Morpho-Structural and magnetic properties of CoFe2O4/SIO2 nanocomposites: effect of the molecular coating

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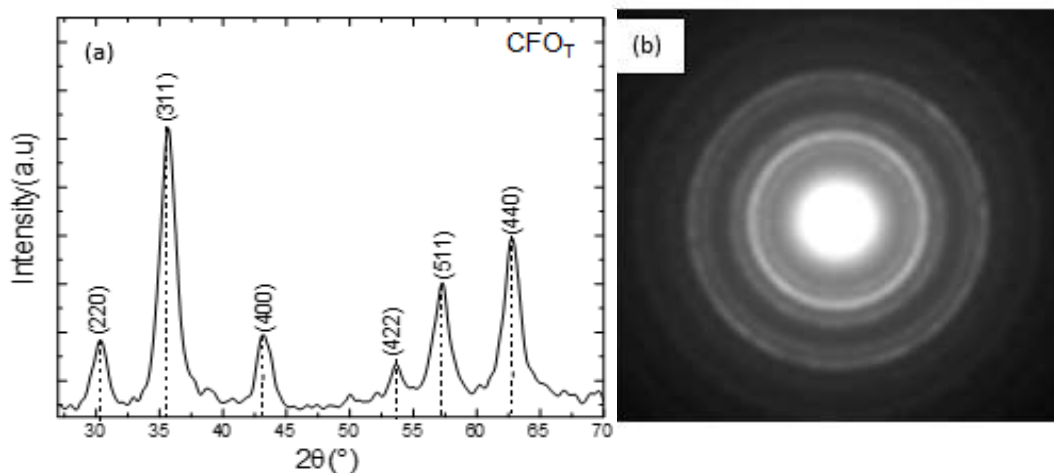
X-Ray Diffraction

Figure S1: **(a)** XRD pattern of as prepared $CoFe_2O_4$ from polyol synthesis (CFO_T), **(b)** selected area electron diffraction (SAED) pattern confirming the good crystallisation of the nanoparticles.

The spinel structure [1] was confirmed by X-ray power diffraction (XRD, Figure S1a, pdf card JCPDS 3-864). The selected area electron diffraction (SAED) measurements, Figure S1b, indicate the good crystallinity of the sample, and the peak profile represents the cubic spinel structure of $CoFe_2O_4$, in accordance with the XRD measurements. Crystallite size was obtained from the Scherrer equation. The formula relates the breadth B_{hkl}, or full width at half-maximum of a certain peak in the X-ray pattern to the average crystallite size D_{hkl}:

$$D_{hkl} = \frac{k\lambda}{B_{hkl} \cos\theta} \qquad (1)$$

where λ is the X-ray wavelength, θ is the Bragg angle expressed in radians and K the Scherrer constant, which is about 0.9 [2]. For our study, intense and symmetrical peaks were chosen and fitted with pseudo-Voight function to calculate the average crystallite size. The obtained average size was about 5.7(2) nm in agreement with the TEM analysis.

M vs (T)

At 5K, the nanoparticle moments are blocked, and the random orientation of them as well as the particle size distribution led to a broad distribution in the anisotropy energy barrier. As the temperature increases, the nanoparticle moments overcome their energy barrier and then the magnetization direction of each thermally activated nanoparticle starts to flip randomly, leading to a decrease in the overall magnetization of the nanoparticles.

$$M_{TRM} = M_{nr} \int_{\Delta E_a}^{\infty} \mathcal{F}(\Delta E) \, dE \qquad (2)$$

M_{nr} is the non-relaxing component of the magnetization and ΔE_a is a critical value of energy, below which all the particles are blocked. An estimation of the anisotropy energy barrier distribution can be given by [3]:

$$\mathcal{F}(\Delta E) \propto -\frac{dM_{TRM}}{dT} \qquad (3)$$

In a real system, where nanoparticles have a distribution of size, the blocking temperature, T_b is defined as the temperature at which 50% of the particles are in superparamagnetic regime [4]. A good approximation of the TRM curve can be obtained from ZFC/FC measurements [5].

$$M_{ZFC}(H,T,t) = M_{rev}(H,T) + M_{IRM}(H,T,t) \qquad (4)$$

$$M_{FC}(H,T,t) = M_{rev}(H,T) + M_{TRM}(H,T,t) \qquad (5)$$

From eq (4) and eq (5) we can write:

$$M_{TRM}(H,T,t) = M_{FC}(H,T,t) - M_{ZFC}(H,T,t) + M_{IRM}(H,T,t) \qquad (6)$$

For an ensemble of nanoparticles M_{IRM} can be negligible and then, eq (6) can be simplified to:

$$M_{TRM}(H,T,t) = M_{FC}(H,T,t) - M_{ZFC}(H,T,t) \qquad (7)$$

For non-interacting system, the distribution of the anisotropy energy barrier can be then estimated from ($M_{FC} - M_{ZFC}$) curve:

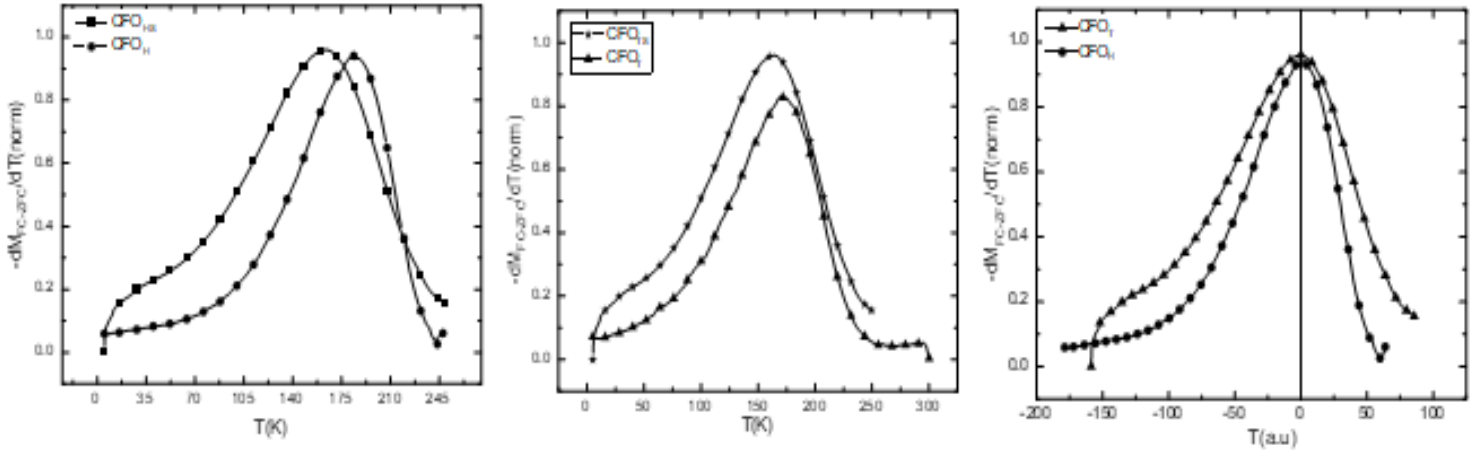$$\mathcal{F}(\Delta E) \propto -\frac{d(M_{FC} - M_{ZFC})}{dT} \qquad (8)$$

Figure S2: Distribution of magnetic anisotropy energy.

ΔM plot

Isothermal remanent magnetization (IRM) and direct current demagnetization (DCD) protocols are two effective tools to investigate interparticle interactions. IRM protocol starts with a sample in a demagnetized state, a positive and small magnetic field H is applied for a short time, which is then removed and M_{IRM} is measured at zero field. This experimental process is repeated by increasing the applied field until the remanence takes the saturation value. In DCD measurement, we start from a saturated sample, then a small field in the opposite direction of magnetization is applied for few seconds, the field is switched off and M_{DCD} is measured. The process is repeated until the sample reaches the saturation in the opposite direction increasing the magnetic field. For non-interacting single-domain particles with uniaxial anisotropy and magnetization reversal by coherent rotation, the IRM and DCD curves are related via the Wohlfarth equation [6]:

$$m_{DCD}(H) = 1 - 2m_{IRM}(H) \qquad (9)$$

where $m_{DCD}(H)$ and $m_{IRM}(H)$ represent the reduced terms $M_{DCD}(H)/M_{DCD}(H_{max})$ and $M_{IRM}(H)/M_{IRM}(H_{max})$, with $M_{DCD}(H_{max})$ and $M_{IRM}(H_{max})$ being the remanence values for the DCD and IRM curves for a large reversal field H_{max} capable of fully saturate the sample. Kelly et al. [7] have proposed :

$$\Delta M = m_{DCD}(H) - 1 + 2m_{IRM}(H) \qquad (10)$$

The plot is equal to zero and deviates from this value in case of interactions: positive or negative deviations are indicative of the predominance of interactions promoting the magnetized (e.g., exchange interaction) or demagnetized state (dipolar interaction), respectively.

The derivative of the remanence curves with respect to the magnetic field H represents the irreversible susceptibility ,or susceptibility of the irreversible magnetization[8]:

$$\chi_{irr}(H) = \frac{dm}{dH} \qquad (11)$$

χ_{irr} can be considered as a measure of the energy barrier distribution, which is in a real system of nanoparticles the energy barrier distribution is associated with a distribution of particles coercivities, generally called switching field distribution (SFD). The remanence coercivity in IRM is defined as the field where IRM curve reaches its half maximum value and as the field where DCD is equal to zero, which corresponds to the maximum of the maximum of SFD.
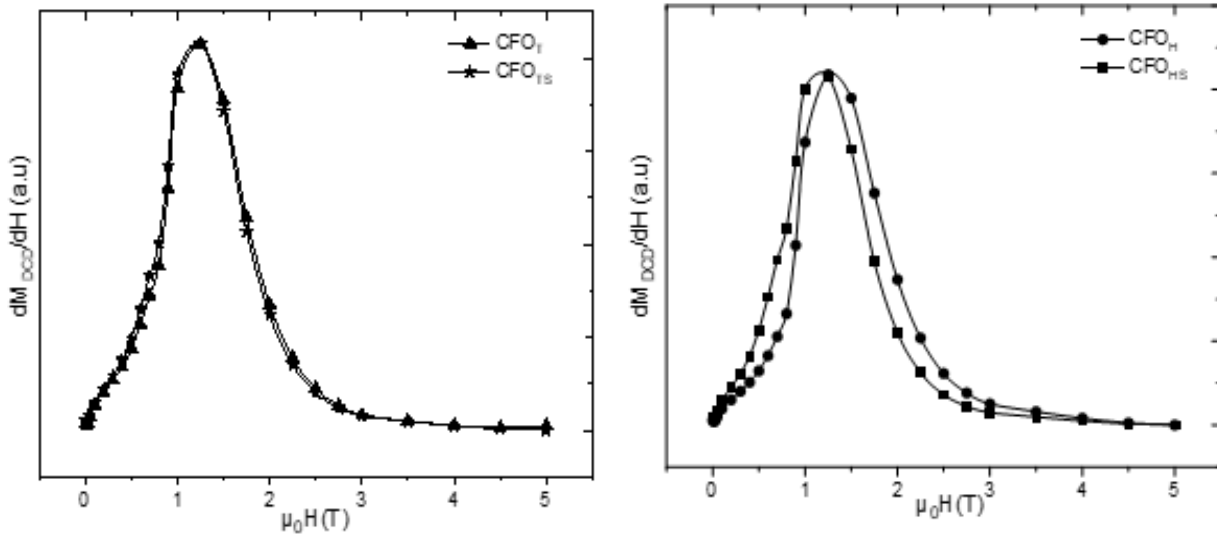

Figure S3: switching field distribution (SFD) from DCD curves.

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