Magnetic domain interactions of \( \text{Fe}_3\text{O}_4 \) nanoparticles embedded in a \( \text{SiO}_2 \) matrix

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Currently, superparamagnetic functionalized systems of magnetite (\( \text{Fe}_3\text{O}_4 \)) nanoparticles (NPs) are promising options for applications in hyperthermia therapy, drug delivery and diagnosis. \( \text{Fe}_3\text{O}_4 \) NPs below 20 nm have stable single domains (SSD), which can be oriented by magnetic field application. Dispersion of \( \text{Fe}_3\text{O}_4 \) NPs in silicon dioxide (\( \text{SiO}_2 \)) matrix allows local SSD response with uniaxial anisotropy and orientation to easy axis, \( 90^\circ < \text{<001}> \) or \( 180^\circ < \text{<111}> \). A successful, easy methodology to produce \( \text{Fe}_3\text{O}_4 \) NPs (6–17 nm) has been used with the Stöber modification. NPs were embedded in amorphous and biocompatible \( \text{SiO}_2 \) matrix by mechanical stirring in citrate and tetraethyl orthosilicate (TEOS). \( \text{Fe}_3\text{O}_4 \) NPs dispersion was sampled in the range of 2–12 h to observe the \( \text{SiO}_2 \) matrix formation as time function. TEM characterization identified optimal conditions at 4 h stirring for separation of SSD \( \text{Fe}_3\text{O}_4 \) in \( \text{SiO}_2 \) matrix. Low magnetization (\( M_s \)) of 0.001 emu and a coercivity (\( H_c \)) of 24.75 Oe indicate that the embedded SSD \( \text{Fe}_3\text{O}_4 \) in amorphous \( \text{SiO}_2 \) reduces the \( M_s \) by a diamagnetic barrier. Magnetic force microscopy (MFM) showed SSD \( \text{Fe}_3\text{O}_4 \) of 1.2 nm on average embedded in \( \text{SiO}_2 \) matrix with uniaxial anisotropy response according to \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) electron spin coupling and rotation by intrinsic Néel contribution.

The addressable \( \text{Fe}_3\text{O}_4 \) NPs in functionalized systems are of interest for the development of applications in magnetic hyperthermia, drug delivery and diagnosis agents and alternative cancer treatments due to their high biocompatibility\(^1\)—\(^3\), bioactivity\(^4\)—\(^5\), driving accumulation\(^6\)—\(^7\) and magnetic excitation\(^8\)—\(^10\) features. The systems based on superparamagnetic NPs behaviour have either biological or technological potential applications. \( \text{Fe}_3\text{O}_4 \) NPs have been extensively studied due to their interesting properties, which allow their evaluation and potential application as catalytic agents\(^11\)—\(^13\), gas sensors\(^14\), water treatment agents\(^15\), environmental remediation agents\(^16\)—\(^18\) magnetic resonance contrast agents\(^19\)—\(^21\), ferrofluids\(^22\), data storage devices\(^23\), and electronic devices\(^24\). Superparamagnetic \( \text{Fe}_3\text{O}_4 \) NPs with SSD have crystal anisotropy in the order 1.1, which allows easy reorientation and energy exchange to generate magnetic hyperthermia in presence of a magnetic field AC\(^25\). However, avoiding \( \text{Fe}_3\text{O}_4 \) NPs agglomeration due to interactions between neighbours is a challenge for biological applications. One alternative is separating the \( \text{Fe}_3\text{O}_4 \) SSD considerable distances by embedding them in a negatively charged, amorphous \( \text{SiO}_2 \) matrix\(^24\). This method allows a local response orientation of SSD to be obtained, according to Majetich S. A. et al.; if neighbouring superparamagnetic particles with a low anisotropy are coupled by exchange or dipolar interactions, their optimal separation for the maximum coercivity will allow the configuration of individually addressable SSD\(^25\). The local interactions will be the same, if the \( \text{Fe}_3\text{O}_4 \) particle size is similar. Then, SSD will have coherent rotation and contribute to the effective energy exchange by hyperthermia.

Current implementation of these systems depends on the superparamagnetic particle size (\(< 20 \text{ nm}) and SSD anisotropy, which directly influence the stability, dissipated energy and magnetic properties as function of time, such as the magnetic susceptibility and coercive field\(^30\). For this reason, different investigations have developed different methods to stabilize \( \text{Fe}_3\text{O}_4 \) NPs while preserving the main SSD properties\(^27\)—\(^29\). V Reichel et. al. showed that the magnetic properties of magnetite are dependent on Néel relaxation. These depend on the particle size, morphology and interparticle interactions as well as the temperature and time-scale of the measurement in \( \text{Fe}_3\text{O}_4 \) NPs (9 ± 3 nm)\(^30\). The \( \text{SiO}_2 \) media can be used to give \( \text{Fe}_3\text{O}_4 \) NPs specific accumulation in organs or tissues.
through bio-functionalization\cite{31–35} because it is an interaction-capable surface with ligands related to biological molecules.

Successful stabilization of Fe\textsubscript{3}O\textsubscript{4} NPs with SiO\textsubscript{2} can be achieved by using citrate as a dispersing agent. The polymerization time of SiO\textsubscript{2} was considered in the range of 2–12 h. However, Fe\textsubscript{3}O\textsubscript{4} functionalization and interaction media barriers with organic products can reduce Ms. The magnetic response will depend on the volume, particle form and SSD population density in the system\cite{36}. Rotation SSD Fe\textsubscript{3}O\textsubscript{4} will depend on the intrinsic structure defined Néel interactions and magnetic moment distribution per volume unit by the easy axis crystal orientation, <100> or <111> and the coercivity terms, which are crucial for SSD uniaxial response\cite{37}. The routes to control the dispersion Fe\textsubscript{3}O\textsubscript{4} NPs embedded in SiO\textsubscript{2} help to consolidate well defined the local SSD and their magnetic interactions. Superparamagnetic Fe\textsubscript{3}O\textsubscript{4} NPs dispersions in an inorganic matrix allow the creation of a functional target or hyperthermia generators with potential applications in nanomedicine\cite{38,39}.

**Results and Discussion**

The key to obtaining Fe\textsubscript{3}O\textsubscript{4} NPs is the ion relation \(\frac{1}{2}\) Fe\textsuperscript{2+}; Fe\textsuperscript{3+} by co-precipitation and the additional dispersion reaction by Stöber route. These ions were dispersed with citrate and TEOS to produce Fe\textsubscript{3}O\textsubscript{4} in an amorphous SiO\textsubscript{2} matrix according to the methodology described by L. Yang et al\cite{40} with some modifications.

XRD results show the main crystalline reflections of Fe\textsubscript{3}O\textsubscript{4} NPs with a cubic inverse spinel structure, forming a close packing fcc (\(a = 8.396\) Å)\cite{41}, Fig. 1a. Ferromagnetic spin interactions are defined by divalent Fe\textsuperscript{2+} and trivalent Fe\textsuperscript{3+} occupying octahedral sites and a double-exchange mechanism, while Fe\textsuperscript{3+} tetrahedral sites form an antiferromagnetic response, Fig. 1b. Because of superexchange, oxygen-mediated coupling, all the magnetic moments of the tetrahedral iron ions are aligned in a specific direction, while all the octahedral iron magnetic moments are aligned in the opposite direction\cite{42}.

The spectra (Fig. 1a (2–12 h)) show the amorphous contribution of the SiO\textsubscript{2} matrix and the Fe\textsubscript{3}O\textsubscript{4} NPs, which do not lose their crystalline quality. Wide diffraction peaks from the Fe\textsubscript{3}O\textsubscript{4} NPs are observed in an amorphous curve for the entire stirring range of 2–12 h. The fluorescence increased and the intensities decreased for each reflection in the patterns corresponding to the Fe\textsubscript{3}O\textsubscript{4} NPs embedded in the SiO\textsubscript{2} matrix. This is attributed to the confinement of the Fe\textsubscript{3}O\textsubscript{4} NPs inside the amorphous SiO\textsubscript{2} matrix.

Additionally, wide peaks are related to the nanometric particle size. Some changes in the NPs size were observed as a function of the reaction time, Fig. 1a. Supplementary information (s1) shows the FWHM values and sizes obtained through a modified Scherrer analysis by using a pseudo–Voigt function\cite{43}. In some cases, the size of the particle increased due to agglomeration and the dynamic stirring energy. When the SiO\textsubscript{2} matrix does not complete the polymerization, the uncoated Fe\textsubscript{3}O\textsubscript{4} NPs form aggregates and reassemble\cite{39}. Peaks of smaller

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**Figure 1.** Structure and bonds of Fe\textsubscript{3}O\textsubscript{4} NPs embedded in SiO\textsubscript{2} matrix. (a) XRD shows the evolution with the stirring time; Fe\textsubscript{3}O\textsubscript{4} NPs reference; Fe\textsubscript{3}O\textsubscript{4} NPs + SiO\textsubscript{2} matrix at 2, 4, 8, and 12 h. Background at these time is associated with the amorphous SiO\textsubscript{2} matrix and small displacement of peaks due to Fe\textsubscript{3}O\textsubscript{4} surface oxidation. (b) Ferromagnetic structure with octahedral sites of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} contributes to the magnetic alignment of Fe\textsubscript{3}O\textsubscript{4} NPs under magnetization. (c) FT-IR spectra of uncoated Fe\textsubscript{3}O\textsubscript{4} NPs and those in the SiO\textsubscript{2} matrix at 2, 4, 8 and 12 h of the coating reaction.
particle sizes were defined after the stabilized reaction of the NPs in the SiO₂ matrix with 4 h of processing. Average size in Fe₃O₄ NPs was 16.73 nm and a = 8.394 Å. Average sizes and lattice parameters in Fe₃O₄ NPs + SiO₂ matrix were (a) 16.49 nm and 8.360 Å at 2 h, (b) 15.37 nm and 8.364 Å at 4 h, (c) 16.92 nm and 8.3619 Å at 8 h, and (d) 17.07 nm and 8.3614 Å. The lattice parameters showed small distortions as Fe₃O₄@γ-Fe₂O₃ by surface NPs oxidation.

The FT-IR spectra of different samples are presented in Fig. 1c. The interactions of the functional group Fe₃O₄ NPs in the SiO₂ matrix can be observed. Characteristic iron-oxygen bond (Fe-O) signals at approximately 585 cm⁻¹ are in the five spectra. Crystalline Fe₃O₄ is conserved after the embedding process. Also, it is possible to identify the SiO₂ contributions in Fig. 1c; a broad band centred at 1048 cm⁻¹ is observed. There are also two interactions of interest at 1113 cm⁻¹, which is attributed to the Si-O-Si bonds, and another at 986 cm⁻¹, which is due to the Si-OH groups from the matrix. These interactions slightly increased in intensity with the reaction time, which promoted the SiO₂ layer thickness. No additional linkage interactions were observed for the functional groups characteristic of citrate and the stabilizing agents used during the experiment. These were completely removed during the particle washing step. This indicates that the reaction parameters, such as the concentration of the solutions and the reaction times, allow the dispersed particles to be obtained without adsorbed citrate molecules on the surface of the Fe₃O₄ NPs.

TEM results for Fe₃O₄ NPs embedded in SiO₂ matrix as a function of time are shown in Fig. 2. The evolution of the processing was observed at 2, 4, 8 and 12 h of stirring: (1) Agglomeration of Fe₃O₄ NPs at 2 h, Fig. 2(a–c). Selected area of electron diffraction (SAED) results correspond to Fe₃O₄ structure with a low amorphous contribution from SiO₂. (2) Good dispersion of individual Fe₃O₄ NPs at 4 h, Fig. 2(d–i). Under these conditions, the small, agglomerated nanoparticle entities are dispersed, and the TEOS polymerization is consolidated. SiO₂ contributes a negative charge to the NPs to form individual SSD of Fe₃O₄ NPs and the amorphous matrix of SiO₂. The crystalline Fe₃O₄ structure diffracted in the planes (220), (311) and (440). (3) The regions of agglomerated Fe₃O₄ NPs plus SSD dispersed for 8 h of stirring, Fig. 2(g–i). Under these conditions, there are NPs linked by electrostatic interactions and/or dipolar coupling. SAED shows the crystalline contribution of Fe₃O₄ NPs with diffraction planes in (311) and (440)⁴⁴. The agglomerates increased in size. (4) Agglomerates plus isolated SSD were obtained in the SiO₂ matrix after 12 h of stirring, Fig. 2(j–l). This phenomenon is associated with the strong interaction between neighbours. SAED shows the rings of the diffraction planes of Fe₃O₄, which are very similar in intensity to those in Fig. 2c. It could be said that the matrix of SiO₂ formed at 4 h stirring is a negatively charged film that confines the SSD as individual entities. As the agitation time is increased to 8–12 h, the dynamic movement increases the coalitions between NPs and their interactions. As a consequence, the attraction between NPs increases the agglomeration with a long agitation time.

The main challenge in potential applications of Fe₃O₄ NPs lies in their superparamagnetic properties, uniaxial anisotropy, particle size and form. Typically, bulk Fe₃O₄ has a Mₛ of 91 emu/g, and its inner structure forms multilayers with magnetic anisotropic axial ratios larger than 5⁵⁶. In superparamagnetic NPs, the magnetic anisotropic energy barrier is reduced and allows the rotation of SSD from a spin-up state to spin-down state to readily rotate the magnetic spin direction on the easy axis⁴⁵. The magnetization from Fe₃O₄ NPs embedded in a SiO₂ matrix shows superparamagnetic, closed hysteresis loops⁴⁶. As the particle size of Fe₃O₄ decreased below the superparamagnetic diameter, Mₛ decreases as well, and the magnetic fluctuation leads to a small Hc near zero with a low remanence at 300 K⁴⁶. Samples as a function of the stirring time were Mₛ = 0.0015 emu, Hc = 26.480 Oe at 2 h; Mₛ = 0.0010 emu, Hc = 24.000 Oe at 4 h; Mₛ = 0.0013 emu, Hc = 24.800 Oe at 8 h; and Mₛ = 0.0015 emu, Hc = 25.570 Oe at 12 h, Fig. 3a. Additionally, the TEM image showed the separation of the Fe₃O₄ NPs SSD embedded in the SiO₂ matrix at 4 h of stirring. These parameters and the particle size are directly related to the descending Hc value as follows: (a) agglomerations of NPs 11.70 nm on average at 2 h; (b) fragmentation and dispersion of 5.64 nm NPs with distances from 5.54 to 29.21 nm as individual SSD in SiO₂ at 4 h; (c) aggregates of 15.45 nm NPs on average and individual 4.47 nm NPs on average separated by 3.54 nm to 6.00 nm in SiO₂ at 8 h; and (d) 13.7 nm average agglomerates and 6.02 nm NPs on average separated by distances 5.20 nm to 6.43 nm in SiO₂ at 12 h. Coherent results were obtained by Mₛ and Hc with 4 h of stirring. This means that individual SSD have uniaxial anisotropy and are addressable by the separation between the NPs, Fig. 3c. However, in the case of the polydispersity of NPs, Mₛ and Hc increase due to the major volume contribution from the neighbouring interactions and thermal fluctuations. The diamagnetic SiO₂ barrier around the Fe₃O₄ NPs reduces Mₛ. However, separation between the monodispersed NPs maintains the Hc as local SSD. These effects can also be observed in encapsulated Fe₃O₄ NPs with organic chains. Some organic coating media have important roles due their permeability, specificity and individual drive of the magnetic domains that can be accumulated in tumours⁵⁶. The integration of SSD as functionalized systems at optimal distances and relatively high Hc values would increase the hyperthermia efficiency by magnetic field AC excitation in the frequency range 100 kHz–500 MHz⁴¹. Fe₃O₄ NPs distribution embedded in the SiO₂ matrix were observed by atomic force microscopy. The 3D images show the differences in the dispersed nanoparticles according the stirring time for 2 and 12 h. Figure 4. The sample obtained with 4 h of stirring had local, isolated particles in the SiO₂ matrix, Fig. 4a. The topography profiles show an estimated particle size of 6 nm and roughness of MRS= 4.53 nm. The images with 12 h of stirring showed 21.8 nm agglomerated particles and their neighbouring interactions with an MRS= 3.07 nm, Fig. 4b. The profiles below 3D images are associated to particle size and their agglomerations in both cases.

MFM shows the magnetic moment density per volume unit. The 3D images are generated by the interaction of magnetic tip polarization, which is normal with respect to the NPs surface, and sensing of the attractive and repulsive states⁵⁸. SSD are NPs that can be aligned in parallel by exchanging forces of the electron spins from applied magnetic field. Inner magnetic structure Fe₃O₄ SSD with Fe⁺³ and Fe⁺² electron spin coupling respond uniaxially because magneto-crystalline anisotropy forces tend to align in a preferred direction based on the easy axis. For superparamagnetic sizes, the relative magnitude of the boundary energy becomes larger than the magnetostatic energy. At a critical size, the spin direction can be oriented by exchange interactions in the SSD⁵⁷.
MFM 3D images showed surface of NPs by magnetization $H^\uparrow$ and demagnetization $H = 0$ effects from Fe$_3$O$_4$ SSD embedded in the SiO$_2$ matrix. The magnetic interaction at the tip in the lift mode shows the disorder from the intrinsic structure at $H = 0$. Under the saturation measurement conditions $H \sim 1200$ Oe for the Co-Ni tip, the SSD uniaxial orientation of the magnet is shown with the domains oriented at $90^\circ$ for the majority $n^\uparrow$ and minority $n^\downarrow$ states with $H^\uparrow$. Finally, domain disorder is observed by demagnetization under the initial conditions $H = 0$.

When the magnetic field AC is applied to these systems, the magnetic domains will fluctuate with local vibrations and will transform this energy into thermal energy. The orientation was observed in a non-continuous media

Figure 2. TEM images show the dispersion of Fe$_3$O$_4$ NPs at different reaction times in the SiO$_2$ matrix: (a,b) Agglomeration of NPs at 2 h and (c) SAED with characteristic rings of the Fe$_3$O$_4$ NPs: the intensity depends on the population density of NPs; (d,e) individual SSD in the SiO$_2$ matrix after 4 h and (f) SAED with dispersion in amorphous SiO$_2$ plus Fe$_3$O$_4$ NPs; (g,h) SSD+agglomeration of NPs at 8 h, and (i) SAED with dispersion in amorphous SiO$_2$: agglomeration increases the intensity of the electron diffraction; (j,k) SSD+agglomeration of NPs; (l) diffraction is increased by the groups of NPs agglomerates.
with local SSD interactions at 4 h of stirring, Fig. 5(a–c). In the case of NPs agglomeration, the surface interactions showed a global response by addition of all magnetic domains in the 12 h stirring sample, Fig. 5(d–f).

Zoom was performed under the saturation conditions $H^\uparrow$ to show the uniaxial behaviour. Parallel stripes from attractive and repulsive interactions define the magnetic domains. The exchange forces of the parallel alignment are result from the internal magnetic structure in Fe$_3$O$_4$ NPs, which are defined by Neél interactions, Fig. 6. The profiles show the $\theta$ (deg) and domains oriented in the normal direction, 90°, with average domain sizes of 1.2 nm and uniaxial anisotropy from main crystalline direction. The anisotropy energy is given by $E_a = KV\sin^2\theta$, where $K$ is a typical constant of the material, $V$ is the volume of the particle, $\theta$ is the angle between the magnetization and the easy axis. The local response of Fe$_3$O$_4$ NPs showed magnetic domains with an average size of 1.2 nm surrounded by the SiO$_2$ matrix with stirring for 4 h. The profile defines the parallel interactions of the uniaxial response, Fig. 6a–c. However, the neighbouring interactions of Fe$_3$O$_4$ NPs in SiO$_2$ matrix with 12 h of stirring show well-defined interactions in the same direction as the sum of local interactions with similar magnetic domains in the range of 1.2 nm, Fig. 6d,e. The Fe$_3$O$_4$ SSD in the SiO$_2$ matrix show a local response of addressable superparamagnetic behaviour, which is mainly governed by particle size and shape of Fe$_3$O$_4$ cores in a monodispersion at magnetic field saturation. The degree axis in the profiles shows the deflection propensity in attraction and repulsion generated by $H^\uparrow$, and these values can change based on the roughness topography and $H^\uparrow$ intensity to form field lines between the tip and sample. The differences in the tip deflections from the SSD were $−33.1°$–$−39.1° = 6.0°$ at 4 h of stirring, Figs. 6c, and $−9.4°$–$−16.6° = 7.2°$ at 12 h of stirring, Fig. 6f, which are very

**Figure 3.** Magnetization responses from Fe$_3$O$_4$/SiO$_2$: (a) $H$ vs $M$ as a function of the stirring time for well dispersed NPs as individual SSD at 4 h shows a lower magnetization. The amorphous SiO$_2$ barrier between NPs reduces the magnification of 2, 4, 8, and 12 h of processing. Superparamagnetic signals as close loops were observed in all cases. (b,c) Differences in the magnetization due to the changes in the magnetic permeability. The magnetization saturation decreases with the $\mu_r$ of the SiO$_2$ matrix media and the separation of NPs as SSD.
similar. These results show the uniaxial responses of local SSD of individual NPs at 4 h and the sum of the SSD as a continuum in the NPs agglomeration at 12 h.

Typically $H_c$ decreases as a function of particle size in $\text{Fe}_3\text{O}_4$ NPs with close hysteresis loop. However, the superparamagnetic single-domains response of $\text{Fe}_3\text{O}_4$ NPs is maintained by local response SSD as agglomeration phenomena is reduced in the case of SiO$_2$ matrix due to its permeability$^{47}$. According to Dave S., R. Dave and G. Xiaohu, the formation of the domain walls is a process driven by the balance between the magnetostatic energy as a function of the particle size$^{52}$.

**Conclusions**

The synthesis strategy presented is a fast and effective option to avoid the agglomeration phenomenon of $\text{Fe}_3\text{O}_4$ NPs by stabilizing them in SiO$_2$ as a function of the stirring time without altering their crystalline features.

The $H_c$ is maintained in individual $\text{Fe}_3\text{O}_4$ SSD with uniaxial behaviour at 4 h of stirring. MFM showed SSD and that local NPs in the SiO$_2$ matrix have similar responses as the NPs concentration increases. However, $M_s$ is reduced by the distance between the NPs among the SiO$_2$ matrix, and this depends on the permeability of the media. Neél interactions produce local fluctuations and energy transference from reorientable SSD by magnetic fields at high frequencies. The challenge is to control the $\text{Fe}_3\text{O}_4$ SSD as individuals in organic media to increase the response velocity and effective magnetic excitation to produce hyperthermia.

**Figure 4.** Topography by AFM. (a) $\text{Fe}_3\text{O}_4$ NPs immersed in a SiO$_2$ matrix after 4 h of stirring. (b) 12 h of stirring with a high concentration of NPs. Profiles show isolated $\text{Fe}_3\text{O}_4$ NPs signals from (a) SSD at 4 h and agglomeration at 12 h (b).
Fe₃O₄ NPs embedded in a SiO₂ matrix are candidates as functional groups or specific organic linkers for cancer cell interactions and hyperthermia therapy. The development of dispersed SSD is mandatory to improve biological applications.

Materials and Methods
For the synthesis, hydrochloric acid (HCl) (36.5–38.0%, BAKER ANALYZED ACS), deionized water (Millipore, 18.2 MΩ cm), iron chloride II (FeCl₂, 98%), iron chloride III (97%), a tetramethyl ammonium solution (C₁₄H₃NO, 25 wt% in H₂O), tetraethyl orthosilicate (TEOS, 98%), a 28% ammonium hydroxide solution (NH₄OH) and absolute ethyl alcohol (C₂H₅OH) were all from Sigma-Aldrich and used as received without any purification.

Synthesis of Fe₃O₄ NPs. The formation of nanostructured magnetite through a co-precipitation method was realized via the following: an aqueous solution of hydrochloric acid (HCl, 0.64 N) was prepared to dissolve the precursor salts of the Fe²⁺ (ferrous chloride, FeCl₂) and Fe³⁺ ions (ferric chloride, FeCl₃).

After the acidic solution was prepared, 6.25 mL was taken, and 2.52 g of FeCl₂ was added. Another 25 mL of the solution was used to dissolve 6.99 g of FeCl₃, and both solutions were kept under magnetic stirring for 1 h. Then, both solutions were mixed in a round-bottom, three-necked flask and bubbled with Ar for 5 min to remove any dissolved oxygen in the solution. The resultant solutions were stirred at 500 rpm and heated to 70 °C. Once the temperature stabilized, 21 mL of tetramethylammonium hydroxide was added dropwise, providing an alkaline environment for the formation of the magnetite. The solution turned black, which was an indication that iron oxide formed in the solution. After 40 min, the stirring and heating were stopped, and the mixture was allowed to cool to room temperature. The nanoparticles were washed with water and precipitated with the aid of a magnet until the pH of the dispersion was equal to 7. Once the nanoparticles were dispersed in water, they were freeze-dried for 12 h to obtain the magnetite powder.

Synthesis of Fe₃O₄ in a SiO₂ matrix. The Fe₃O₄ NPs powder (0.02 g) was taken and mixed with the same amount of citrate in an aqueous solution (250 mL) and mechanically stirred at 500 rpm for 1 h. Citrate was used as a dispersal agent to avoid agglomeration of the nanostructures prior to the formation of the SiO₂ matrix.

Then, the SiO₂ precursor solution was prepared as follows: 10 mL of water, 50 mL of ethanol, 5 mL of ammonium hydroxide and 0.2 mL of TEOS were mixed by magnetic stirring for 10 min. After that, the solution of magnetite and citrate was mixed with the SiO₂ precursor solution. To modify the thickness of the SiO₂ coating, the mixture reacted for 2, 4, 8 and 12 h under mechanical stirring at 500 rpm. Once the different times passed, the
Particles were washed with ethanol and precipitated with the help of a magnet. They were dried at room temperature, and the powder was characterized.

The analysis of the material allowed determination of the optimal reaction time conditions to reduce the agglomeration in the citrate suspension. Additionally, these samples were processed by the Stöber method to embed the magnetite NPs in the matrix of silicon dioxide. This is an easy methodology to reduce agglomeration and to improve the Fe₃O₄ NPs dispersal in the SiO₂ matrix and the magnetic properties of the magnetite under different stirring conditions.

To determine the properties of the nanostructures, different characterization techniques were used: RIGAKU Smart Lab X-ray diffractometer, XRD, was used in the Bragg-Brentano configuration with 0.02 steps in the range from 25 to 70°, 2θ with a copper source of 1.5424 Å and wavelength to define Fe₃O₄/SiO₂ structures. PowderCell Software was used to analyse experimental diffractograms from XRD. Their dispersion and particle sizes were observed by JEOL-JEM 2010 transmission electron microscope, TEM, with a LaB₆ filament at an acceleration voltage of 200 kV. The functional groups of silicon and magnetite were examined with an FT-IR.

Figure 6. Parallel orientation of magnetic domains with uniaxial behaviour. (a) Fe₃O₄ SSD immersed in a SiO₂ matrix after stirring for 4 h show desirable areas with stripes in the same direction, and the profile indicates the orientation of SSD, 90°; (b) after stirring for 12 h, the sample shows oriented magnetic domains and assembly by neighbouring interactions; profiles show the sum of all local SSD.
spectrophotometer, NICOLET 6700. The magnetic response was determined using a MPMS3 Magnetometer SQUID of Quantum Design with a sensitivity of 5 × 10⁻⁸ emu.

Magnetic force microscopy (MFM) was performed with a scanning probe microscope (SPM) JEO JSPM 5200 multimode. The samples were dispersed in carbon adhesive tape on the holder. An ultra-sharp silicon cantilever NSC14/Co-Cr/15 micro-wire was exposed to a strong neodymium magnet. The voltage and lift conditions were defined according to the magnetic surface interactions of the sample with the tip lift voltage [0.030–0.1 V].

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Author Contributions
J.A.F.G. contributed to the synthesis and characterization of Fe₃O₄ nanoparticles embedded in a SiO₂ matrix, analysed the results and wrote part of the manuscript. A.I.D.C. wrote part of the manuscript. A.G.C. performed the TEM analysis. J.S.S. and MFM-AFM analysed results and wrote part of the manuscript.

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