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Electronic Supplementary Information

Shaping Iron Oxide Nanocrystals for Magnetic Separation Applications

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Experimental Section

Chemicals. Iron(II) stearate (9% Fe, Strem Chemicals), sodium oleate (95%, Aldrich) and oleic acid (90%, Aldrich) were used as received without any additional purification.

Synthesis. Fe(II) stearate (1.24 g, 2 mmol), sodium oleate (0.1 g, 3.1 mmol) and oleic acid (13.72 mL, 39 mmol) were mixed and magnetically stirred under argon flow.[1] The resulting mixture was degassed for 1h at 100°C, subsequently heated up to 380°C (above the decomposition temperature of oleic acid) with a heating rate of ~ 5°C min^{-1}, and then maintained at that temperature for 1h. After cooling to room temperature, the sample was washed several times by sequential precipitation with a mixture of hexane and ethanol. In the last precipitation cycle the nanoparticles were dispersed in n-hexane.

Characterization. Samples for TEM were prepared by depositing them upon a carbon-coated copper grid. TEM images were obtained on a JEOL JEM 1010 microscope operating at 100 kV. HRTEM, STEM and EEL spectra were performed on a JEOL JEM 2010F operating at 200 kV. The XRD pattern of the nanoparticles synthesized was obtained with a PANalytical X'Pert PRO diffractometer using a Cu-K$_\alpha$

radiation in a 2θ range from 20-100°. Raman spectra were collected with a Renishaw in Via Reflex Raman Microscope. Experiments were conducted at room temperature by using two excitation wavelengths of 633 and 785 nm, in order to obtain complementary information. Magnetic measurements were performed using Quantum Design (MPMS XL) SQUID magnetometry. Temperature-dependent magnetization curves of the samples were collected after zero-field cooling (ZFC) and field-cooling (FC) the samples down to 2 K, from 2 to 380K and applying a 5 mT magnetic field. Field-dependent magnetization curves were obtained at H = -4.5 to 4.5 T at 5 and 300 K. In order to study the exchange bias, the measurements were performed after cooling from 340 K in a 4.5 T magnetic field. Size histograms were obtained by manual counting over 300 particles (diagonal length). Size distribution was fitted to a log-normal function and the results appear expressed in terms of mean and standard deviation as x */ σ (68.3%).[2] Dynamic light scattering measurements were performed on a Zetasizer Nano ZS (Malvern Instruments Ltd.) at a detection angle of 173º. All experiments were conducted at room temperature using a 633nm He-Ne laser operating a 4 mW.

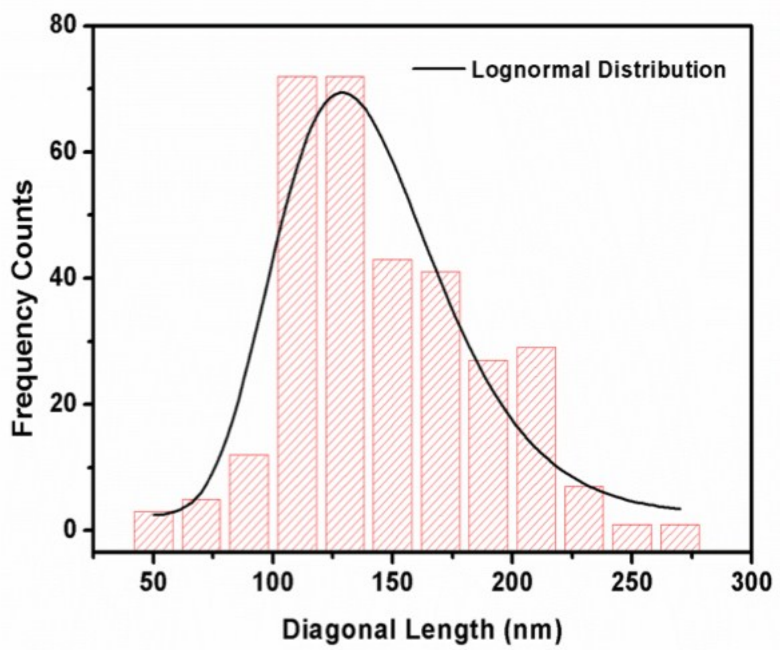

Figure S1. Size distribution (diagonal length) analysis fitted with a lognormal function

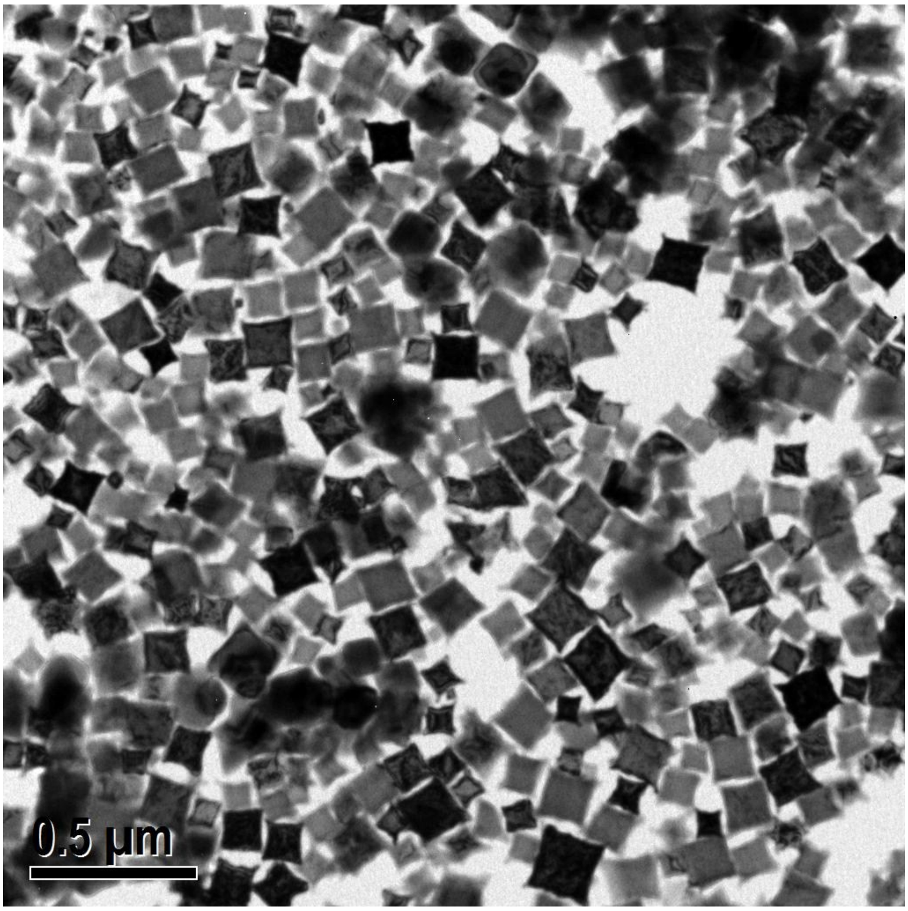

Figure S2. TEM image with a general overview of the nanoparticles.

d_{hkl} values of the spots in the Fourier Transform (figure S3) of the HRTEM image included in figure 2e, were measured using the Digital Micrograph® (GATAN) software. The values obtained are 0.479 nm and 0.282 nm, as it is shown in figure S2. These values match quite well the theoretical d_{hkl} values corresponding to the (111) and (220) reflections of the magnetite respectively (0.4852 and 0.2967 nm), neglecting the associated experimental error. In addition, for a more accurate indexation, the experimental angle between the two spots was determined, with a resulting value of 35.35º in the FFT.

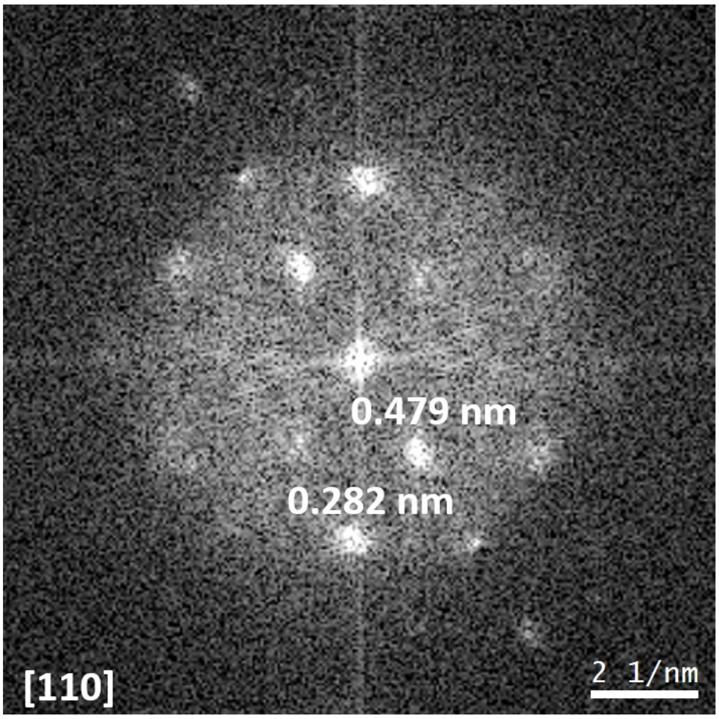

Figure S3. Fourier Transform of the HRTEM image included in figure 2e, indicating the d_{hkl} values corresponding to the (111) and (220) reflections of the crystalline lattice at the tip, confirming the presence of magnetite.

In order to obtain more information about the phase composition, a quantitative Rietveld analysis was performed using the Rietica program.[3] The weight fraction of a phase *p*, W_p, can be written as:

$$W_p = \frac{(SZMV)_p}{\sum_i (SZMV)_i} \qquad (1)$$

where S is the scale factor, Z is the number of formula units per unit cell, M is the molecular weight of the formula unit, V is the unit cell volume and i indicates each phase present in the sample. This analysis yields a weight percentage of 53%, 41% and 6% for Fe_3O_4, FeO and Fe, respectively, with an uncertainty associated to the weight percentages of ± 1.0%.

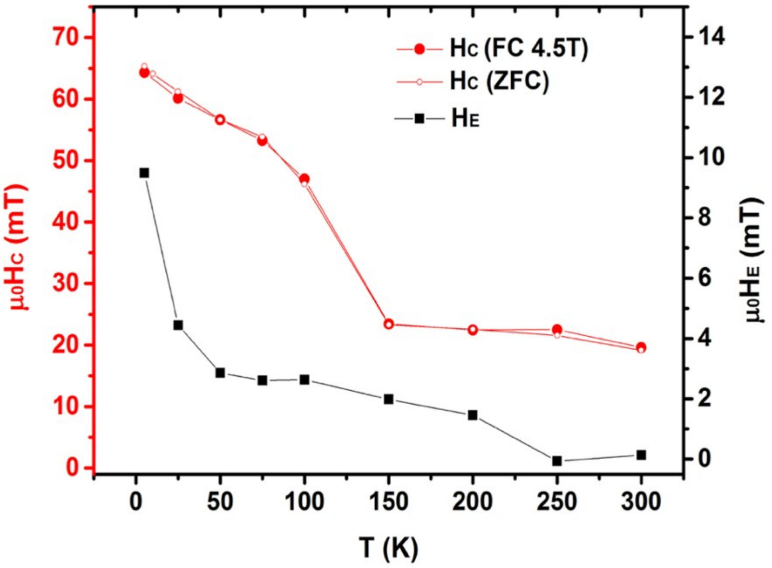

Figure S4. Temperature-dependent exchange bias and coercive field values, obtained from magnetization hysteresis loops recorded after ZFC and FC.

Dynamic light scattering (DLS) measurements were performed, in order to check the variation in the average hydrodynamic size of the octapod-shaped nanoparticles, after transfer to cyclohexane (in red) and after transfer to aqueous solution (in blue). To transfer the nanoparticles to water, tetramethyl ammonium hydroxide (TMAOH) was employed, following a procedure reported elsewhere.[4]

The average hydrodynamic diameter registered with the DLS measurements are 239± 7 nm (in cyclohexane) and 198± 9 nm in aqueous solution, as shown in figure S5. These differences in the values of average hydrodynamic diameter can be justified considering the presence of molecules of oleic acid attached in the surface of the nanoparticles. In order to transfer the nanoparticles to aqueous solution, the sample was washed several times to remove any residual oleic acid molecules, so that the TMAOH can become adsorbed on the surface of the nanoparticles, and create the electrostatic double layer to render the nanoparticles stable in water solution.

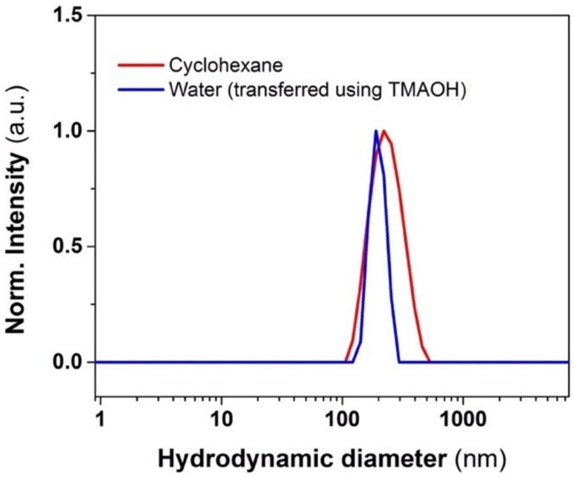

Figure S5. DLS measurements of the nanoparticles in solution; in cyclohexane (red) and in water (blue).

Calculation of the magnetophoretic mobility values in Table I

The magnetophoretic mobility values of the magnetic beads and of the FeO-Fe_3O_4 nanocrystals were calculated using equation (1).

The magnetophoretic mobility values of the magnetic swimmers were calculated using the following equation:

$$\xi = \frac{V_{magnetic-shell}\Delta\chi}{12\pi\eta R_H}$$

on which, $V_{magnetic\text{-}shell}$ refers to half the volume of a concentric shell of one or three layers of $MnFe_2O_4$ nanoparticles thick (as these swimmers have a Janus morphology[5]), $\Delta\chi$ is the relative magnetic susceptibility, η is the viscosity of the solvent, and R_H is the hydrodynamic radius.

References

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