oxide to be confined in size. A handicap of these materials is that it is difficult to show that the nanoparticles are γ-Fe_2O_3 and that there is not a contamination of other iron oxides in the nanocomposite.

Comparing the above reports in the literature, the present work is a direct method for the synthesis of γ-Fe_2O_3 by oxidizing Fe_3O_4 nanoparticles in the aqueous phase without the presence of a surfactant. The oxidation of Fe_3O_4 into γ-Fe_2O_3 was carried out by adjusting the pH of the hydrosol of Fe_3O_4 to a pH of about 3.5. The clear hydrosol was stirred under aeration (with air) for 30 min at about 100 °C. The color of the solution changed from blue-black to clear reddish-brown. The reddish-brown solution was cooled to room temperature, and the supernatant solution was collected after centrifugation for 30 min at 4000 rpm. The clear, reddish-brown supernatant is a hydrosol of γ-Fe_2O_3 nanoparticles. A drop of the hydrosol was dropped on the top of a Formvar-coated copper grid and dried for TEM measurement. A TEM image of γ-Fe_2O_3 nanoparticles is shown in Figure 2. Needlelike γ-Fe_2O_3 nanoparticles with lengths of 20−50 nm and widths of 4−6 nm are visible. These sizes are much greater than those of the magnetite nanoparticles. In this and other TEM images, overlapping nanoparticles of γ-Fe_2O_3 make it difficult to get a precise size distribution of the lengths and widths. What is significant however is that while

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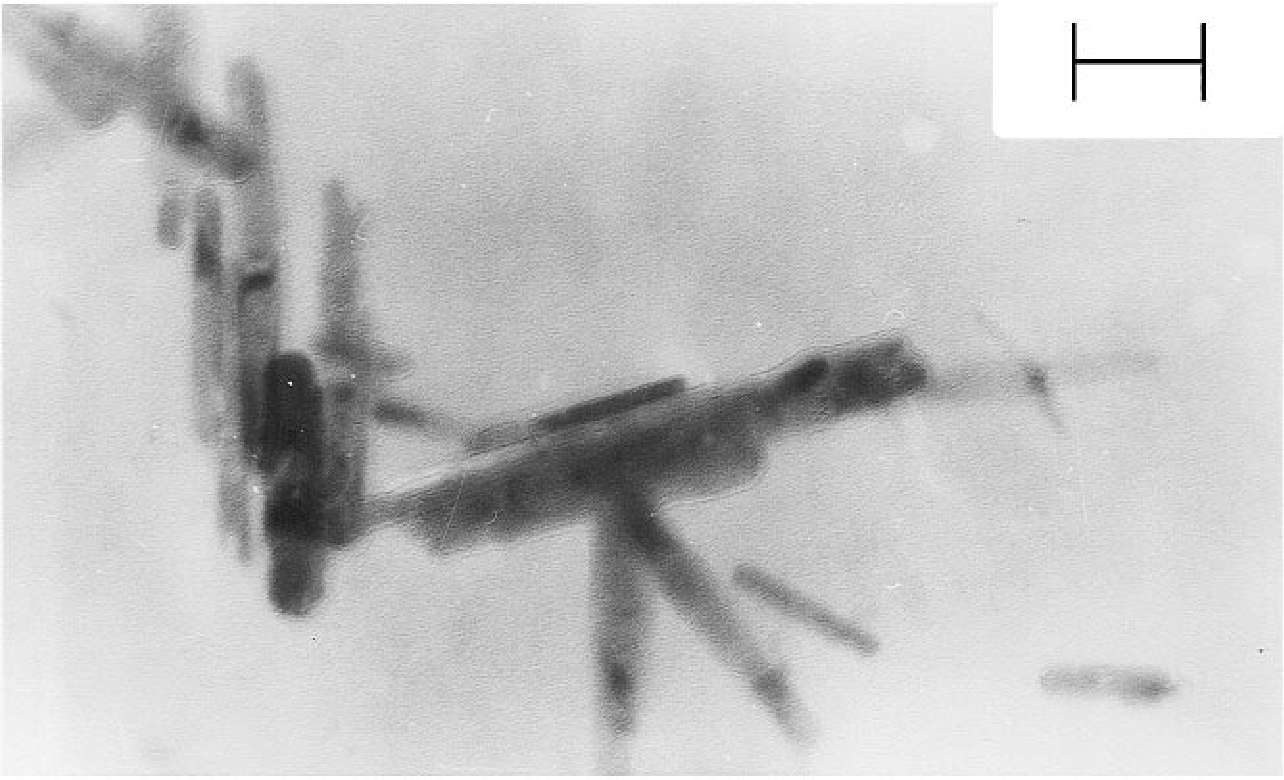

Figure 2. Scanning electron micrograph of γ-Fe_2O_3 particles. Bar length is 30 nm.

needlelike γ-Fe_2O_3 particles in the micrometer size are currently used in magnetic storage media,[2] the size reported here is of nanometer scale. The SAED measurements on isolated nanoparticles indicated that the lattice parameters were consistent with single-crystal γ-Fe_2O_3. The paramagneticity of γ-Fe_2O_3 was checked by increasing the pH of the colloidal solution to about 11 by addition of 1.5 M NaOH solution. At this pH, the colloidal particles of γ-Fe_2O_3 aggregate, and the aggregates are separable in a magnetic field.

In summary, that we have demonstrated the production of clear hydrosols of either Fe_3O_4 or γ-Fe_2O_3. These hydrosols have a particle size considerably smaller than that reported in the literature and no surfactants are necessary to stabilize the sols.

Acknowledgment. This work was supported in part by the MRSEC Program of the National Science Foundation under Award No. DMR-9400354.

CM960157J