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Surface Modification of Ultrafine Magnetic Iron Oxide Particles

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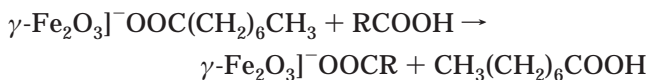
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Nanocrystalline magnetic iron oxide particles (γ -Fe₂O₃ and Fe₃O₄) have attracted an increasing interest in the fields of nanoscience and nanotechnology because of the unique and novel physicochemical properties that can be attained according to their particle size (quantum size effect), shape morphology (spherical or rodlike), and engineering form (films/self-assembled nanocrystals and ferrofluids).^{1–4} In addition, considerable efforts have been devoted to line the surfaces of such magnetic particles with polymeric or inorganic substances in order to receive composite materials with improved properties.⁵ However, in the literature only limited work has been reported for the effective surface modification of magnetic iron oxidic nanoparticles with individual chemical entities that would enable one to combine the magnetic properties of the inorganic support with the chemical functionalities of the particular modifier.^{6–9} For instance, coprecipitation and postsynthetic methods usually fail at this aim because grafting of the modifier onto the particle surfaces is seriously inhibited either by the strong alkaline conditions applied during the synthesis (coprecipitation method) or by the strong aggregated state of the magnetic particles in conjunction with the presence of a small number of defect sites onto their surfaces (postsynthetic method). Recently, we have developed a novel approach for preparing ultrafine γ -Fe₂O₃ particles efficiently capped with caprylate units (C₇H₁₅COO[−]).⁹ More specifically, thermal treatment of a hydrated iron(III) hydroxide caprylate, readily obtained by alkaline coprecipitation of an iron(III) source and caprylic acid in an ethanol solution, in boiling tetraline, and under an inert atmosphere, affords uniform-sized spherical γ -Fe₂O₃ nanoparticles (mean size: 40 Å) that are readily soluble in high quantities in organic solvents, as a result of the organophilic mantle around the particle surfaces. In the present communication, we describe a general and soft route for the surface

modification of magnetic iron oxide particles based on ligand exchange reactions¹⁰ between the caprylate units of the capped γ -Fe₂O₃ particles and multifunctional carboxylic compounds through their carboxylate units, according to the reaction scheme



where γ -Fe₂O₃] denotes the surface of γ -Fe₂O₃ particles and R denotes the part of the inserted modifier that carries specific functionalities. The method has the advantage of easy control of the chemical environment over the particle surfaces and, in turn, of the particle properties.^{10,11} As examples, we present here the modification of γ -Fe₂O₃ nanocrystals using betaine·HCl [**Cl**[−](**H**₃**C**)₃**NCH**₂**COOH**], a molecule of high biological and agricultural importance, and 2,5-dihydroxybenzoic acid [**HOOCC**₆**H**₃(**OH**)₂], an electron-rich aromatic compound, as the starting materials (the bold part of each molecule indicates the R group in the RCOOH ligand).

For the betaine derivative, 100 mg of capped γ -Fe₂O₃ powder (FeOC8)⁹ was dispersed in 10 mL of ethanol containing 150 mg of betaine·HCl, and the mixture was stirred at room temperature for 24 h. The dispersed solid was centrifuged and washed with ethanol to afford after drying a magnetic powder (FeOBET), as indicated by its strong attraction by a permanent magnet, readily soluble at a high concentration in water. For the 2,5-dihydroxybenzoate derivative (FeODHB), 100 mg of FeOC8 was dispersed in 10 mL of ethanol containing 150 mg of **HOOCC**₆**H**₃(**OH**)₂, and the mixture was sonicated for 2 h in an ultrasound bath. The solid was centrifuged and washed with ethanol and acetone to afford after drying a magnetic powder (FeODHB), which was not soluble in organic or aqueous media. The particular solids, after modification, retained the typical for a γ -Fe₂O₃ crystallinity (spinel type) as evidenced from XRD measurements (inset photo, Figure 1).

The exchange reactions were probed by Fourier transform infrared (FT-IR) spectroscopy. In Figure 1 the FT-IR spectra of samples FeOC8 (a), FeOBET (b), and FeODHB (c) are presented. The parent FeOC8 sample exhibits absorptions in three characteristic regions: (i) below 3000 cm^{−1}, associated with vibrations of the **−CH**₃ and **−CH**₂ groups present in the caprylate aliphatic chain, (ii) between 1600 and 1400 cm^{−1}, related to the presence of coordinated **−COO**[−] groups, and (iii) at 600 and 460 cm^{−1}, indicative of a rigid γ iron oxide network.^{12,13} After modification with the capping agents, the bands pertinent to the inorganic support remain unchanged, whereas we discern a considerable decrease in the aliphatic absorption bands of the caprylate units and the appearance of new absorptions in the region

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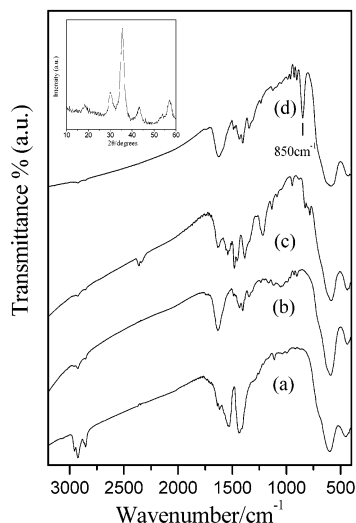


Figure 1. FT-IR spectra of samples FeOC8 (a), FeOBET (b), FeODHB (c), and FeOBET after treatment with PF_6^- ions (d) (the inset XRD photo shows the typical for a $\gamma\text{-Fe}_2\text{O}_3$ crystallinity for all corresponding samples).

$1600\text{--}800\text{ cm}^{-1}$ ascribed to the betaine and hydroxybenzoate molecules. These results clearly demonstrate the displacement of the caprylate units in the parent FeOC8 material by the inserted ligands through their carboxylate groups. When FeOC8 was treated with ethyl acetate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$), a ligand in which the chelation ability of the carboxylic group is absent, the IR bands of the caprylate units remained untouched in intensity and position after the treatment. Note also that postsynthetic treatment of pure $\gamma\text{-Fe}_2\text{O}_3$ particles (40 Å in size, obtained by thermal treatment in tetraline of an iron hydroxide gel) with the particular capping agents does not bring any changes to the surface environment of the particles as evidenced by IR spectroscopy.

As mentioned above, the FeOC8 composite has organophilic properties and therefore can be easily dissolved in high quantities in organic solvents to afford magnetic organosols (stable for more than 6 months). On the contrary, the FeOBET derivative is strongly hydrophilic and thus readily dissolves in high quantities in water to afford stable magnetic hydrosols (stable for ~ 2 months). This behavior is a representative example showing how the particular surface environment affects the properties of magnetic particles, for instance, their solubility. Figure 2 presents the transmission electron microscopy (TEM) micrograph of ultrafine, hydrophilic $\gamma\text{-Fe}_2\text{O}_3$ particles derived after drying of an FeOBET aqueous colloidal solution (0.2% w/v). The size of the spherical particles varies between 30 and 80 Å with an average of ~ 40 Å. The FeOBET derivative, on account of the quaternary ammonium-type structure of the betaine ligand, is also endowed with anion-exchange properties. In this frame, treatment of FeOBET with $(n\text{-Pr})_4\text{N}^+\text{PF}_6^-$ leads to exchange reactions between the pristine chloride ions and the corresponding PF_6^- ions, without affecting the betaine ligand. The particular insertion was evidenced by IR spectroscopy from the presence of an absorption band at 850 cm^{-1} characteristic of the PF_6^- group (Figure 1d). Silver chloride analysis of the FeOBET solid gave an anion-exchange capacity (AEC) in the chloride form of 0.9 mequiv g^{-1} .

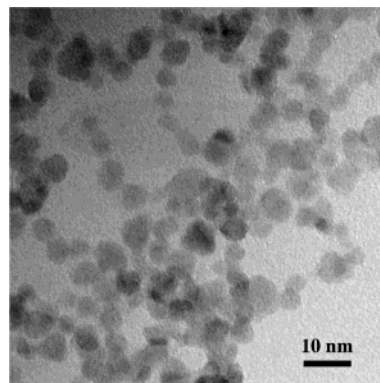


Figure 2. TEM micrograph of the hydrophilic FeOBET derivative after water evaporation.

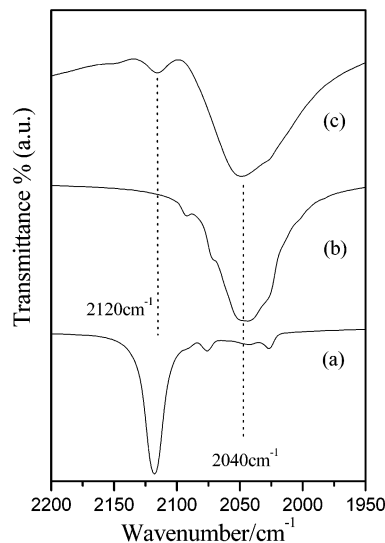


Figure 3. IR spectra of (a) $\text{K}_3[\text{Fe}(\text{CN})_6]$, (b) $\text{K}_2[\text{Fe}(\text{CN})_6]$, and (c) FeOBET after the exchange reaction with $\text{K}_3\text{Fe}(\text{CN})_6$.

Another interesting observation concerns the effect of the inorganic support on the electronic state of a redox-active guest anionic species, e.g., $\text{Fe}(\text{CN})_6^{3-}$. In particular, treatment of the FeOBET solid with $\text{K}_3\text{Fe}(\text{CN})_6$ leads not only to a nondestructive displacement of the chloride ions by the corresponding $\text{Fe}(\text{CN})_6^{3-}$ but also to reduction of the latter to hexacyanoferrate $\text{Fe}(\text{CN})_6^{4-}$. Analogous redox behavior has been reported for hydrocalcite-like materials (layered solids possessing anion-exchange properties) exchanged with $\text{Fe}(\text{CN})_6^{3-}$ ions.¹⁴ The reduction of the inserted ferric cyanide ions was confirmed by IR spectroscopy because the cyanide stretching vibration is sensitive to the iron oxidation state in the complex (Figure 3). The $\text{K}_3\text{Fe}(\text{CN})_6$ salt exhibits a strong absorption band at $\sim 2120\text{ cm}^{-1}$, which, after exchange with the FeOBET solid, is almost suppressed, and a new band at $\sim 2040\text{ cm}^{-1}$, attributed to the formation of $\text{Fe}(\text{CN})_6^{4-}$ species, appears.¹⁴ Thus, the magnetic betaine derivative reflects a system with interesting host–guest properties. On the other hand, the magnetic FeODHB derivative inherits some of the recognition properties of its electron-rich aromatic ligand. Treatment of FeODHB with ethyl viologen dibromide, a bipyridinium quaternary salt, leads to

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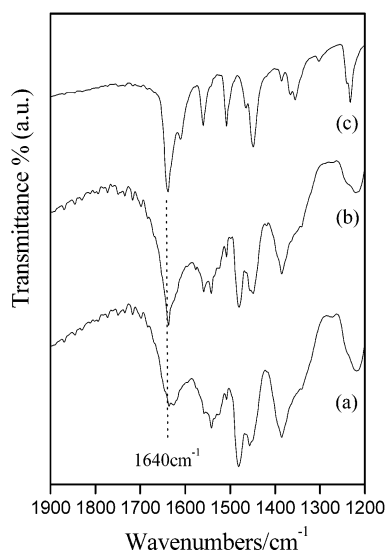


Figure 4. IR spectra of (a) FeODHB, (b) FeODHB after treatment with ethyl viologen, and (c) ethyl viologen dibromide.

binding of the latter onto the particle surfaces, probably through π - π charge-transfer interactions between the electron-deficient bipyridinium moiety (π acceptor) and the electron-rich hydroxybenzoate ligand (π donor) (see graphical abstract).¹⁵ Indeed, the addition of a small amount of 2,5-hydroxybenzoic acid (white crystals) in a diluted aqueous solution of ethyl viologen dibromide

(colorless) gives instantly a deep orange coloration, characteristic of a charge-transfer complex formation.¹⁵ In our case, the recognition of the ethyl viologen by the FeODHB solid was evidenced by the appearance of a strong, sharp absorption band at 1640 cm^{-1} in the treated solid, ascribed to the ethyl viologen compound and in particular to its aromatic constituent (Figure 4). Notice that, in all instances, neither PF_6^- and $\text{Fe}(\text{CN})_6^{3-}$ ions nor ethyl viologen dibromide themselves are directly bound to the surfaces of the $\gamma\text{-Fe}_2\text{O}_3$ particles as evidenced by blank experiments.

These examples demonstrate the wide potentiality of the exchange route to produce valuable magnetic derivatives with interesting host-guest and recognition properties. More than 20 capping agents, including amino acids (arginine, lysine, and ω -aminocaproic acid), substituted carboxylic compounds (imine, hydroxy, and halogen derivatives), carboxylic carbohydrates (gluconic acid), and most interestingly carboxylated fullerenes, were successfully employed to modify the particle surfaces of the magnetic nanocrystals. However, because of the complexity of the inserted ligands in their large majority, e.g., the presence of additional chelating sites such as amine, imine, halogen, and hydroxy groups in the framework, it was difficult to predict the exact way of coordination of these ligands to the particle surfaces. Nevertheless, these results, to be published shortly, show the versatility of surface $\gamma\text{-Fe}_2\text{O}_3$ modifications with simple or complex molecules of high interest.

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