

Synthesis of Monodisperse Superparamagnetic Fe/Silica Nanospherical Composites

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Nanoparticulate magnetic materials exhibit unique properties of interest, for example, in data storage technology.¹ In recent years, special attention has been focused on superparamagnetic nanomagnets because of their potential use in biotechnology.² Many applications of these materials require the preparation of magnetic fluids stable against the aggregation induced by the magnetic dipolar attraction.³ Encapsulation in silica provides the nanomagnets with several benefits (apart from screening the magnetic dipolar attraction) for their use in biomedical applications, compatibility in biological systems,⁴ functionality,⁵ high suspension stability under different conditions,⁶ modulation with heating of magnetic properties,⁷ and hydrophilic character.⁸ All of these benefits are especially useful when dealing with metallic instead of oxidized compounds. Silica, as we will see below, also stabilizes α -Fe nanocrystals against corrosion.

We here report the synthesis of monodisperse air-stable superparamagnetic α -Fe nanocrystals encapsulated in nanospherical silica particles of 50 nm in diameter (Figure 1). The development of strategies to produce magnetic metallic particles encapsulated in inorganic diamagnetic matrixes is not only important in biotechnology but also in recording applications. For example, an unusual magnetic behavior (beating the superparamagnetic limit) in metallic magnetic nanocrystals embedded in inorganic matrixes has been recently observed.^{2b} Our approach to screen the dipolar attraction term was to design a microstructure with a core containing superparamagnetic α -Fe nanocrystals dispersed in a silica matrix, and a shell only containing silica that is ultimately responsible for screening the magnetic dipolar attraction (magnification in Figure 1).⁹ The absence of dipolar chains in Figure 1 suggests that this type of microstructure is adequate for screening dipole–dipole interactions between nanocomposites.³

The experimental method selected to build the microstructure displayed in Figure 1 was based on the subtle interplay controlling the formation of nanospherical silica particles by the ammonia base-catalyzed hydrolysis of tetraethoxysilane (TEOS) in water-in-oil (W/O) microemulsions.¹⁰ In this system, TEOS molecules, easily dissolved in the external oil phase, interact with water within the micellar aggregates to produce hydrolyzed species (Si–OH groups) that remain bound to the micelles due to their amphiphilic character. The formation of particles then occurs not only through polymerization of monomeric reactants into polymeric reacting species but also through interdroplet dynamic exchange. After reaching a critical size, surfactants deformations are improbable (interdroplet exchange is no longer possible), and the nuclei grow by adsorption of small monomeric or oligomeric species.

Therefore, to obtain the desired microstructure, it was necessary at first to favor interdroplet exchange of matter, that is, to favor homogeneous dispersion. Another factor to control was the solubility of the cationic species, which are the precursors of the final metallic particles, in the aqueous phase. High solubility at neutral or slightly acidic conditions allows us to prepare aqueous cationic

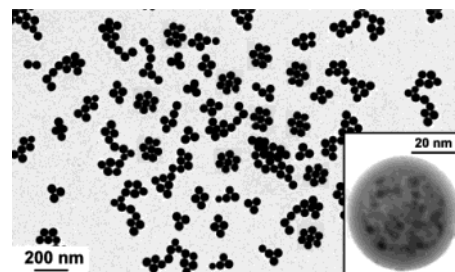


Figure 1. Typical TEM microstructure of Fe–silica nanocomposites showing also details of a single particle. According to TEM microanalyses, the outer shell is composed of silica. The dark spots correspond to the nanoparticles with an α -Fe metallic core.

solutions, avoiding a strong acidic pH that could favor gel-like structures.¹¹ Finally, we should bear in mind that even under conditions in which interdroplet exchange is favored, there is a critical size above which the exchange is not longer favorable, and thus a silica shell free of metallic precursor must grow naturally by adsorption of small monomeric or oligomeric species. To implement these conditions, we have selected nonionic surfactants instead of ionic surfactants because of their faster exchange rates.^{10d} Particularly, the nonionic surfactant Igepal CO-520 (polyoxyethylene(5) nonylphenyl ether) in heptane forms interconnected lamellar-like structures, which favor interdroplet exchange.^{10c} Interdroplet exchange is also favored for water concentrations close to the upper-phase boundary limit for the formation of microemulsions. For the surfactant concentration we have selected (0.2 M), the upper limit is about 0.8 M.^{10c} We have also used an Fe(II) precursor instead of an Fe(III) precursor because of its higher solubility. Details of the experimental conditions and methodology are described in ref 12.

Strategies to prepare metallic nanoparticles from microemulsions are mainly based on a two-step process that requires the use in a first step (when the metallic precursors in the form of cationic species are dissolved) of reducing agents, normally leading to microstructures consisting of a single metallic core surrounded by an outer shell.¹³ In particular, sodium borohydride was used for the production of Fe nanocrystals. However, this method leads to stable suspensions when the main component of the nanoparticles was an amorphous iron boron phase.^{13b} Meanwhile, when the main component was α -Fe, aggregation due to dipole–dipole interactions is observed.^{13c}

We have previously found that during the thermal reduction of iron oxide nanoparticles encapsulated in polydisperse silica particles (150 ± 100 nm) prepared by aerosol-assisted methods, an Fe_2SiO_4 layer surrounding the Fe metallic core is formed.¹⁴ This protective layer along with the thermal sealing of pores produced in the silica matrix are responsible for the high stability against corrosion of the metallic α -Fe nanocrystals. Thus, the powder obtained after the hydrolysis process carried out within the nanocavities of the

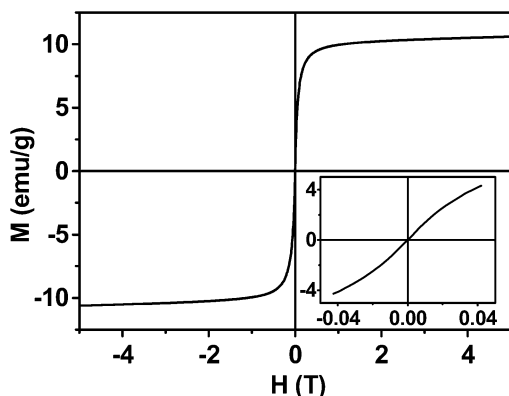


Figure 2. Magnetization curve of the nanocomposite. The inside plot is the low field part that clearly shows the absence of remanence.

reverse micelles was heated at 450 °C for 5 h in a H_2 (99.99%) atmosphere to produce α -Fe/silica nanospherical composites.

X-ray diffraction (XRD) (Supporting Information) only showed diffraction peaks associated with α -Fe. The crystallite size estimated from the FWHM of the reflection (110) was 4.9 nm, which is similar to the diameter estimated from TEM (Figure 1). XRD cannot discard the presence of other Fe-containing nanophases, which makes it essential to register the Mössbauer spectrum of this sample (Supporting Information). The spectrum consisted of a single line (superparamagnetic fraction) and a sextet (blocked fraction) with parameters associated with α -Fe and a doublet with an isomer shift of 1.08 $mm\ s^{-1}$ and a quadrupole splitting of 1.68 $mm\ s^{-1}$ that is associated with Fe(II) cations located in an environment similar to that of Fe_2SiO_4 .¹⁵ Assuming equal Debye–Waller factors, we could estimate the total content in phases to be about 6 wt % α -Fe, 17 wt % Fe_2SiO_4 , and 77 wt % SiO_2 . These results suggest that an Fe_2SiO_4 layer surrounding the α -Fe nanomagnets indeed exists.

Finally, we registered the hysteresis loop of the sample at room temperature to check for superparamagnetic behavior (Figure 2). The zero coercivity field (absence of remanence) indicates that the spherical nanocomposites are superparamagnetic. It is worthy of mention that the value of the saturation magnetization after keeping the sample in air for about 6 months remained almost invariant (change of less than 5%). Moreover, the first studies carried out in these particles indicate that indeed the surface can be functionalized following standard protocols. For example, using 3-aminopropyl-triethoxysilane, we have been able to obtain a surface enriched in amino groups.

In summary, we have developed a method to prepare monodisperse air-stable superparamagnetic Fe nanocrystals encapsulated in nanospherical silica particles that could be useful in biotechnology. A possible advantage of the method is its versatility, which could allow us to change particle size (both for nanomagnets and for the composite) and the spatial arrangement of the nanomagnets in the matrix. In this way, we are trying to extend this methodology to produce nanocomposites containing metallic nanoparticles encapsulated in inorganic matrixes of different size and nature.

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Supporting Information Available: X-ray diffraction and Mössbauer spectroscopy (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) For biomedical applications, it is important to have a hydrophilic surface. Thus, the use of methods based on the decomposition at high temperatures of iron precursors in the presence of organic surfactants (see for example: Hyeon, T.; Lee, S. S.; Park, J.; Chung, Y.; Na, H. *J. Am. Chem. Soc.* **2001**, *123*, 12798) is excluded because they produce highly hydrophobic surfaces.
- (9) Having this particular microstructure instead of the typical core–shell microstructure (a magnetic core surrounded by a silica shell) could be beneficial in some applications because we can have a similar load of magnetic material with a lower number of particles, that is, reduce the probability of collision between particles.
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- (11) This microemulsion method can be considered as a confined sol–gel method. Thus, spherical colloids are formed in ammonia-base-catalyzed conditions, while in acidic conditions we can expect gel-like structures.
- (12) We prepared a microemulsion at room temperature by the addition of the appropriate amount of a 2 M $FeCl_2$ deaerated aqueous solution set to a pH of 5.5 to a mixture containing the surfactant Igepal Co-520 (Aldrich) and heptane (Aldrich, 99%, dehydrated with molecular sieves). The resulting mixtures were shaken until becoming optically transparent, that is, until formation of the microemulsion. To this microemulsion, we first added TEOS (Aldrich, 99%) and then a second microemulsion with ammonium hydroxide (Fluka, 29%) under stirring. Given that we work at water concentrations close to the upper-phase boundary limit for microemulsion formation, and the content in water of the two microemulsions is different, we have distributed the content in heptane in such a way that we keep constant in both microemulsions the water and surfactant concentration. The system was stirred for about 7 days, and later the suspension was centrifuged at 10 000 rpm. The powder thus obtained was washed with CH_2Cl_2 several times and then with $EtOH/H_2O$ five times, further refluxed at 70 °C in $EtOH$ under constant stirring for 24 h, and finally dried. The microemulsion reactant concentrations were 0.2 M Igepal CO-520, 0.05 M TEOS, 0.01 M $FeCl_2$, 0.14 M NH_3 , and 0.6 M water. Our criterion to obtain these conditions was to set the surfactant concentration to a value of 0.2 M and the concentration of water to a value of 0.6 M (close to the upper-phase boundary limit of 0.8 M). We then found the concentration of TEOS, thus of $FeCl_2$ (Fe/Si molar ratio set to 0.2), based on values described in ref 10 to obtain monodisperse nanospherical silica particles.
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