

## Facile synthesis of capped $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles

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**Abstract** Facile methods for the selective preparation of capped iron oxide nanoparticles ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) are described. The magnetic oxides are obtained via oxidative transformation of an iron hydroxide gel using H<sub>2</sub>O<sub>2</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solutions as oxidants. Capping with oleic or other aliphatic acids is established simultaneously in one step by adding a toluene solution of the capping agent and refluxing the resulting biphasic system. The method is simple, soft and affords nanoparticles of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> of controlled size depending on the reaction conditions. The capped nanoparticles are readily soluble in organic or aqueous media according to the nature of the sheath surrounding the surface of the particles, providing stable and high concentration ferrofluids.

### Introduction

The magnetic iron oxides, magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), define a strategic class of chemically stable materials exhibiting numerous and important industrial, technological and environmental applications [1]. Processes related to the surface functionalization of such magnetic nanoparticles in order to become soluble in organic or aqueous media are of prime importance since their solubilization gives access to ferrofluids and related technologies [2], including films formation and self-assembled

nanocrystals [3]. In particular the wide application of ferrofluids in a variety of biomedical applications [4–8], renders the in-situ formation of magnetic iron oxide nanoparticles with their surface coated with polymers or individual chemical entities an emerging and attractive research topic [5–10]. Two main objectives are: (i) to design and develop simple and reproducible methods leading to functionalized nanoparticles that are easily soluble in a carrier liquid at high concentrations, and (ii) to enable the control of the surface environment of the particles with a wide range of simple or complex molecules in order to attain valuable derivatives that combine the magnetic properties of the inorganic support with the chemical functionalities of a particular modifier [11, 12]. Nevertheless, the synthetic methods developed so far employ either complex entities as surface modifiers [5] or drastic, and in some cases time consuming, solvothermal conditions, e.g. reaction temperatures above 200 °C under an inert atmosphere [6–10]. In the present work we report softer and simpler routes for the rapid and selective synthesis of organophilic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles readily soluble in high concentration in polar organic solvents.

The method for producing the capped magnetic iron oxides relies on treating an iron(II) hydroxide gel with H<sub>2</sub>O<sub>2</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in strongly alkaline environment in presence of an aliphatic acid as coating agent and under biphasic conditions. A somehow similar procedure has been applied for the synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles embedded in ion-exchange resins [13]. The method is simple and reproducible yielding stable and high concentration organo- or aqueous-based ferrofluids according to the organophilic or hydrophilic nature of the capping agent. Furthermore, the method allows for particle size control according to the reaction conditions. The materials were

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extensively characterized and identified by XRD, FT-IR, TGA, Mössbauer, magnetic and TEM measurements.

## Experimental

### Materials

Oleic acid (60%) and H<sub>2</sub>O<sub>2</sub> solution (30%) were purchased from Panreac. Concentrated NH<sub>3</sub> solution (25%) and (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O were from Merck. The chemicals KOH, FeSO<sub>4</sub>·7H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were purchased from Riedel-deHaën. The silanes (CH<sub>3</sub>O)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl and carboxyethylsilanetriol (25% in water, sodium salt) were provided by Gelest. Caprylic acid, lauryl acid, betaine, glycolate and glycolic acid ethoxylate lauryl ether [C<sub>12</sub>H<sub>25</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>OCH<sub>2</sub>COOH] were bought from Aldrich.

### Capped $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>

In a typical preparation, 7 mL of NH<sub>3</sub> (25%) were added to a magnetically stirred solution of 5 g of FeSO<sub>4</sub>·7H<sub>2</sub>O in 60 mL of de-ionized water followed by 0.5 mL of H<sub>2</sub>O<sub>2</sub> aqueous solution (30%) and by 100 mL of toluene containing 8 mL of oleic acid (60%). The resulting biphasic system was refluxed for 45 min. The temperature at reflux was measured at 95 °C. After reaction accomplishment, the deep brown organic layer was separated and poured slowly into 50 mL of acetone or ethanol, both serving to precipitate the organophilic particles. The precipitate was centrifuged, washed well with acetone and finally air dried to afford a strongly magnetic organosoluble solid with the stoichiometry ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)<sub>10.27</sub>(C<sub>18</sub>H<sub>33</sub>O<sub>2</sub>), according to TGA (15% w/w organic content). Color: brownish; Yield: 0.8 g capped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

### Capped Fe<sub>3</sub>O<sub>4</sub>

To a solution of 2 g (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 50 mL of de-ionized water were added 1.14 g of KOH in 20 mL of H<sub>2</sub>O followed by the dropwise addition of 0.38 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 10 mL of H<sub>2</sub>O. Subsequently, 1.5 mL of oleic acid in 30 mL of toluene was added and the mixture heated at reflux for 30 min (95 °C). After cooling the reaction mixture, the organic phase was separated and poured slowly into 50 mL of acetone. The precipitate was separated by centrifugation, washed with acetone and air dried to afford a strongly magnetic organosoluble solid with the stoichiometry (Fe<sub>3</sub>O<sub>4</sub>)<sub>3.65</sub>(C<sub>18</sub>H<sub>33</sub>O<sub>2</sub>), according to TGA (25% w/w organic content). Color: black; Yield: 0.8 g capped Fe<sub>3</sub>O<sub>4</sub>.

### Ligand exchange reactions

For the betaine-based magnetic derivative, 100 mg of capped magnetic iron oxide were dispersed in 10 mL of ethanol containing dissolved 150 mg of betaine hydrochloride. The mixture was stirred for 24 h at room temperature and then centrifuged, washed with ethanol and dried. The resulting solid is easily dispersible in water affording clear hydrosols of high concentration.

For the silane-based derivative, 100 mg of capped magnetic iron oxide were dispersed in 10 mL of ethanol containing dissolved 0.5 mL carboxyethylsilanetriol (25% in water, sodium salt). Similarly as above, the mixture was stirred for 24 h at room temperature and then centrifuged and washed with ethanol to afford the corresponding derivative as a highly hydrophilic solid (dispersible in high concentrations in water).

### Analytical methods

X-ray powder diffraction (XRD) patterns were taken on a D-500 Siemens diffractometer using CuK <sub>$\alpha$</sub>  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. TGA measurements were obtained on a Seiko Instruments TG/DTA 320 model analyzer. The samples were measured against an alumina standard under N<sub>2</sub> flow with a temperature ramp of 20 °C/min to 500 °C. Magnetic measurements were carried out at room temperature with a VSM magnetometer. Mössbauer spectra were recorded with a constant acceleration spectrometer with a 50 mCi <sup>57</sup>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 toluene solution of each powder (0.1% w/v) was placed on a copper grid surface and dried before analysis.

## Results and discussion

### General comments

The oxidative transformation of ferrous hydroxide gels to Fe<sub>3</sub>O<sub>4</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is known in the iron chemistry. For instance, the hydroxide is oxidized by KNO<sub>3</sub> in neutral or basic solutions to give magnetite [14], while Fe<sup>2+</sup> incorporated to an ion-exchange resin [13] or to cellular fibers [15] are oxidized by H<sub>2</sub>O<sub>2</sub> in strong alkaline environment to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

In the present work we have studied the oxidation in presence of aliphatic carboxylic acids (caprylic, oleic) that bind covalently through their  $-\text{COOH}$  group the iron surface atoms thus producing uniformly dispersed and stable ferrofluids. Hydrogen peroxide or ammonium persulfate were used as oxidants, the latter being preferred because of its stability and easiness in handling. The results of many experimental trials established that: (i) biphasic conditions are necessary for the generation of organophilic  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$ ; all attempts to carry out the transformation in a single phase were proved unsuccessful. Specifically, in absence of the organic phase the reaction resulted in magnetic nanoparticles that were not dispersible in organic solvents, thus implying an even smaller organic content. Therefore, it seems that the organic phase protects the capped nanoparticles from the detrimental action of the strongly alkaline aqueous environment towards detachment of the surface modifier, (ii) determining factor for developing the magnetite or maghemite phase is the base used in the reaction; magnetite is produced in presence of  $\text{KOH}$ , whereas maghemite only in excess of  $\text{NH}_3$ .

#### Capped $\gamma\text{-Fe}_2\text{O}_3$

Upon addition of the oxidant the  $\text{Fe}(\text{OH})_2$  turns black and then, through the intervention of the capping agent, the partially oxidized hydroxide is instantly transferred to the organic layer where dehydration and condensation reactions give the corresponding capped magnetic nanocrystals. Oleic acid can be equally replaced by caprylic, lauryl, ethoxylate lauryl ether [ $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OCH}_2\text{COOH}$ ] or other long chain carboxylic acids resulting in nanocrystals of comparable particle size. As a result of the organophilic sheath around the particle surface, the fresh-prepared magnetic solid is readily soluble (50 mg/ml) in

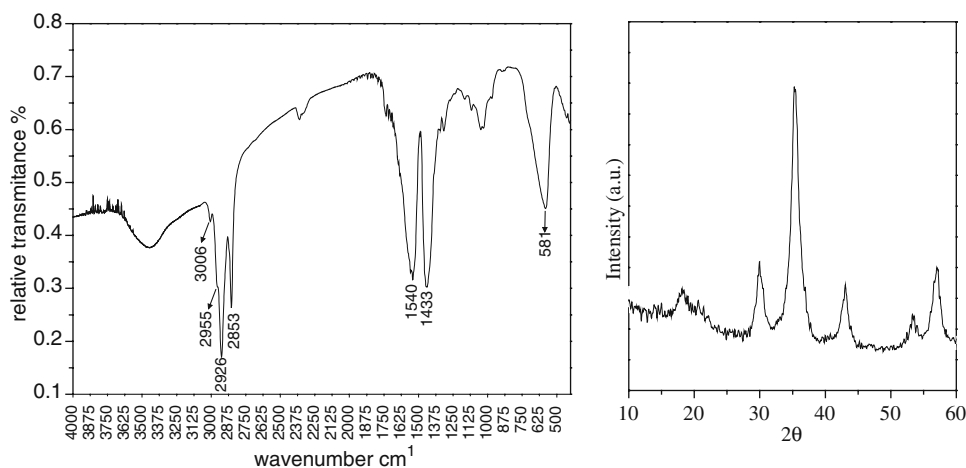
chloroform, tetrahydrofuran and toluene affording stable dark brown organosols (stable for at least 2 months).

A two-fold concentration of reactants afforded an insoluble magnetic powder, most likely due to detachment of the capping agent from the surface under the more severe alkaline conditions (base in double concentration). On the other hand, half concentration reactants lead to highly organosoluble maghemite nanoparticles with 6-nm average diameter as evidenced by the corresponding X-ray line broadening. We have also examined whether the nature of the organic solvent affects particle size. As expected, organic solvents such as xylene (bp:  $140^\circ\text{C}$ ) and mesitylene (bp:  $160^\circ\text{C}$ ) had no effect on the refluxing temperature of the biphasic system (almost equal to the boiling point of water) and in turn on particle size. In contrast, when benzene is the organic layer the refluxing temperature (almost equal to the boiling point of benzene, i.e.,  $80^\circ\text{C}$ ) is lower than that of the toluene biphasic system and so the particle size (6 nm).

The IR spectrum of the oleic acid capped magnetic nanoparticles in Fig. 1, left, shows a weak band at  $3006\text{ cm}^{-1}$  characteristic of the *cis*- $\text{HC}=\text{CH}$  arrangement in oleic acid, intense absorptions at  $2955\text{ cm}^{-1}$ ,  $2926\text{ cm}^{-1}$ ,  $2853\text{ cm}^{-1}$  ascribed to  $-\text{CH}_2-$  and  $-\text{CH}_3$  aliphatic groups and absorptions at  $1540\text{ cm}^{-1}$ ,  $1433\text{ cm}^{-1}$  from  $-\text{COO}^-$  stretching vibrations. The presence of both antisymmetric and symmetric carboxylate vibrations and their separation of  $110\text{ cm}^{-1}$  suggest a bridging configuration of the  $-\text{COO}^-$  groups [16]. The peak at  $580\text{ cm}^{-1}$  indicates the formation of iron oxide network. These bands clearly demonstrate covalent bridging of the oleate groups to the iron oxide surface. Similar vibrations, except that at  $580\text{ cm}^{-1}$ , were recorded in the spectrum of barium oleate complex.

Figure 1, right, presents the XRD pattern of the capped nanoparticles revealing a spinel type structure and a mean

**Fig. 1** IR spectrum (left) and XRD pattern (right) of the capped  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles



size for the core particles of 8 nm according to the Scherrer equation. Analytically, the Scherrer equation is given by:

$$d = k \times \lambda / B_{hkl} \times \cos \theta$$

where  $d$  is the mean diameter in Å,  $k$  a unit-less constant equal to 0.9,  $\lambda$  the wavelength of  $\text{CuK}_{\alpha 1}$  equal to 1.54 Å,  $B_{hkl}$  the full width at half maximum of an individual peak and  $\theta$  the peak position. In our case, the particle size was calculated by the most intense 311 reflection centered at  $2\theta = 35.5^\circ$  with  $B_{311} = 3.14/180$  rad.

Since the XRD technique cannot witness the formation of  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  (both having spinel type structure) the nature of the magnetic solid was unveiled by Mössbauer spectroscopy. The spectrum at 78 K (Fig. 2, left) displays full magnetic hyperfine structure exhibiting zero quadruple interaction, isomer shift of  $0.44 \text{ mm s}^{-1}$  and hyperfine magnetic field of 490 kOe. These values are indicative of  $\gamma\text{-Fe}_2\text{O}_3$  [1a]. The variable temperature spectra demonstrate clearly the superparamagnetic nature of the capped  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles from the gradual growth of the magnetic sextet at the expense of the paramagnetic doublet as temperature reduces. Furthermore, the magnetization versus

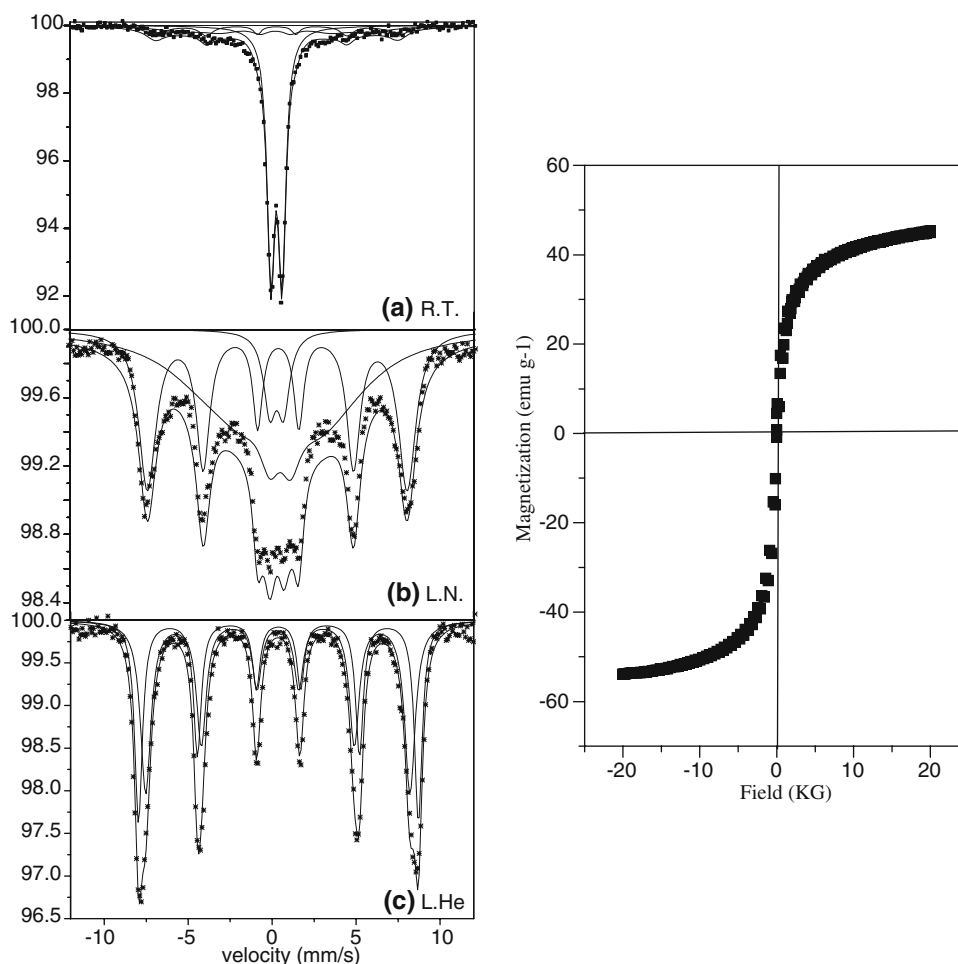
applied field curve of the sample at room temperature (Fig. 2, right) is typical of super paramagnetic particles exhibiting zero values of coercivity and remanence magnetization above their blocking temperature, with saturation magnetization of  $M_s = 40 \text{ emu g}^{-1}$  (extracted by fitting the data with the Langevin function). By a simple conversion-based on the TGA-derived inorganic content (85% w/w), we find a magnetization value of 40 emu per 0.85 g of net maghemite or 47 emu per gram of net maghemite, a value that corresponds well to the particle size [17].

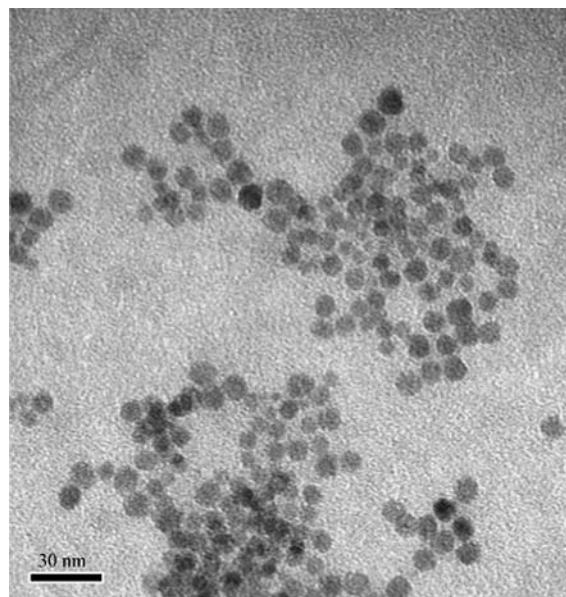
Figure 3 depicts the TEM micrograph of the organophilic  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles derived after drying a 0.1% w/v colloidal solution in toluene. The morphology of the magnetic nanoparticles is spherical with an average diameter near to 8 nm (in agreement with the XRD results) and a good size distribution.

### Capped $\text{Fe}_3\text{O}_4$

The iron(II) salt  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  or  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in water and by adding KOH the as-formed slurry became strongly alkaline. Addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,

**Fig. 2** Left part: Mössbauer spectra at R.T. (a), L.N. (b) and L.He (c) temperature. Right part: magnetization versus applied field curve at room temperature of the organophilic magnetic solid





**Fig. 3** TEM image of the capped  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles

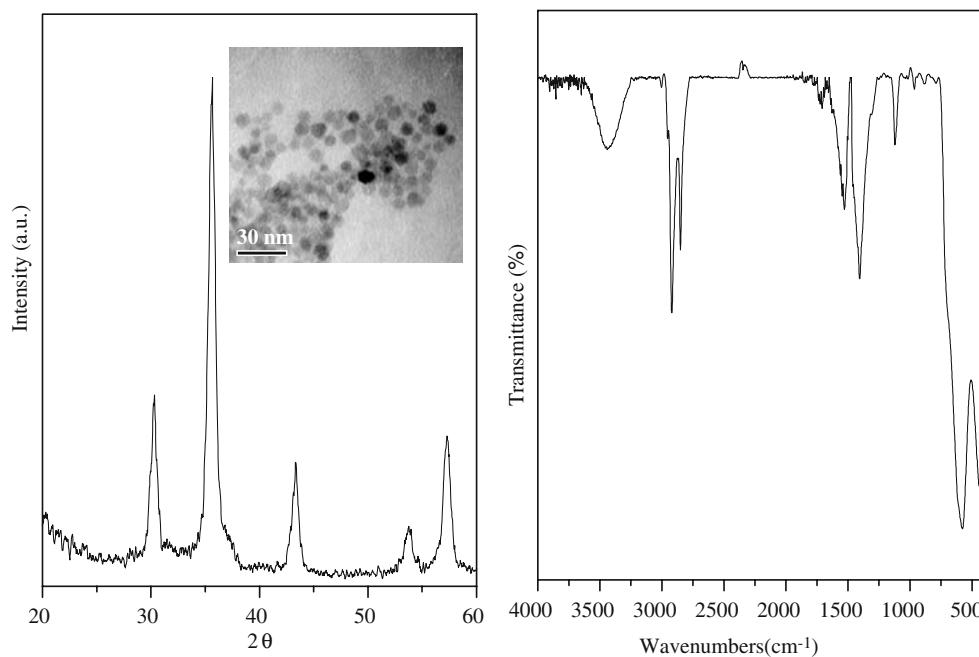
used as oxidant, turned the mixture black. Then, oleic acid in toluene was immediately added to the reaction mixture and upon heating the capped magnetic nanoparticles migrated to the organic phase. The capped magnetite nanoparticles were isolated by precipitation in acetone and washed. The magnetic solid is highly soluble in toluene, chloroform and tetrahydrofuran giving stable organosols without sign of precipitation after 2 months.

Similarly to the maghemite case, the ferrous hydroxide gel first decomposes to Fe<sub>3</sub>O<sub>4</sub> by partial oxidation with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and then remains stable against oxidation to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Although it is not clear the mechanism of magnetite stabilization [5](b), it is possible that intermediate radicals derived from (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in addition to pH have a main contribution. It is worth to note that addition of the oleic acid toluene solution after a 30 min aqueous reflux pretreatment, which allows the magnetic nanoparticles to grow before capping, produced organosoluble magnetite nanocrystals of higher dimension (i.e. 12 nm vs. 8 nm). Therefore, the method demonstrates another alternative way to control particle size.

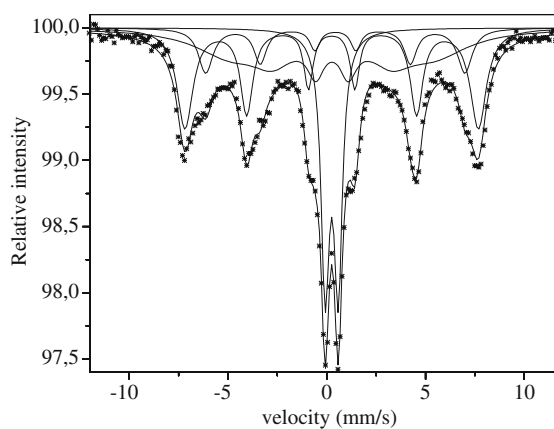
The XRD pattern of the magnetic solid is characteristic of spinel type iron oxide with a mean diameter of 8 nm (recall that both  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> have identical XRD patterns due to their common spinel type structure). This size was also confirmed by TEM analysis. The presence of the capping agent grafted to the surface of the nanoparticles and the iron oxide formation were evidenced by IR absorptions similar to those of the maghemite analogue. The corresponding XRD, TEM (inset) and IR data are shown in Fig. 4. Lastly, the solid is strongly magnetic with  $M_s = 42 \text{ emu g}^{-1}$  or 56 emu per gram of net magnetite at room temperature (TGA inorganic content: 75% w/w). Once again, the value agrees well with particle size [17].

The Mössbauer analysis of the prepared capped magnetic solid revealed the presence of divalent iron cations and therefore formation of magnetite [18]. The spectrum at 140 K (Fig. 5) was fitted with four sites: two magnetic

**Fig. 4** XRD pattern (left) and IR spectrum (right) of the capped Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The inset presents the TEM image of the nanoparticles



**Fig. 5** Mössbauer spectrum and parameters at 140 K of the organophilic magnetite



	$\delta$	$H$	$DH$	$\Gamma/2$	$U$	$P$
(sextet) $\text{Fe}^{+3}$	0.36	463	16	0.23	0	28.5
(sextet) $(\text{Fe}^{+2})_{\text{Oh}}$	0.54	409	10	0.28	0	22
$\text{Fe}^{+3}$	0.37	324	119	0.21	0	26.5
Superpara. $\text{Fe}^{+2}$	0.43	0	0	0.25	0.33	23.0

sextets, one super-paramagnetic doublet and another poorly resolved magnetic sextet. The first magnetic sextet with isomer shift at  $0.36 \text{ mm s}^{-1}$  corresponds to ferric cations in the magnetite lattice. The second magnetic sextet with isomer shift  $0.54 \text{ mm s}^{-1}$  corresponds to the divalent iron cations in the octahedral sites. This value is lower than the theoretically expected for ferrous cations because of the electron hopping that occurs between  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  cations in the octahedral sites and because of the non-stoichiometric composition of the particular magnetite product. The third component depicts a weak hyperfine field interaction and a very large hyperfine field distribution (DH). The characteristics of this component and of the superparamagnetic doublet can be correlated with the size distribution of the particles and with relaxation phenomena that appear when size is constricted to the nanometer scale. Particularly, larger particles give rise to the well resolved magnetic sextets (sites I and II) while particles of intermediate and very small size correspond to the poorly resolved magnetic sextet (site III) and to the superparamagnetic doublet (site IV), respectively.

#### Exchange reactions of capping agents

An interesting aspect of the present work refers to ligand exchange reactions between the oleate units of the capped  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles with other multifunctional carboxylic compounds, as has been described elsewhere for analogous systems [11]. These exchange reactions allow the easy control of the surface environment of the particles

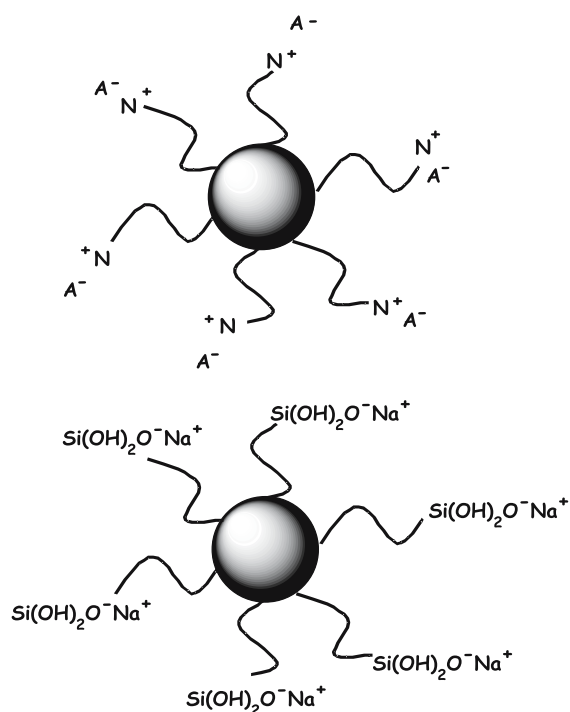
and thus of their properties. For instance, replacement of the oleate units by  $\text{Cl}^-(\text{CH}_3)_3\text{NCH}_2\text{COO}^-$  (chloride salt of betaine) or  $\text{HOCH}_2\text{COO}^-$  (glycolate) affords hydrophilic magnetic derivatives, readily soluble in high quantities in water. Furthermore, the quaternary ammonium type structure of betaine delivers anion-exchange properties to this ferrofluid [11].

Similarly, replacement of the oleate ligand by the silane  $\text{NaO}(\text{OH})_2\text{SiCH}_2\text{CH}_2\text{COONa}$  (carboxyethylsilanetriol, sodium salt) results in a magnetic derivative that forms stable hydrosols of high concentration (stable for at least 3 weeks). In this case, the carboxylate tip of the silane is attached to the iron oxide surface thus leaving the hydrophilic silanetriol group exposed. Covalent grafting of the silane via the silanetriol group onto the iron oxide surface is another alternative, however, the following facts exclude such a grafting mode. First, the sol dried at  $100^\circ\text{C}$  is not re-dispersible in water thus signaling formation of Si–O–Si bridges (also evident by IR) among neighboring particles. Second, the silane group is exchangeable by other carboxylate ligands, as for instance, by sodium palmitate which leads to an aqueous precipitate after exchange. Therefore, it seems that the affinity of the iron centers towards the carboxylate group is higher than that towards the formation of Si–O–Fe bonds.

Such a silanization process is valuable since enables the formation of multifunctional magnetic derivatives. For instance, the magnetic nanoparticles can simply adhere on substrates through covalent bonding between the substrate and the silanetriol moieties. Condensation reactions in the

outer shell with other functional silanes are expected to give a variety of core/shell nanostructures. Characteristically, addition of  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  leads to grafting and peptization of the sol. Besides this functionality, the sodium silicate type structure of the silane endows the functionalized nanoparticles with cation-exchange properties, e.g. they precipitate upon addition of quaternary ammonium surfactants, dye cations (methylene blue) and viologen derivatives.

Finally, exchange reactions with carboxylate polymers like polyacrylate and carboxymethylcellulose afford the corresponding polymer nanocomposites that, however, are not dispersible in organic or aqueous media. Figure 6 shows a proposed schematic for the betaine- and silane-based magnetic derivatives.



**Fig. 6** Schematic of the betaine- and silane-based magnetic derivatives (the carboxylate tips are attached on the surface via coordination with local iron centers)

## Conclusions

One step treatment of an iron hydroxide gel with either  $\text{H}_2\text{O}_2$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in alkaline environment and in

presence of a capping agent under biphasic conditions leads to the selective synthesis of organophilic  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ , respectively. The capped magnetic nanoparticles are highly soluble in organic solvents thus providing stable ferrofluids. Hydrophilic and other derivatives are easily obtained by ligand exchange reactions with suitable carboxylate molecules. The method is simple, soft and enables for particle size tailoring of the corresponding magnetic phases.

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