Thermal Route for the Synthesis of Maghemite/Hematite Core/Shell Nanowires

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Abstract

Nowadays, iron oxide-based nanostructures are key materials in many technological areas. Their physical and chemical properties can be tailored by tuning the morphology. In particular, the possibility of increasing the specific surface area has turned iron oxide nanowires (NWs) into promising functional materials in many applications. Among the different possible iron oxide NWs that can be fabricated, maghemite/hematite iron oxide core/shell have particular importance since they combine the magnetism of the inner maghemite core with the interesting properties of hematite in different technological fields ranging from green energy to biomedical applications. However, the study of these iron oxide structures is normally difficult due to the structural and chemical similarities between both iron oxide polymorphs. In this work we propose a route for the synthesis of maghemite/hematite NWs based on the thermal oxidation of previously electrodeposited iron NWs. A detailed spectroscopic analysis based on Raman, Mössbauer and X-ray absorption shows that the ratio of both oxides can be controlled during fabrication. Transmission Electron Microscopy has been used to check the core/shell structure of the NWs. The biocompatibility and capability of internalization of these NWs have also been proven to show the potential of these NWs in biomedical applications.

Introduction

The physical and chemical properties of iron oxides can be tailored by tuning stoichiometry and morphology, making them promising functional materials for many applications. In particular, the large specific surface of iron oxide nanowires (NWs) can be exploited in energy applications, as anode material for lithium-ion batteries\(^1\) or as photo electrode for water splitting,\(^2\) or in gas sensing.\(^3\) Biomedical applications take also advantage of the elongated geometry and the magnetic response of iron oxide NWs to external magnetic fields, together with the recent studies that do not show any additional toxicity related to the
In fact, they have already shown their potentiality in axonal and cells guidance\textsuperscript{6,7} and hyperthermia treatments\textsuperscript{8,9} among other applications. Spin-dependent transport measurements carried out in iron-oxide NWs\textsuperscript{10,11} have also shown the potentiality of these nanomaterials in Spintronics. Template-assisted electrodeposition is one of the most suitable techniques for the controlled growth of NWs.\textsuperscript{12} This fabrication route allows independent control of morphological parameters such as length and diameter. However, although extensively used for the synthesis of metallic NWs, it has been scarcely used for the synthesis of iron oxides,\textsuperscript{13} probably due to the inherent difficulties in the electrodeposition of oxides.\textsuperscript{14,15} A possible option is the combination of electrodeposition and thermal annealing, which has been already used to produce iron oxide NWs\textsuperscript{16} as well as iron-iron oxide core-shell NWs.\textsuperscript{17,18} In fact, core-shell nanostructures are quite interesting structures since they combine properties of inner and outer materials to generate multifunctional capabilities.

Among the iron oxides, hematite and maghemite are excellent candidates for the fabrication of these core/shell structures.\textsuperscript{19} Maghemite is a ferrimagnetic material and provides nanostructures with a response to applied magnetic fields. Hematite exhibits a high hydrophilic surface\textsuperscript{20} which is essential in water-based applications as well as for a strong interaction with the cell membrane in biomedical applications. However, the structure of these core-shell nanomaterials is usually difficult to determine precisely due to the polycrystalline character of both, core and shell, as well as to the similarities between both iron oxide polymorphs.

In this work we propose a thermal route to obtain core/shell maghemite/hematite NWs starting from previously electrodeposited iron NWs. The structural properties have been carefully studied as a function of annealing temperature and time, to show the existence of a maghemite/hematite core-shell structure. This structure, as well as the maghemite/hematite ratio can be controlled by tuning the oxidation parameters. We show, as an example, the potential use of these NWs in biomedical technology by studying their interaction with living cells.
Materials and methods

Iron oxide NWs were synthesized from previously electrodeposited iron NWs. These iron NWs were grown by template assisted electrodeposition that was carried out in a three-electrode vertical cell, with a Pt mesh as counter electrode and a Ag/AgCl electrode as reference, using polycarbonate nanoporous membranes, with 30 nm of pore diameter, as templates. A Au thin film was thermally evaporated on one side of the template to use it as working electrode. The electrolyte contained 0.5 M iron sulphate (Fe$_2$SO$_4$·7H$_2$O) and 0.5 M boric acid (H$_3$BO$_3$) supplied by Panreac. pH was adjusted to 2.5 by dropping sulphuric acid to the solution. All samples were synthesized with a constant plating potential of −1.15 V (vs. Ag/AgCl). After electrodeposition, the template was removed on a Si (100) substrate using dichloromethane (CH$_2$Cl$_2$) from Sigma-Aldrich.

Afterwards, the iron NWs were thermally oxidized in a tubular furnace under air atmosphere. The annealing temperature was varied from 350°C to 500°C and the annealing time from 10 to 240 min. Table 1 collects the synthesis parameters for three selected samples.

Table 1: Representative samples selected for this work

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>350</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>400</td>
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<td>C</td>
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<td>120</td>
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Sample morphology was studied by Scanning Electron Microscopy (SEM), using a JEOL JSM 6335F microscope and Transmission Electron Microscopy (TEM), using a JEOL JEM 3000F microscope. Grazing Incident X-Ray Diffraction (GIXRD) measurements were carried out in a Philips X’Pert PRO system using Cu K$_\alpha$ radiation ($\lambda_{k\alpha} = 1.54$ Å). The X-ray incident grazing angle for measurements was fixed at 0.4°.

To evaluate the oxidation state of the iron in the NWs, we employed Confocal Raman Microscopy, Mössbauer Spectroscopy and X-ray Absorption Spectroscopy (XAS).

Raman experiments were carried out in a Confocal Raman microscope (Witec ALPHA
300RA) at room temperature using a Nd:YAG laser (532 nm) in p-polarization. Raman measurements were performed fixing the laser excitation power at 0.5 mW and using an objective with a numerical aperture (NA) of 0.95. Samples were analyzed mapping regions on the plane (XY scans, \(5 \times 5 \, \mu\text{m}^2\)) and in-depth (XZ scans, \(5 \times 2 \, \mu\text{m}^2\)). The XZ scan was carried out to identify the plane with higher Raman intensity for each sample, followed by a XY scan in the selected plane. Average Raman spectra were obtained from the in-plane scans, where single Raman spectra were recorded each 100 nm in the spectral range 0 – 3600 cm\(^{-1}\). Collected spectra were analyzed by using Witec Control Plus Software. Raman bands of each spectrum were fitted using Lorentzian functions.

Conversion Electron Mössbauer data were recorded at room temperature with a parallel plate avalanche counter\(^{21}\) and a constant acceleration spectrometer equipped with a \(^{57}\)Co(Rh) source. The velocity scale was calibrated using a 6 \(\mu\)m thick \(\alpha\)-Fe foil and the isomer shifts were referred to the centroid of the spectrum of \(\alpha\)-Fe at room temperature.

XAS measurements were carried out at the Fe K-edge (7112 eV) in fluorescence yield mode at the beamline BM25A of The European Synchrotron (ESRF) in Grenoble (France). Samples were placed at 45\(^\circ\) from the incoming X-ray beam and forming 45\(^\circ\) with the dispersive X-ray fluorescence detector (13 elements Si (Li)). From three to five spectra were acquired from each sample and merged in order to improve the signal-to-noise ratio. A Fe foil was measured at the beginning and end of the experiment for energy calibration. The BM25-Spline has a double Si(111) crystal monochromator in pseudo channel-cut configuration refrigerated at 200 K by a homemade ethanol cooling system. Due to the optical configuration, the energy resolution was close to 0.8 eV. The acquisition time for each energy scan was about 30 min. XAS data were processed using the Demeter package and applying standard methods.\(^{22}\)

Core/shell structure of NWs was analyzed by Electron Energy Loss Spectroscopy (EELS) in the TEM JEM 3000F microscope, which is fitted with an ENFINA spectrometer. EELS spectra were acquired in diffraction mode (\(\beta \simeq 5.3\) mrad), with a dispersion of 0.1 eV/pixel.
and an acquisition time of 2 s. Plural-scattering events were removed following the Fourier-ratio deconvolution method. The oxidation state of iron was obtained from the corresponding Fe-L$_{2,3}$ edges using the white-line ratio method.

Interaction of NWs with biological systems was also analyzed. In particular, the internalization of NWs in glioblastoma cells was studied following two methods: the Direct Incubation (DI) and Centrifugation-Mediated Internalization (CMI). The protocols used for the experiments can be found in the Supplementary Information. To study the internalization, the cells were marked with prussian blue and neutral red and studied using optical microscopy (Leica DMI3000B).

Results and discussion

Morphology

Figure 1.a shows a SEM image of the electrodeposited Fe NWs after removing the Au seed layer and the polycarbonate template, in which an averaged diameter of 50 nm and a large density of NWs can be observed. After the oxidation process, the density of NWs remains almost unaltered for all studied samples (see Figure 1 and Figure S.1), but the diameter and the morphology change. These morphological features can be more easily seen in the TEM images shown in Figure 2. The diameter of the iron oxide NWs (see Figure 2.d) was estimated from both SEM and TEM images. The trend is similar in both analyses. The clear change in the diameter of NWs can be associated with the temperature and duration of thermal annealing. Considering the TEM results as an example, for the same annealing time (10 min), the diameter increases from 79 nm to 113 nm when the annealing temperature changes from 350°C (sample A) to 400°C (sample B), while increasing the time up to 120 min (sample C) the diameter increases up to 128 nm. The oxidation process that takes place during the annealing produces an increase in the volume of the NWs.

A first approach of the crystalline structure and characterization of the different iron
Figure 1: SEM images of a) a collection of electrodeposited Fe NWs after removing the template, b) sample A (annealed at 350°C for 10 min.), c) sample B (annealed at 400°C for 10 min.) and d) sample C (annealed at 400°C for 120 min.)

Figure 2: TEM images of a single iron oxide NW of a) sample A, b) sample B and c) sample C. d) Average diameter (calculated from SEM and TEM images) and grain size (calculated from XRD patterns) as a function of annealing temperature and time.
oxide polymorphs can be extracted from the XRD patterns (Figure S2). Two features can be distinguished. First, the XRD patterns are compatible with the presence of hematite. It should be noted in particular the presence, in sample A, of reflections that may be indexed as the (422) and (511) reflections of maghemite. However, due to the lack of other reflections from maghemite as well as the weakness of the maghemite reflections, these results are not conclusive and the use of other spectroscopic techniques is compulsory to corroborate the presence of maghemite in the NWs and not other iron oxide phases. Secondly, the intensity of the diffraction maxima, related to the hematite phase increases when increasing the annealing temperature and time, which could be an indication of an increase of the content of this iron phase as well as of a better crystallinity. The average crystallite sizes were calculated using the Scherrer formula. A Gaussian function was used to obtain the full width at half maximum (FWHM) of the most intense diffraction maxima. Results for samples A, B and C are collected in Figure 2.d, where we observed an average crystallite size of 6.6 nm, 8.1 nm and 9.8 nm respectively. As expected, the grain size increases for higher annealing temperatures and longer annealing times.

**Oxidation state: Raman, Mössbauer and X-ray Absorption spectroscopies**

Raman spectroscopy is a suitable technique for the identification and discrimination of different oxides. In Figure 3.a we show the average Raman spectra for samples A, B and C obtained from mapping areas on the sample surface together with a Raman spectrum of a sample fully oxidized to hematite (annealed at 500° for 120 min, see Figure S1.f). In order to improve the spectral resolution and resolve overlapped bands, Fourier Self-Deconvolution (FSD) was performed. The purpose of FSD is making the spectra narrower but preserving the frequency and the integrated intensity of each line. Therefore, FSD have been performed as a mathematical tool to differentiate the hematite and maghemite vibrational modes. We have followed the FSD method previously used by J. K. Kauppinen et al., with
small modifications that concern to the implementation of the Fourier Transform, taking in
consideration different parameters in order to have the best compromise between spectral
resolution and the deconvolution of the Raman modes (see Supplementary Information).
FSD was applied to the Raman spectra from 0 cm$^{-1}$ to 2000 cm$^{-1}$ (see Figure S3), however
in Figure 3.b we represent a magnification of both, the original Raman and FSD spectra for
each sample in which it is possible to distinguish the Raman bands in the region of interest
more clearly.

After FSD, Lorentzian fits were made using the FSD spectra and the bands assignment
was performed taking into account just hematite and maghemite as the iron oxides present
in the samples (marked in Figure 3.a). For hematite, we found the allowed Raman modes at
229 cm$^{-1}$ ($A_{1g}(1)$), 245 cm$^{-1}$ ($E_{g}(1)$), 295 cm$^{-1}$ ($E_{g}(2)$), 300 cm$^{-1}$ ($E_{g}(3)$), 410 cm$^{-1}$ ($E_{g}(4)$),
496 cm$^{-1}$ ($A_{1g}(2)$) and 612 cm$^{-1}$ ($E_{g}(5)$). The vibrational mode at 670 cm$^{-1}$ ($E_u$), a
longitudinal optical mode, is forbidden in Raman scattering. However, this mode can be
activated due to the lattice disorder of hematite. The band at 817 cm$^{-1}$ can be associated
with the excitation of a magnon. The different Raman modes for maghemite were at
382 cm$^{-1}$ ($T_{2g}$), 520 cm$^{-1}$ ($E_{g}$) and 726 cm$^{-1}$ ($A_{1g}$). The $A_{1g}$ mode of maghemite is
the most characteristic of this iron oxide. Overtones for both hematite (at 1320 cm$^{-1}$) and
maghemite (at 1430 cm$^{-1}$) were also observed. The Raman spectrum of the fully oxidized
sample shows all vibrational bands for hematite. When decreasing the annealing temperature
from 500 °C to 350 °C, the hematite Raman signal decreases while the intensity of the
peaks corresponding to maghemite increases. Similar behavior is observed on decreasing the
annealing time (Figure 3.a).

In order to study the presence of hematite and maghemite in each sample we analyzed the
area of the Raman band $E_{g}(5)$ for hematite and $A_{1g}$ for maghemite. The $A_{1g}^{\gamma}/E_{g}(5)_{\alpha}$
ratio was calculated from relative areas to each Raman band and can be associated with
the relative variation of both iron oxide phases when changing the annealing conditions
(Figure 3c). From the figure, it is clear that the maghemite content in the samples increases


Figure 3: a) Raman spectra from 100 cm$^{-1}$ to 1500 cm$^{-1}$ for samples A, B and C and for hematite NWs. The position for the different active vibrational modes has been marked with vertical blue (hematite) and orange (maghemite) lines. b) A magnification of Raman bands and FSD spectra from 100 cm$^{-1}$ to 900 cm$^{-1}$ for samples A, B, C, and hematite NWs. The position for the $E_g(5)$ and $A_{1g}$ active vibrational modes are marked with a vertical blue and orange lines. c) Estimation of the maghemite/hematite ratio for different samples.
when decreasing the oxidation time or temperature.

As Figure 3.a evinces, slight variations can be also appreciated in the FWHMs and the Raman mode positions. We observed that hematite Raman bands are broadened and shifted towards lower wavenumbers for NWs prepared using lower annealing times and temperatures. As above mentioned, taking into account that all studied NWs have the same length and are randomly oriented on the substrate, these changes might be associated with changes in diameter,\textsuperscript{33,39} which in average increases with the duration and temperature of thermal treatment (Figure 2.d).

Raman spectra were also measured in samples annealed at higher temperature for longer times. In all cases we only found modes corresponding to hematite similar to the one depicted as hematite NWs in Figure 3.a.

The maghemite/hematite ratio of sample A was also analyzed by Mössbauer spectroscopy. The Mössbauer spectrum recorded for this sample is depicted in Figure 4. It was fitted to two magnetic sextets and a broad central paramagnetic doublet. The Mössbauer parameters of the most intense sextet ($\delta = 0.35 \text{ mm s}^{-1}; 2\epsilon = -0.22 \text{ mm s}^{-1}; \text{H} = 51.0 \text{T}$), which accounts for 32% of the total spectral area, are characteristic of hematite.\textsuperscript{40} The other sextet has Mössbauer parameters ($\delta = 0.31 \text{ mm s}^{-1}; 2\epsilon = -0.09 \text{ mm s}^{-1}; \text{H} = 48.4 \text{T}$) that can be assigned, on the basis of the smaller isomer shift, quadrupole shift and magnetic hyperfine field, to maghemite.\textsuperscript{40} That accounts for 43% of the total spectral area. The paramagnetic doublet ($\delta = 0.39 \text{ mm s}^{-1}; \Delta = 0.84 \text{ mm s}^{-1}; \text{Area} = 25\%$) is characteristic of high spin Fe$^{3+}$ in octahedral oxygen coordination and, most probably, corresponds to superparamagnetic Fe$^{3+}$ oxides. Whether this doublet is due to superparamagnetic hematite, superparamagnetic maghemite or both, is something that cannot be decided solely on the basis of a room temperature measurement.\textsuperscript{41,42}

For that reason, the oxidation state and quantification of the different iron oxides in the samples have been also evaluated by XAS. Due to the penetration depth of X-rays and the experimental configuration used in this study, the information obtained by this technique
gives an average chemical state of the NWs for each sample. In Figure 5.a, XAS spectra of representative samples A, B and C are compared with the corresponding hematite and maghemite standards. Some common features are observed between the NWs spectra and the iron oxides references. For instance, in all samples we observe an intense pre-peak, which appears with different intensity, corresponding to electric dipole transitions $1s \rightarrow 3d$ in $3d$-$4p$ hybridized orbitals. Other similarities are the resonance at 7140 eV and the large resonance at 7180 eV, which make NWs spectra very similar to each other. The intensity of the pre-peak in samples resembles more likely to maghemite, but the intensity and shape of main peak have more common features with the hematite.

We can obtain quantitative information from different analyses of the experimental data. Following the Kunzl’s empirical rule, the chemical shift of the absorption edge is somehow proportional to the oxidation state in the case of most transition elements. Hence, if the position of the absorption edge is determined for the zero-valence compound (metallic state), and for selected reference standards, the formal oxidation state of a problem sample can be estimated. In the case of $\alpha$- and $\gamma$-phases, the relative energy shift must be zero, or negligible, because both phases have Fe in formal oxidation state of $3^+$. An alternative way of estimating the phase proportion is by fitting the problem spectra by least-square method with the reference spectra. In this way, we have obtained the phase proportions
in the samples and the results are shown in Figure 5.b. The calculated $\gamma$-Fe$_2$O$_3/\alpha$-Fe$_2$O$_3$ ratio shows that the relative amount of $\gamma$-Fe$_2$O$_3$ increases with lower annealing time and temperature, in accordance with the Raman analysis. The $\gamma$-Fe$_2$O$_3$ content in the NWs is about 34% (Sample B) and increases to 42% (Sample A) when we decrease the annealing temperature. The proportion of $\gamma$-Fe$_2$O$_3$ phase increases in a 10% when decreasing the annealing time at 400°C from 2 h (24%) to 10 min. (34%).

Figure 5: a) XAS spectra of representative NWs samples, obtained at three different synthesis conditions (samples A, B and C), along with those corresponding to a hematite and maghemite standards. b) Calculated maghemite percentage of selected samples.

**Measuring individual nanowires: EELS**

The area sampled by Mössbauer spectroscopy corresponds mostly to the whole sample, while XAS measurements comprise areas of a few mm$^2$. Raman spectroscopy can explore regions of several µm$^2$. Therefore, with the above-mentioned techniques, we cannot discriminate whether there are hematite and maghemite NWs in the samples of whether we have NWs composed by both oxides in a core/shell structure.

In order to characterize the NWs structure with high spatial resolution, individual NWs were studied by TEM. EELS data were obtained from the inner part (core) and the outer part (shell) of individual NWs. Spectra, including the iron-L$_{2,3}$ edge have been used to calculate the oxidation state of both areas, using the L$_3$/L$_2$ white-line ratio method. Figure 6 displays the Fe-L$_{2,3}$ edge of the core and the shell of samples A, B, C. The white-line ratio is very
similar, indicating that the oxidation state of iron is the same in both the core and the shell for NWs synthesized under the different conditions. The calculated value is always very close to $3^+$. This result is compatible with the coexistence of maghemite and hematite (oxidation state of iron is $3^+$ in both phases).\(^{43}\)

Figure 6: EELS spectra of Fe $L_3/L_2$ edge (left panel) and the O K-edge (right panel). Measurements performed on an individual NW, core (black) and shell (red), for samples A, B and C.

The energy-loss near-edge structure (ELNES) of the Oxygen K-edge allows distinguishing both iron oxides.\(^{43}\) Maghemite displays a distinctive peak at an energy-loss around 550 eV (c band), that is absent in the hematite. Right panel of Figure 6 shows the EELS spectra at the O K-edges of the core and the shell of a NW. In all samples, the core can be identified as maghemite since the peak at around 550 eV of energy-loss is clearly observed. The absence of this peak identifies the shell as hematite. This study was performed for several individual NWs, and results were similar. Therefore, these EELS results confirm that the NWs present a maghemite/hematite core/shell nanostructure.
Interaction of NWs with biological systems

Finally, as an example to show the potential of these NWs in biomedical technology, we have studied one of the most relevant features in the majority of biomedical application: their internalization capability. To this aim, we used the U373 glioblastoma cell line, and the NWs uptake was conducted by two different methodologies: DI and CMI. While most cell-labeling methods are based on DI method, which consists of endocytosis-mediated internalization and requires at least 24 h of incubation,\(^4\) the CMI mediates an endocytosis-independent internalization in less than 5 min.\(^{25}\)

First, we conducted a set of experiments in order to find the optimal NWs concentration for both the CMI and the DI methods using from 1000 to 30000 NWs by cell. The cells did not show cytotoxicity signals due to the internalization of maghemite/hematite core/shell NWs at any concentration and in the range of times of the essay. For 5000:1 (NWs by cell) concentration we yielded detectable internalization results by CMI, as revealed by using Prussian blue staining. Moreover, at this concentration we observed a higher amount of NWs in contact with the cells, and internalized, using the CMI method (Figure 7c,d.) than DI one (Figure 7a,b).

The different internalization methods depend on the sedimentation and diffusion velocities of the materials.\(^{44}\) Due to the magnetic core and the elongated shape of NWs, using the CMI method at 1500 rpm for 5 min, we may have higher diffusion and sedimentation velocities than using DI. For that reason, we suppose that the amount of NWs internalized is higher using CMI than DI. Due to the highly hydrophilic surface of the hematite shell,\(^{20}\) these core/shell NWs have a stronger interaction with the cell membrane. It is not necessary to functionalize the NWs using CMI method because of the higher speed of the method compare with DI.
Figure 7: Optical microscopy images of U373 glioblastoma cells after NWs internalization by a) DI method and c) CMI method. NWs were used in a concentration of 5000:1 (NWs:cell) and revealed by Prussian blue staining. b) and d) are magnifications of areas marked on a) and c) respectively.

Conclusions

To sum up, we have reported in this work a route to produce $\gamma$-$\text{Fe}_2\text{O}_3/\alpha$-$\text{Fe}_2\text{O}_3$ core/shell NWs by thermal annealing of previously electrodeposited iron NWs. Raman, Mössbauer and XAS spectrosopies show the possibility of tuning the $\gamma$-$\text{Fe}_2\text{O}_3/\alpha$-$\text{Fe}_2\text{O}_3$ ratio in the samples by controlling the annealing parameters, temperature and time. The diameter of the NWs and the grain size also depend on the annealing parameters. The nature of the core/shell structure has been clearly proved by EELS experiments. These maghemite/hematite core/shell structures do not show toxicity in contact with living cells. This paves the way to the use of these NWs in biomedical applications like cells guidance, separation experiments or manipulation of living cells in which the potentiality of their elongated shape together with their magnetic nature can be exploited.

Acknowledgments

This work was funded by Spanish MINECO under projects MAT2013-48009-C4-1-P, MAT2014-52477-C5-2-P and MAT2015-64110-C2-1-P. We acknowledge the European Synchrotron Ra-
diation Facility (ESRF), MINECO and CSIC for provision of synchrotron radiation facilities and the financial support for the beam line (PIE-2010-OE-013-200014). We would like to thank the BM25-SpLine staff for the technical support beyond their duties. We also acknowledge the use of the XRD facilities of the ISOM-UPM and thank A. Prados for her help during the XRD experiments. We also thank G. Pieplow for his help with the analysis using the FSD method. Belén Cortés acknowledges MINECO (FPI program) for her pre-doctoral fellowship.

Supporting Information Available

Description of the protocol for the biological study. Complementary SEM images of different iron oxides annealed under different conditions. XRD study of samples A, B and C. Details on the analysis of Raman spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Figure 8