Synthesis of Capped Ultrafine γ-Fe_2O_3 Particles from Iron(III) Hydroxide Caprylate: A Novel Starting Material for Readily Attainable Organosols

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Received September 14, 2001. Revised Manuscript Received November 14, 2001

The synthesis of capped γ-Fe_2O_3 ultrafine particles from thermal treatment of iron(III) hydroxide caprylate in boiling tetraline with retention of the integrity of the caprylate units during the reaction process is reported. This novel material due to the organophilic mantle around the particle surfaces can be easily dissolved in organic solvents and thus the availability of stable magnetic organosols is straightforward. The formation of capped magnetic particles is accomplished only under anaerobic conditions, while the state of hydration of the starting iron(III) hydroxide caprylate precursor was found to play a critical role for the magnetic-phase formation. The various steps in the synthesis as well as the nature of the magnetic particles were studied by means of X-ray powder diffraction and IR and Mössbauer spectroscopies, while the morphology and particle size of the final magnetic nanocrystallites were evaluated by the TEM technique. Finally, ESR spectroscopy provided strong evidence for the isolated state of the magnetic particles in their solvated state.

Introduction

Ferrofluids define a unique class of ferromagnetic liquids in which an inorganic magnetic solid is homogeneously dispersed in a liquid carrier, thus forming a stable colloidal dispersion that exhibits magnetic response when a magnetic field is applied.[1] The availability of magnetic fluids constitutes a topic of interest not only to colloid chemists[2−4] but also to the observation of a number of novel phenomena and applications, including magnetocaloric power cycle,[5] magnetoviscous effect,[6] magnetic imaging,[7] magnetic[8] and magneto-optic[9] data storage media, biology and medicine,[10] formation of mono- or multilayered magnetic films,[11] and others.

The common ferrofluids comprise a colloidal dispersion of magnetite (Fe_3O_4) fine particles with a diameter <150 Å in an aqueous or organic carrier liquid (hydrosol or organosol, respectively). In general, aqueous ferrofluids are easily obtained either by acid peptization of magnetite[12] or by immobilization of small magnetite particles in the matrix of a water-soluble polymer, for example, poly(vinyl alcohol).[13] In the case of ferrofluids based on organic solvents, the coupling of the insoluble magnetic solid to the bulk liquid phase is accomplished by adding a chemical whose structure is such that it can be adsorbed by the surface of the particle and simultaneously become solvated by the carrier liquid. This chemical is usually a molecule having a polar carboxylic end group that binds to the particle surface and a hydrocarbon chain that is dispersed in the organic medium. However, a main drawback of the method relies on the fact that stable colloidal ferrofluids can be obtained only after grinding the magnetic substance together with the organic carrier liquid and the stabilizing agent for a prolonged period of time, usually from 1 to 6 months.

Recently, a new nonhydrolytic route based on the thermal decomposition of iron complexes in the presence of a surfactant has led to the formation of capped γ-Fe_2O_3 nanoparticles that are soluble in organic solvents.[14] In the present work we describe a simpler method that leads to magnetic particles, the surfaces of which are capped by the carboxylate group of caprylic acid. The resulting organically modified magnetic particles are easily dissolved in organic media to provide stable organosols.

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10.1021/cm010794w CCC: $22.00

Experimental Section

Materials. For the synthesis of the iron(III) hydroxide caprylate precursor the following reagents were used: $Fe(NO_3)_3{\cdot}9H_2O$ (Merck) and caprylic acid (octanoic acid) (Riedel deHaën). Distilled tetraline (Fluka) was used for the magnetic-phase formation.

Precursor Agent.[15] In 5 mL of commercial ethanol, 6 g of the salt $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved. To this solution, 2.14 g of caprylic acid in 10 mL of ethanol was added, followed by a rapid addition of 3 mL of concentrated NH_3 (37%) under vigorous stirring. The as-formed precipitate was centrifuged and washed well with hot ethanol (6−7 times). The washed precipitate was re-dispersed in a few milliliters of ethanol and finally dried at room temperature for 24 h by spreading over a glass plate (FeOHC8). The presence of caprylate groups ($C_7H_{15}COO^-$) in the precipitate was verified by the characteristic infrared absorption bands at 1600−1400 cm^{-1}.

Capped Magnetic Particles. Eight hundred milligrams of FeOHC8 was suspended in 40 mL of tetraline and the mixture was purged with flowing argon for 20 min. Following, the suspension was subjected to an intense reflux (boiling point of tetraline: 210 °C) under an argon atmosphere for 9 h. After reaction was accomplished, the obtained brown solution was cooled to room temperature and an excess of commercial acetone (200 mL) was added to it. A brown precipitate formed immediately, which was isolated by centrifugion, washed with acetone, and finally dried over a glass plate at room temperature. The obtained powder possessed bulk magnetic properties, as indicated by its attraction by a permanent hand magnet. Iron elemental analysis[16] gave 40% of Fe, while the organic matter in the material was estimated to be 40 wt % from the weight difference before and after calcination of a certain amount of the powder at 450 °C for 2 h in air. These findings indicate the formula $(\gamma\text{-}Fe_2O_3)_{1.31}(C_8H_{15}O_2)$, which is consistent with the results obtained from iron and carbon elemental analysis of the sample [Fe/C molar ratio: 0.29 (exp.) versus 0.32 (calc.)].

Physical Methods. X-ray powder diffraction (XRD) patterns were taken on a D-500 Siemens diffractometer using Cu Kα radiation. Infrared spectra were taken with a FT-IR spectrometer of Bruker, Equinox 55/S model. The samples were measured in the form of KBr pellets. Electron spin resonance (ESR) measurements were obtained at room temperature on a Bruker 200D-SRC spectrometer with a resonance cavity of 9.6 GHz. Mössbauer spectra were recorded with a constant acceleration spectrometer with a 50 mCi $^{57}Co(Rh)$ source moving at room temperature, while the sample (absorber) was kept in a variable temperature cryostat. The parameters were obtained by a least-squares fitting program assuming Lorentzian line shapes. Isomer shift values are given with respect to metallic iron. TEM measurements were carried out in a CM20 Phillips microscope operating at 200 kV. To this purpose, a drop from a $CHCl_3$ solution of the powder (0.2% w/v) was carefully placed on a copper grid surface and dried before analysis.

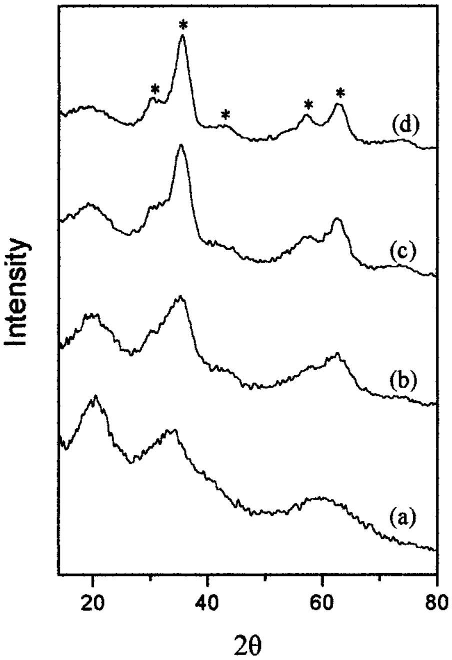

Figure 1. XRD patterns of FeOHC8 as received (a) and after its thermal treatment in tetraline for 1 h (b), 6 h, (c) and 9 h (d) [asterisks in pattern (d) indicate reflections from γ-Fe_2O_3].

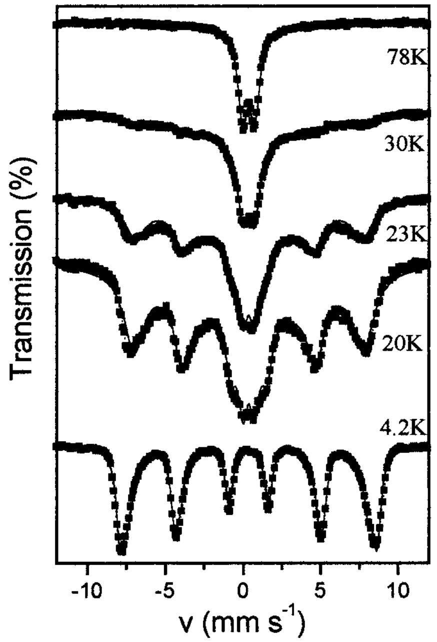

Figure 2. Variable temperature Mössbauer spectra of the capped magnetic particles.

Results and Discussion

Characterization. Figure 1 presents the XRD patterns of the FeOHC8 precursor before (as received) and after reflux for various periods of time in tetraline. We observe that the initial FeOHC8 material exhibits very broad reflections associated probably with the formation of small-sized particles (30−40 Å) showing partial crystallinity.[17] Upon thermal treatment for various times in tetraline, the initial broad reflections weaken gradually in intensity and finally gave their place to well-discernible broad signals, pointing to the formation of ultrafine iron oxide particles, 40 Å in size as estimated from the Scherrer equation.

Since the XRD technique cannot actually discern between magnetite (Fe_3O_4) and γ-Fe_2O_3 (both magnetic oxides have a spinel-type structure), the nature of the iron oxide particles in the final sample was unveiled by Mössbauer spectroscopy. Mössbauer spectra were taken in the temperature range 4.2−300 K (Figure 2). The spectra from room temperature to 78 K (L.N.) consist of a paramagnetic doublet with broad line widths and with an isomer shift of 0.50 mm s^{-1}, which is typical of trivalent iron. The L.He (4.2 K) spectrum displays full

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magnetic hyperfine structure. This spectrum has been analyzed with two magnetic components with hyperfine magnetic fields of 516 and 480 kOe, respectively, and zero quadrupole interaction. The lack of isomer shift contribution from divalent iron sites, the values of hyperfine fields, and the zero quadrupole splitting advocate for the formation of maghemite particles (γ-Fe$_2$O$_3$). With increasing temperature there is a gradual collapse of the magnetically split component to a doublet. These spectral changes are characteristic of superparamagnetic behavior in which thermal fluctuations of the fine particles cause the direction of the associated atomic spins to vary with a frequency depending upon the particle size, anisotropy energy, and temperature. If this frequency is greater than the Larmor frequency of the ^{57}Fe nucleus (10^8 s^{-1}), the magnetic hyperfine splitting collapses to give a single line or a doublet if a quadrupole interaction is present. In the slow relaxation limit of the iron spins, a complete magnetic hyperfine splitting is observed. However, because of particle size distribution in a sample, the spectra typically consist of a doublet, owing to small particles with short relaxation times and a sextet from larger particles with longer relaxation times. Furthermore, the doublet is expected to gain intensity at higher temperature as a result of the increasing relaxation frequency and the magnetic sextet to increase with lowering temperature as the relaxation frequency slows down. The temperature at which the area of the doublet is equal to the sextet is defined as Mössbauer blocking temperature. An important result in the present study is the temperature evolution of the spectral lines in the narrow interval of 20−30 K. This result is rather unusual for magnetic particles. The drastic spectral changes are typical of an intermediate spin relaxation rate manifested by the rapid temperature variation. This variation implies that in this temperature range the relaxation time falls within the Mössbauer time window (10^{-7}−10^{-9} s). Such a rapid evolution can be ascribed to superparamagnetic behavior of magnetic particles with a rather narrow particle size distribution. Judging from the temperature variation of the central "paramagnetic" part, we can estimate that the Mössbauer blocking temperature lies within the temperature range of 20−30 K, corresponding to a particle diameter of 30−40 Å.[18]

In Figure 3 the IR spectra of FeOHC8 before (a) and after reflux in tetraline (b), in the region 3100−400 cm^{-1}, are presented. As seen, the FeOHC8 precursor exhibits, apart from the absorption bands below 3000 cm^{-1} ascribed to $-$CH$_2-$ and $-$CH$_3$ aliphatic moieties, two other absorptions at 1540 and 1430 cm^{-1}, characteristic of the presence of $-$COO$^-$ groups. These data clearly demonstrate the anchoring of the caprylate anions to the particle surfaces. Moreover, the frequency separation between the bands at 1540 and 1430 cm^{-1} (110 cm^{-1}) indicates that the caprylate moieties bind the surface iron centers in a chelating or bridging mode of coordination.[19] The bands at 600 and 460 cm^{-1} are indicative of an iron oxide hydroxide network.[20] After thermal treatment of FeOHC8 in tetraline, the characteristic bands of the caprylate groups are still observable, while an enhancement of the band at 600 cm^{-1} at the expense of that at 460 cm^{-1} was also observed. These results unveil the preservation of the organophilic sheath around the magnetic solid and also the formation of a rigid γ iron oxide network.[20,21]

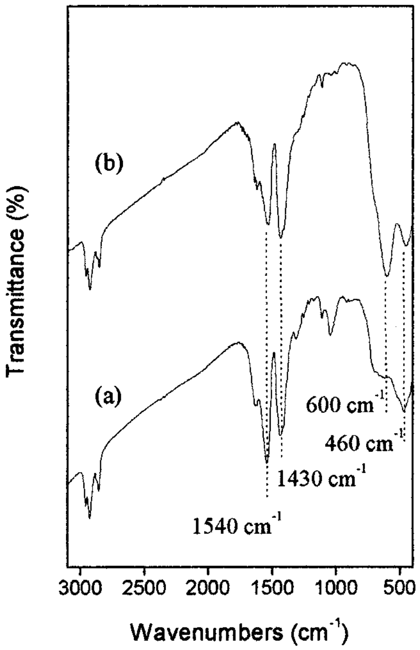

Figure 3. IR spectra of FeOHC8 as received (a) and after its thermal treatment in tetraline for 9 h (b).

Synthesis. There are two basic factors affecting the magnetic-phase formation. The first refers to the anaerobic conditions needed during the thermal treatment of the precursor in the tetraline solvent and the second to the state of hydration of the precursor compound. Indeed, when FeOHC8 was treated in boiling tetraline (not purged with argon) under an air atmosphere, a pure hematite (α-Fe$_2$O$_3$) phase was obtained. On the other hand, when the as-synthesized iron(III) hydroxide caprylate gel was dried at 80 °C for 24 h in air and then thermally treated in boiling tetraline (purged with argon) under an argon atmosphere, the phase was a mixture of hematite/γ-Fe$_2$O$_3$. Furthermore, drying the sample at a higher temperature (150 °C, 24 h) yielded mainly the hematite phase. A similar behavior was observed when a small amount (5% v/v) of 2,2-dimethoxypropane, the latter acting as a dehydrating agent,[22] was added to the tetraline solvent prior to thermal treatment of the as-synthesized precursor compound under an argon atmosphere. In this case, a pure hematite phase was received, which upon addition of a few drops of water to the boiling solution turned to a hematite/γ-Fe$_2$O$_3$ mixture. Therefore, the anaerobic conditions in conjunction with the hydrated state of the precursor compound are critical factors for the magnetic-phase formation.

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An interesting question concerns the mechanism leading to the magnetic-phase formation. We propose that the key step for this formation is the partial reduction of the trivalent iron centers to their divalent state by a reducing agent to first form magnetite through ion reorganization and subsequently γ-Fe_2O_3 via oxidation.[23] It is well-known that iron(III) carboxylate compounds upon pyrolysis under an inert atmosphere are transformed into crystalline magnetite nanoparticles through partial reduction of trivalent iron to its divalent state by the carboxylate groups.[15,24,25] The same reactions also take place when a solid sample of the FeOHC8 precursor was calcined at 210 °C for a few hours in an argon atmosphere. A black magnetic powder consisting of large magnetite particles was received which lacked, as expected, the IR bands from the caprylate anion owing to its thermal decomposition. In boiling tetraline reduction of trivalent iron in the FeOHC8 precursor can be affected either by the caprylate anions or tetraline itself, the reducing properties of the latter being well-established in the literature.[26] Since the majority of the caprylate units retain their structural integrity throughout the reaction process, we assume that tetraline must play the role of the reducing agent. The following blank experiments justify this hypothesis. In the first experiment, a precursor prepared under the same conditions as those applied for the FeOHC8 but without caprylic acid, that is, an iron hydroxide gel, gave in refluxing tetraline a pure, insoluble in organic solvents, γ-Fe_2O_3 phase (40 Å in diameter). In contrast, when nitrobenzene (boiling point: 210 °C) was used instead of tetraline, no magnetic phase was obtained regardless of whether the iron hydroxide gel was modified with caprylic acid or not. These results strongly support the essential reducing action of tetraline for the exclusive formation of the γ-Fe_2O_3 phase. Furthermore, it is important to state that we were unable to isolate magnetite crystallites from the reaction mixture, even after purging boiling tetraline thoroughly with flowing argon. So a crucial remaining question is what causes the reoxidation of divalent iron centers back to trivalent and thus finally to γ-Fe_2O_3. We cannot provide a clear answer for it but, tentatively, we suggest the possible generation of reactive oxidative species, for example, hydroxyl radicals, due to the large number of surface hydroxyl groups in the ferrogeneous nanocrystallites. However, a nonredox process, for example, direct crystallization of the noncrystalline FeOHC8 precursor to γ-Fe_2O_3 in refluxing tetraline, could constitute another possible path as suggested by one of the reviewers.

Solubility of the Capped Magnetic Particles—TEM Examination. The capped γ-Fe_2O_3 powder is slightly soluble in hexane but readily soluble in chloroform, tetrahydrofuran, and toluene (>50 mg/ml). In the latter cases, the dissolution process proceeds rapidly and leads to clear and transparent brown organosols that remain stable even after 6 months. In addition, by appropriate dilution of the powder (about 0.1% w/v), homogeneous films could be obtained by solvent evaporation over the film support. It is important to note that when a pure iron hydroxide gel (not modified with caprylate units) was treated in tetraline in the presence of the required quantity of caprylic acid, we received a magnetic phase that was sparingly soluble in the abovementioned organic solvents. The same behavior was observed when γ-Fe_2O_3 (obtained by thermal treatment in tetraline of an iron hydroxide gel) was dispersed, for example, in chloroform and sonicated in the presence of the capping agent. Therefore, to obtain highly soluble in organic solvents magnetic particles, modification of the initial iron hydroxide gel with the capping agent is necessary before transformation to the magnetic phase.

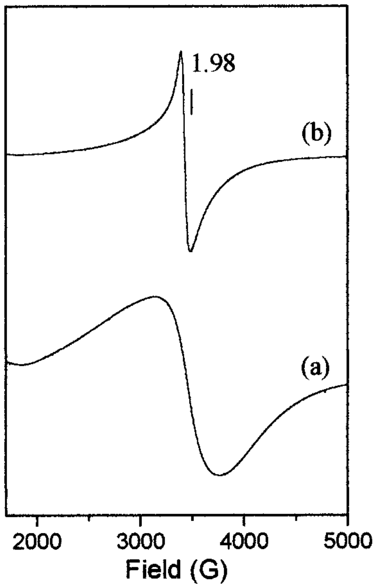

Figure 4. ESR spectra of capped γ-Fe_2O_3 particles in powder (a) and in solution (b), recorded at room temperature.

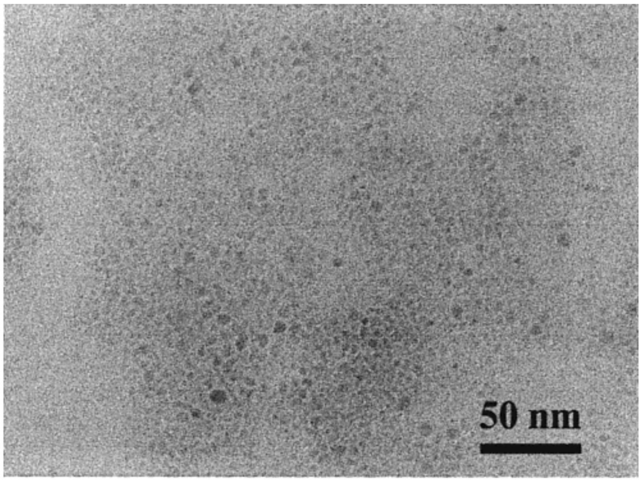

Figure 5. TEM micrograph of the capped γ-Fe_2O_3 ultrafine particles after solvent evaporation.

An interesting finding was revealed by comparing the ESR spectra of the capped γ-Fe_2O_3 particles in powder and in solution (0.2% w/v in toluene) (Figure 4). The powder exhibits a broad signal at $g \sim 1.98$, which is typical for a magnetic substance.[27] The broadening of the ESR line arises from strong interparticle dipolar

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interactions that provide an effective spin relaxation mechanism. Upon dilution of the powder in toluene, the signal's line width is decreased, giving a narrow line ($g \sim 1.98$). This change depicts not only the ultrafine size of the capped magnetic particles (line width proportional to the particle volume) but also their isolated state, which weakens the interparticle interactions and make feasible the observation of the narrow signal.[27]

Finally, the morphology and size of the capped γ-Fe_2O_3 particles were evaluated by their TEM examination. The bright-field TEM micrograph of the dried sample is shown in Figure 5. Apparently, solvent evaporation leads to the formation of a monolayer of particles, the latter being nearly spherical in shape, exhibiting a rather uniform size distribution with particle diameters ranging between 30 and 80 Å and an average of 40 Å.

Conclusions

Capped ultrafine γ-Fe_2O_3 particles were prepared under anaerobic conditions by the thermal treatment of a hydrated iron(III) hydroxide caprylate gel in boiling tetraline and by retention of the organophilic mantle around the parent particles throughout the final solid. The capped particles, which possessed a spherical morphology and an average size of 40 Å, were easily solvated in organic solvents to provide stable and homogeneous magnetic organosols. These unique properties in conjunction with the uniform and ultrafine size of the particles make them valuable for many technological and other applications. Surface modification of magnetic particles with other capping agents of high biological importance, bearing also in their structure functional groups different from the carboxylic, will be the subject of a future work.

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