Spinel iron oxide by the co-precipitation method: effect of reaction atmosphere

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Electron Diffraction
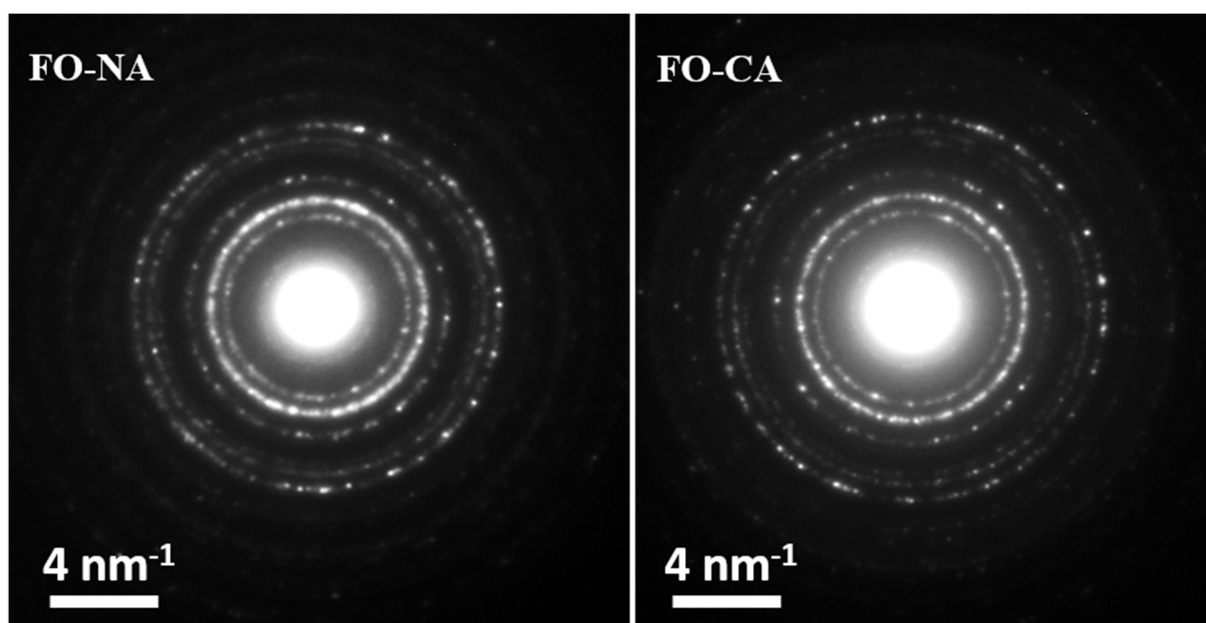
FigureS1.Selected area electron diffraction (SAED) patterns of FO-NA and FO-CA.

Selected area electron diffraction (SAED) patterns of FO-NA and FO-CA taken under the same microscope conditions. The diffraction rings have the same diameters and intensities indicating the presence of the same kind of particles into both samples. The interplanar distances associated to the diffraction rings agree with the spinel iron oxide structure (JCPDS cardNo.75-449), confirming XRD results.

Size evaluation
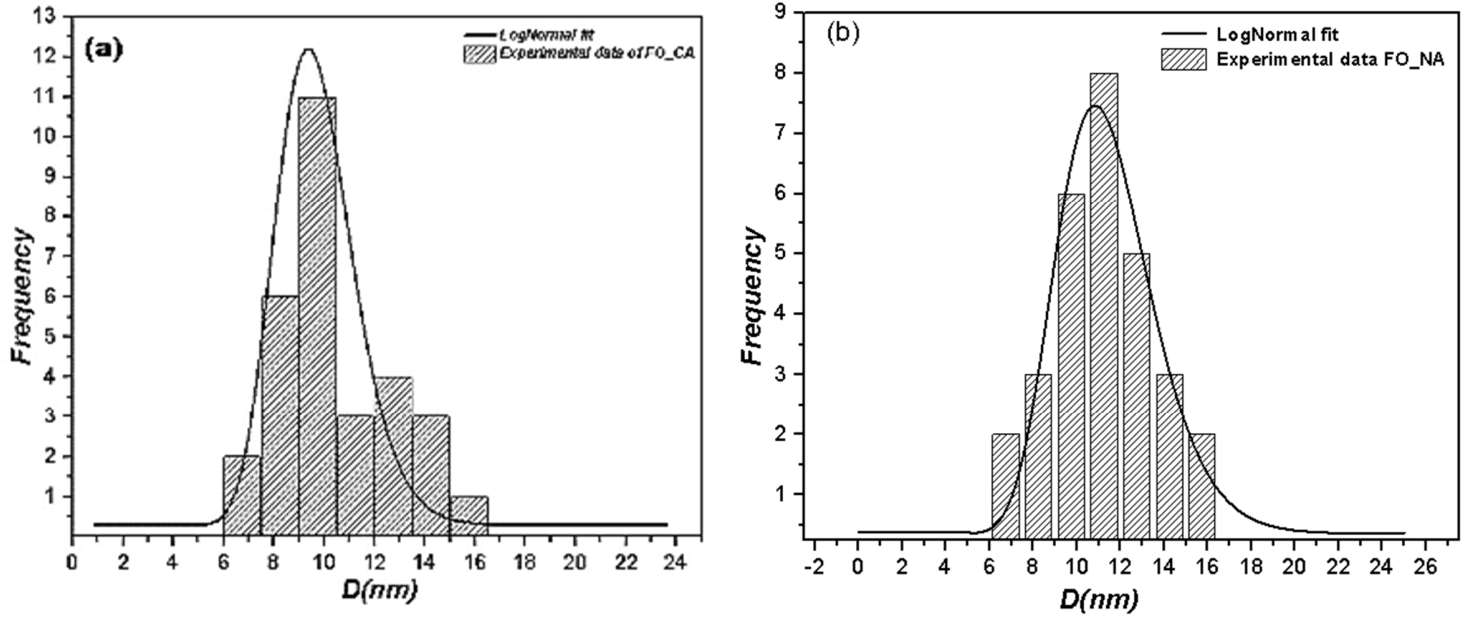
**FigureS2**.Particle size distribution fitted with log-normal function.
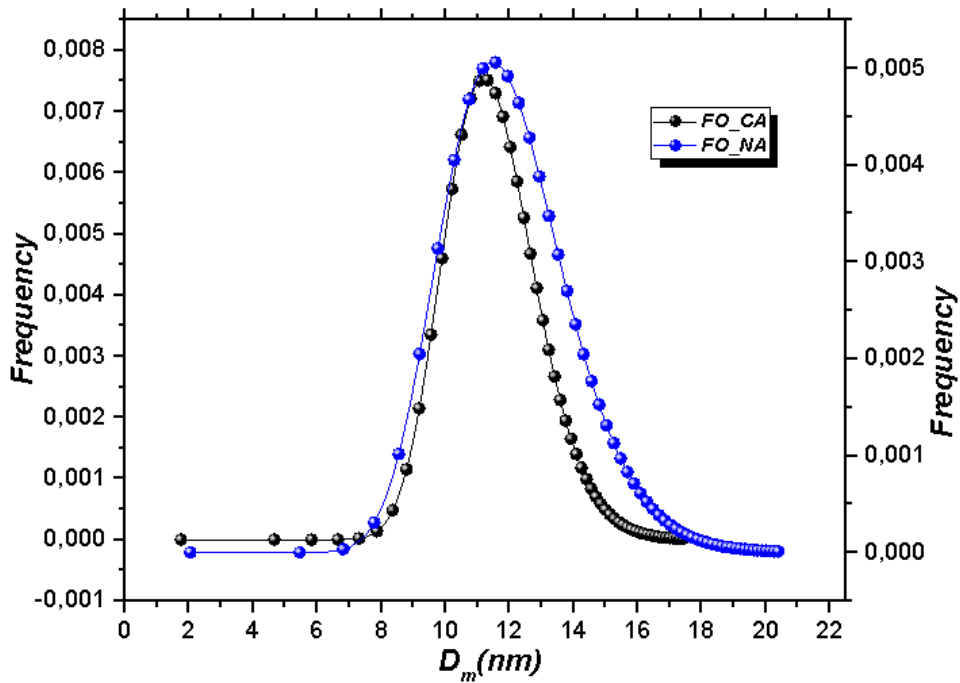
FigureS3.Magnetic size distribution for FO-CA and FO-NA nanoparticles using Langevin function at 300K.

More than one trial of synthesis of spinel iron oxide nanoparticles via co-precipitation under different reaction atmosphere have been performed in order to test repeatability of the results. As an example, in the table below we report the particle size, saturation magnetization of three experiments under nitrogen atmosphere (CA) and air (NA).

TableS2: Summary of obtained values of particle size and saturation magnetization at 5K of the three experimental trials under nitrogen atmosphere (CA) and air (NA).

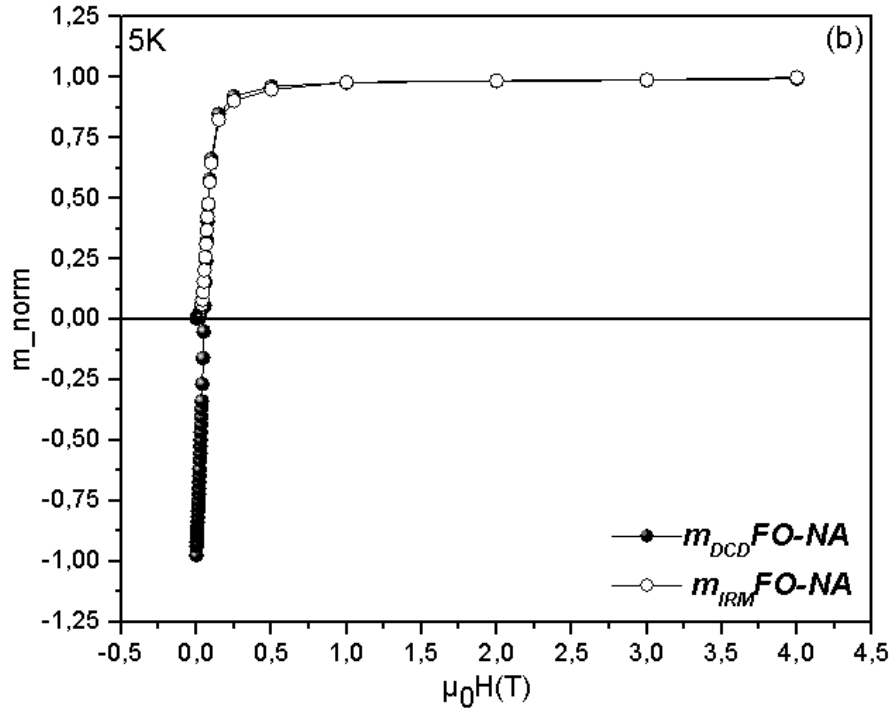| Sample	D_{XRD}(nm)	Error	Ms_5K(Am^2Kg^{-1})	Error
FO-CA(1)	9	0.9	88	0.3
FO-CA(2)	9.3	0.7	85	0.2
FO-CA(3)	8.7	0.9	92	0.6
FO-NA(1)	9	0.9	77	0.3
FO-NA(2)	8.8	0.8	74	0.3
FO-NA(3)	8.9	0.6	90	0.9

Interparticle interactions
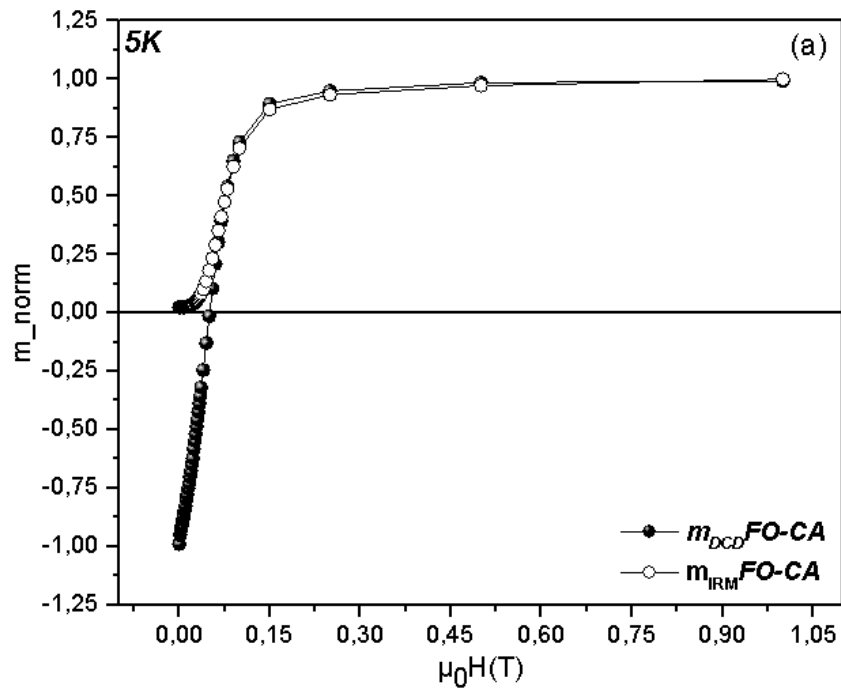
FigureS4.Remnant magnetization curves according to DCD and IRM protocols for (a) FO-CA and (b) FO-NA samples.

In order to investigate magnetic nanoparticle interactions, low temperature remnant magnetization (5K) is carried out by the direct current demagnetization (DCD) and isothermal remnant magnetization (IRM) protocols (Figure S4). In a typical DCD measurement, after cooling the sample to 5K, an external magnetic field of 5T is applied to saturate the sample, then the field is removed, and the remanence magnetization (M_{rDCD}) is recorded. After, a small external field (H_{rev}), opposite to the magnetization is applied for few seconds, then switched off and the remanence magnetization is recorded. The process is repeated several times, each time with a higher H_{rev}, up to 5 T. IRM protocol is similar to DCD protocol, but it starts with the sample in demagnetized state. $M_{rIRM}(H)$ and $M_{rDCD}(H)$ represent the same energy barriers in the case of an ensemble of non-interacting monodomain particles with uniaxial anisotropy. This is clearly expressed by the Wohlfarth relation[1]:

$$m_r^{DCD}(H) = 1 - 2m_r^{IRM}(H) \quad (S.1)$$

Kelly et al. rewrote the Wohlfarth's relation in order to show more clearly the deviation of a real system from the non-interacting case[2]:

$$\delta m(H) = m_r^{DCD} - [1 - 2m_r^{IRM}] \quad (S.2)$$

where the δm parameter has zero value for a non-interacting system. Interactions promoting the magnetized state such as exchange and other positive interactions lead to a positive value of δm parameter whereas negative deviation is due to demagnetizing interactions (e.g. dipole–dipole interactions).

Mössbauer Spectroscopy
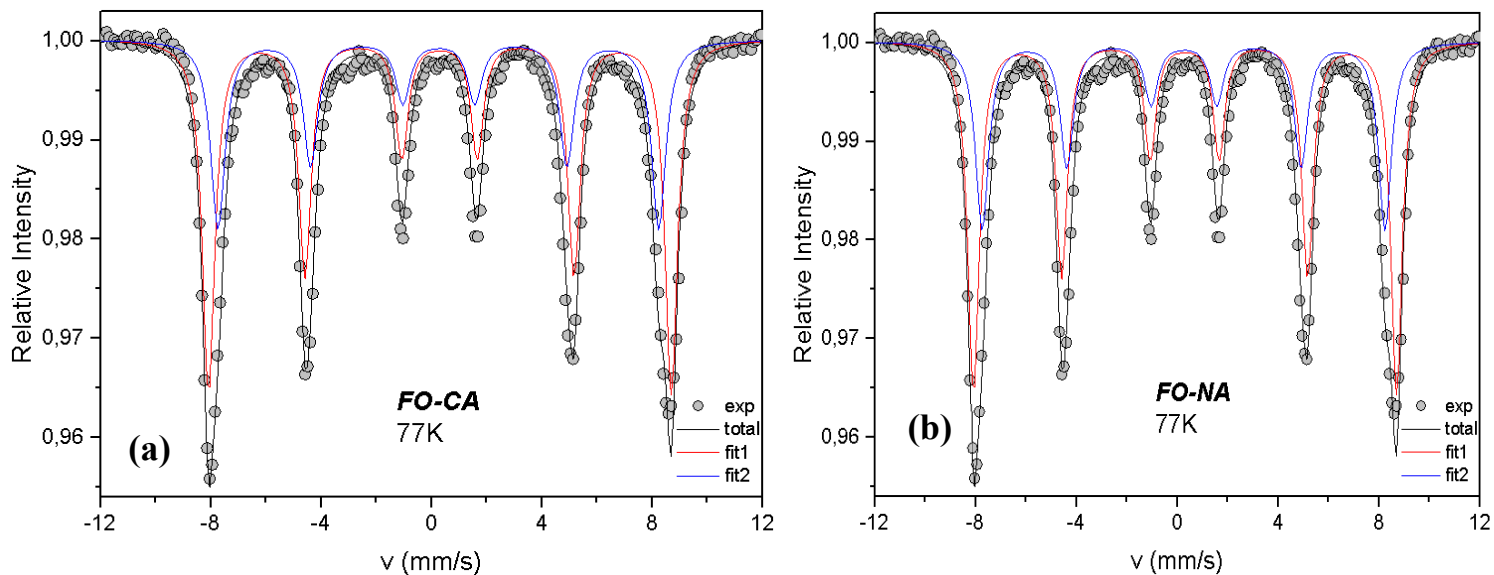
FigureS5.[57]Fe Mössbauer spectra measured at 77K for (a) FO-CA and (b) FO-NA; the spectra are fitted with 2 sextets corresponding to A-site and B-site (fitted using a Lorentzian distribution).

TableS2.Summary of obtained values of hyperfine parameters (Isomer Shift, Quadrupolar Shift, Effective and Hyperfine fields, and weight) obtained at 77K.

Sample	Sites	δ (mm.S^{-1})	2ε (mm.S^{-1})	B_{hyp} (T)	%
FO-CA	A	0.42	0.01	49.6	36
	B	0.47	-0.04	52.1	64
FO-NA	A	0.42	0.02	49.4	38
	B	0.47	0.02	51.8	62

X-ray Absorption Near-Edge Structure (XANES) spectroscopy
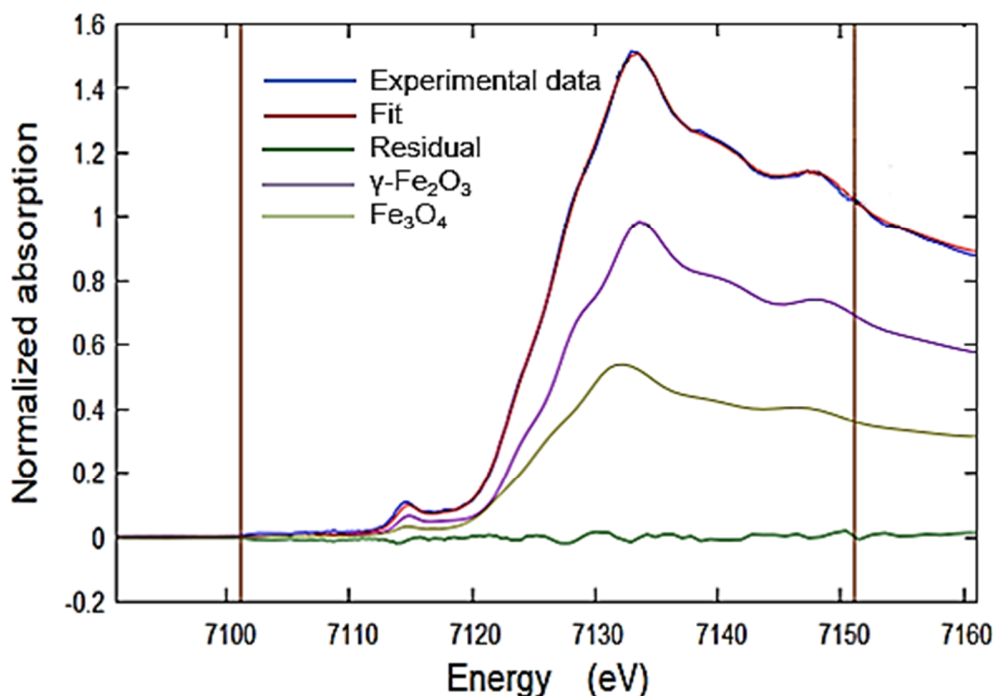
FigureS6.Linear Combination fit analysis of FO-CA nanoparticles.

X-ray Absorption Fine Structure (XAFS) spectroscopy is a chemically selective powerful technique to study the properties of local atomic structure around the absorbers[3]. In particular the near edge region (XANES) of the absorption spectrum is strongly sensitive to the oxidation state and coordination chemistry of the absorber and can provide accurate chemical speciation in multi-phase compounds[4]. In this study we used Fe-K edge XANES analysis to individuate and quantify the maghemite and magnetite phases in iron oxide NPs.

The oxidation state and average local coordination chemistry of the Fe cation in maghemite (γ-Fe_2O_3) is 3+ with 6 Oxygen nearest neighbors octahedrally coordinated ($Fe^{3+}O_6$). In magnetite (Fe_3O_4) Fe is found either as octahedral coordinated ($Fe^{2+}O_6$) 2+ cations and as a combination of octahedral ($Fe3+O6$) and tetrahedral ($Fe^{3+}O_4$) coordinated cations. Such a different local coordination chemistry and valence state, make the Fe K edge XANES of maghemite and magnetite clearly distinguishable.

In this study we used the Linear Combination Fit (LCF) method to understand the Fe phase composition of NPs. In LCF the experimental XANES spectrum of unknown sample μ_{exp} is fitted to a linear combination of XANES spectra of reference compounds μ_i^{ref}: $\mu_{exp} = \sum_i \alpha_i \mu_i^{ref}$, here the α_i represent the fraction of Fe in the sample being in the i-th phase. The LCF was performed using Athena program (from Demeter software package[5]), data were fitted in the 7090-7160 eV energy region around the Fe K edge (7112 eV). After preliminary check we found a combination of γ-Fe_2O_3 and Fe_3O_4 reference spectra enough to achieve satisfactory fit (shown in Figure S6) and the best fit gives 65% γ-Fe2O3 and 35% Fe3O4 meaning that in this sample about 2/3 of Fe ions reside in a local environment close to that of γ-Fe2O3 and about 1/3 close to that of Fe3O4 local structure[6].

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