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MDPI

Supporting Information

Significant Surface Spin Effects and Exchange Bias in Iron Oxide-Based Hollow Magnetic Nanoparticles

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1. Spin-Glass-like Behaviour

The magnetic dynamics for core/void/shell (C/V/S) MNPs and hollow MNPs were studied using real $\chi'(T)$ and imaginary $\chi''(T)$ components of the AC susceptibility. Figures S1 shows the temperature dependence of the real part $\chi'(T)$ (figure S1.a for C/V/S MNPs and Figure S1b for hollow MNPs) and the imaginary part $\chi''(T)$ (Inset in figure S1.a for C/V/S MNPs and inset in figure S1.b for hollow MNPs) of the ac susceptibility at different frequencies (10, 200, 500 and 1000 Hz). These curves show a maximum for both $\chi'(T)$ and $\chi''(T)$ components, defined as T'_{max} and T''_{max}. For $\chi'(T)$ component, a shift to higher temperatures when the frequency ω increases is observed, while the value of χ' decreases. It is typical in disordered systems such as spin glasses [1]. However, $\chi'(T)$ is frequency independent at $T>T'_{max}$, indicating a superparamagnetic behaviour for both MNPs. For $\chi''(T)$ component, a shift to higher temperatures is also observed, but the value of χ'' increases. The blocking temperature, T_B, is obtained as the temperature where the maximum happens in the $\chi'(T)$ curve. The T_B values obtained are 111.61 K (ω = 10 Hz), 118.72 K (ω = 200 Hz), 119.61 K (ω = 500 Hz) and 120.50 K (ω = 1000 Hz) for C/V/S MNPs and 100.00 K (ω = 10 Hz), 108.88 K (ω = 200 Hz), 109.77 K (ω = 500 Hz) and 111.55 K (ω = 1000 Hz) for hollow MNPs.

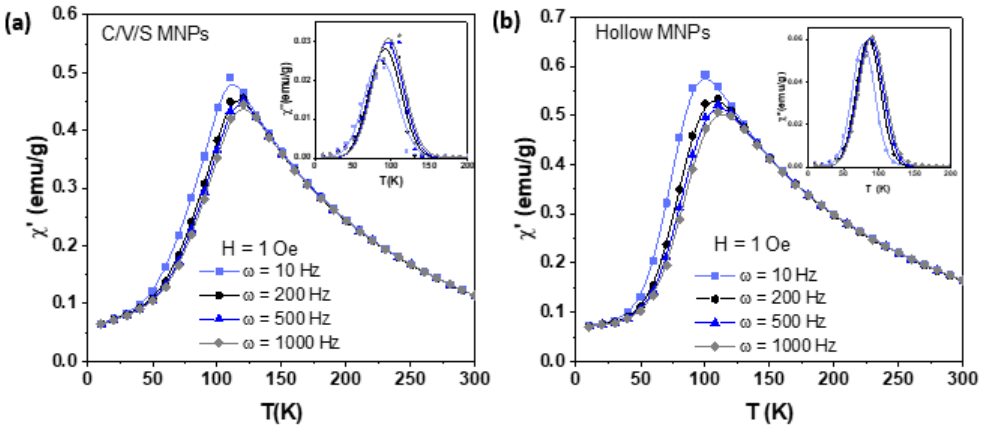

Figure S1. Temperature dependence of the real component $\chi'(T)$ of (**a**) C/V/S MNPs and (**b**) hollow MNPs at 1 Oe. Insets show the imaginary component $\chi''(T)$ of the magnetic susceptibility of C/V/S MNPs and hollow MNPs.

From AC measurements the spin-glass-like behavior of MNPs was obtained using the ϕ parameter from the relation [1]:

$$\Phi = \frac{\Delta T'_{max}}{T'_{max} \cdot \Delta \log(\omega)} \quad \text{(S1)}$$

Where $\Delta T'_{max}$ is the difference between the maximum values of T'_{max} in an interval $\Delta\log(\omega)$. Depending on the values obtained from Φ, it is possible to differentiate whether the MNPs behave as a spin-glass-like system (if Φ <0.06) [2]. In our case, values of Φ = 0.04 were obtained for C/V/S MNPs and Φ = 0.05 for hollow MNPs, suggesting a spin-glass-like surface behavior in both MNPs.

2. Hysteresis Loops under FC Conditions of Solid and Hollow Fe_3O_4 MNPs

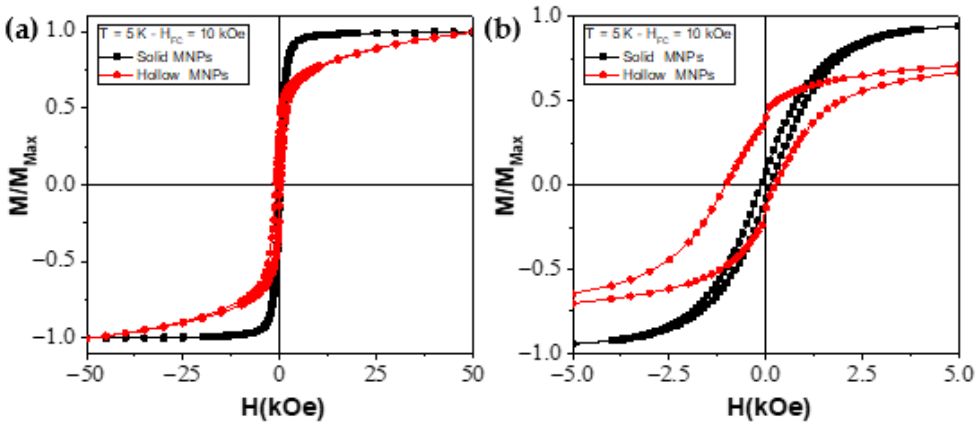

Figure S2. Hysteresis loops of solid iron oxide based MNPs (black points) and hollow iron oxide based MNPs (red points) at 5 K and with H_{FC} = 10 kOe in the range of (**a**) −50 and 50 kOe. For clarity the range between −5 and 5 kOe is shown in (**b**).

References

1. Masunaga, S.H.; Jardim, R.F.; Fichtner, P.F.P.; Rivas, J. Role of dipolar interactions in a system of Ni nanoparticles studied by magnetic susceptibility measurements. *Phys. Rev. B* **2009**, *80*, 184428, https://doi.org/10.1103/physrevb.80.184428.
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