Electronic supplementary information

Thermal relaxation and collective dynamics in interacting aerosol-generated hexagonal NiFe$_2$O$_4$ nanoparticles

D. Ortega,$^{a,b,*}$ M. V. Kuznetsov,$^c$ Yu. G. Morozov,$^d$ O. V. Belousova$^d$ and I. P. Parkin$^e$

$^a$ Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Cantoblanco 28049, Madrid, Spain
$^b$ Institute of Biomedical Engineering, University College London, WC1E 6BT London, UK
$^c$ N. P. Ogarev Mordovian State University, Saransk, Republic of Mordovia, 430005 Russia
$^d$ Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Moscow Region, 142432, Russia
$^e$ Department of Chemistry, Materials Chemistry Centre, University College London, 20 Gordon Street, London, UK, WC1H 0AJ

*E-mail address: d.ponce@ucl.ac.uk

Fig. S1 Bright TEM images of samples M10 (a) and M13 (b).
Fig. S2. Room temperature XPS spectra from sample M19 showing Ni (a) and Fe (b) contributions.

Table S2. Summary of the main magnetic properties for selected samples prepared under zero field. Synthesis conditions can be found in Table 1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\sigma_s$, A m$^2$kg$^{-1}$</th>
<th>$\sigma_r$, A m$^2$kg$^{-1}$</th>
<th>$\mu_0H_c$, 10$^{-2}$ T</th>
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<tbody>
<tr>
<td>M01</td>
<td>145</td>
<td>52.0</td>
<td>8.6</td>
</tr>
<tr>
<td>M02</td>
<td>105</td>
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</tr>
<tr>
<td>M03</td>
<td>25.0</td>
<td>8.9</td>
<td>2.6</td>
</tr>
<tr>
<td>M04</td>
<td>79.5</td>
<td>6.6</td>
<td>1.2</td>
</tr>
<tr>
<td>M05</td>
<td>47.0</td>
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<td>2.5</td>
</tr>
<tr>
<td>M09</td>
<td>35.0</td>
<td>13.0</td>
<td>1.6</td>
</tr>
<tr>
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</tr>
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<td>22.5</td>
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<tr>
<td>M18</td>
<td>70.5</td>
<td>18.0</td>
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Fig. S3 ZFC and FC (after applying a field $\mu_0H_{FC} = 5$ T) magnetization curves at 5 K of samples M13 (a), M15 (b) and M19 (c). Insets show the corresponding low field regions.

APPENDIX A: APPLIED FIELD AND SAMPLE HOLDER CORRECTION IN SQUID MEASUREMENTS

All magnetic measurements obtained with the hybrid SQUID-VSM magnetometer had to be corrected for field errors. The superconducting electromagnet of the instrument can never be completely discharged and, as a consequence, flux is trapped in the magnet at field values above 1000 Oe. The formation of pinning sites leads to errors on the measured field, which consequently is reflected as a virtual increase of the sample’s coercive field. This effect can be corrected post-measurement by using a highly stable paramagnetic salt, dysprosium (III) oxide (Dy$_2$O$_3$). As a paramagnet, the corresponding magnetization curve at 300K of Dy$_2$O$_3$ should consist in an anhysteretic loop showing a linear relationship with the applied field. However, upon measuring the sample, the obtained data shows a quasi-linear response with a coercive field of about 30 Oe. This field error is then corrected by estimating the real value of the field for the Dy$_2$O$_3$. The gradient of each of the magnetization curve quadrants is calculated ($\chi'$) and the theoretical field value is obtained as the product of the
measured gradient by the measured field \( (H_t = \chi' H') \). The field error is expressed as the difference between the measured and theoretical field values divided by the measured gradient:

\[
H_{\text{err}} = \frac{H - H_t}{\chi}
\]  

(A.1)

The true field is the sum of the error and the measured fields. The obtained correction is valid for any samples measured using the same field steps. An example of the field correction on a \( \text{Dy}_2\text{O}_3 \) standard sample measured at 300 K is shown in Fig. S4.

![Fig. S4 Magnetization vs field plot of a standard sample of \( \text{Dy}_2\text{O}_3 \) at 300K. Raw and field-corrected data are shown.](image)

APPENDIX B: CHARACTERISTIC LENGTHS CALCULATIONS

The size threshold value from which a multidomain magnetic particle becomes single domain \( (R_{sd}) \) can be expressed as a function of the exchange length\(^{35} \) \((l_{\text{ex}})\) through \( R_{sd} = 36\kappa l_{\text{ex}} \) (B.1), where

\[
l_{\text{ex}} = \left( A / \mu_0 S^2 \right)^{1/2}
\]

(B.2), and \( \kappa = \left( K / \mu_0 M_s^2 \right)^{1/2} \) (B.3), being \( K \) the first anisotropy constant at room temperature, \( \kappa \) the dimensionless hardness parameter, \( \mu_0 \) the permeability of the free space \( (1.2566 \times 10^{-6} \text{ J/A}^2\text{m}) \) and \( A \) the exchange stiffness constant. The latter is given by:

\[
A = n J S^2 / a
\]

(B.4)

Where \( n \) is the number of atoms per unit cell, \( a \) the lattice parameter, \( S \) the spin momentum and \( J \) the exchange constant. \( J \) is not directly measurable, but can be in turn estimated from:\(^{53} \)

\[
J = 0.3 k_B T_c
\]

(B.5)
being $T_C$ the Curie temperature. For NiFe$_2$O$_4$, $T_C = 858$ K, and hence $J = 3.55 \times 10^{-21}$ J. On the other hand, the nickel ferrite structure has 8 Ni, 16 Fe and 32 O atoms in its unit cell; that means $n = 56$. As only Ni effectively contributes to the net magnetization, $n = 8$. Substituting $J$, $n$ and $a$ (8.35 $\times 10^{-10}$ m) in Eq. (B.4), we have $A = 8.50 \times 10^{-12}$ J/m.

Inserting the corresponding values for NiFe$_2$O$_4$ (considering $K = 0.7 \times 10^4$ J/m$^3$ and $M_s = 2.71 \times 10^5$ A/m at room temperature) in Eqs. (B.2) and (B.3), it follows that $\kappa = 0.27$ and $l_{ex} = 9.58$ nm, and using these values in Eq. (B.1) we finally obtain $R_{SD} = 93.11$ nm. Additionally, the theoretical superparamagnetic size limit ($R_{SPM}$) can be easily calculated from the first anisotropy constant through the expression $R_{SPM} = \left(6k_B T / K\right)^{1/3}$ (B.6). For NiFe$_2$O$_4$ NPs we obtain $R_{SPM} = 15.25$ nm.