## Supplementary Materials:

Mössbauer spectroscopy results:

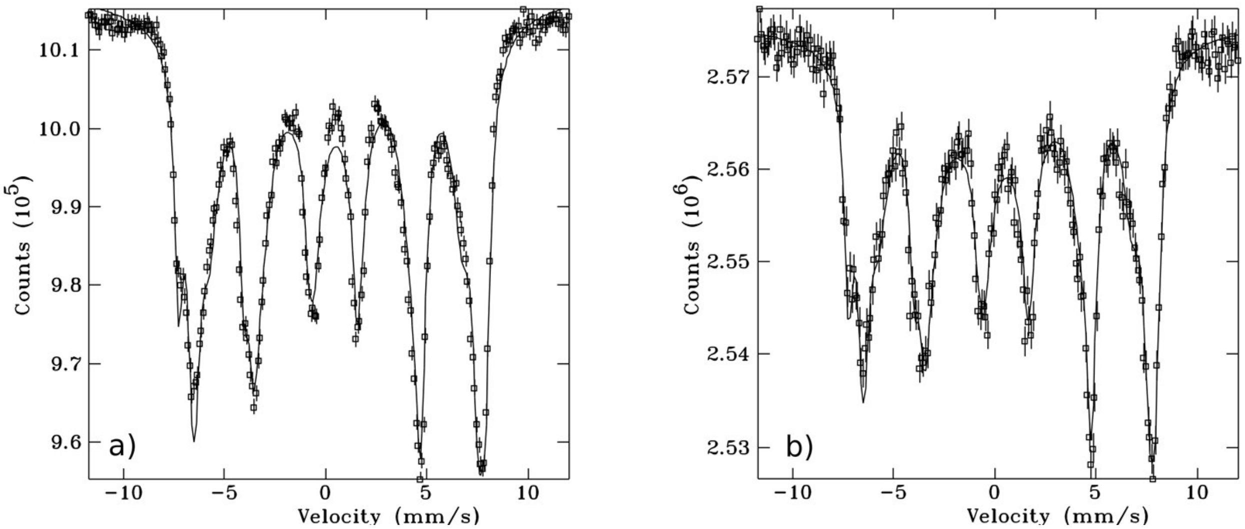

Figure SM1: Mössbauer spectra collected at room temperature for 10 nm Fe-oxide (a) and Fe-oxide/$SiO_2$ nanoparticles (b). Solid lines are fits described in the text.

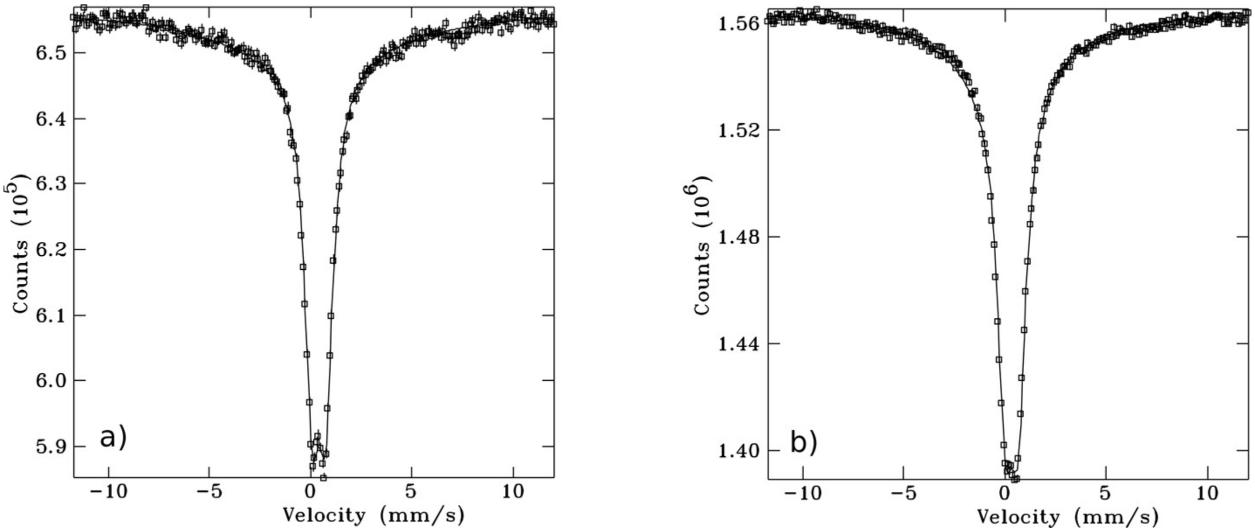

Figure SM2: Mössbauer spectra collected at room temperature for 3 nm Fe-oxide (a) and Fe-oxide/$SiO_2$ nanoparticles (b). Solid lines are fits described in the text.

Figures SM1 and SM2 show the spectra at room temperature of the 10 and 3 nm Fe-oxide bare and $SiO_2$ coated nanoparticles, and Table SM1 summarizes the hyperfine parameters determined from non-linear least-squares fit to the spectra using first-order perturbation theory to determine the energy splittings and Lorentzian linewidths ($\Gamma$ = FWHM). Firstly, the spectra reflect the degree of magnetic relaxation of the nanoparticle (i.e. relative proximity to the superparamagentic blocking temperature), and identify the Fe species via the hyperfine parameters. The sextet splitting of a Mössbauer spectrum is due to the local magnetic field experienced by $^{57}$Fe nuclei. For nanoparticles, the onset of superparamagnetism results in a collapse of the spectrum, since the hyperfine field becomes zero with increasing 180 degree spin flip rates as the temperature increases. Since both nanoparticles consist spinel Fe-oxide, the large difference in the degree of collapse for the two nanoparticles was consistent with the significant difference in the particle size (3 nm vs 10 nm diameters). The hyperfine field ($B_{hf}$ resulting in the sextet splitting of the 10 nm MNPs) isomer shift ($\delta$), and relative abundance (proportional to the relative areas of the sites) for the Fe-sites in the large particles were typical of a non-stoichiometric spinel Fe-oxide, containing octahedral $Fe^{2+}$ and $Fe^{3+}$, and tetrahedral $Fe^{3+}$, and suggested more strongly a $Fe_3O_4$-like composition. The broadened line widths ($\Gamma$ vs. $\Gamma_{nat}$ = 0.13(3) mm/s of the source) result from structural and chemical disorder; however $\Gamma > \sim 0.4$ mm/s line broadening in nanoparticles is due to the onset of superparamagnetic relaxation. For the 3 nm diameter MNPs, relaxation effects clearly dominate the spectrum, and the large quadrupole split doublet ($\Delta$) and $\delta$ values are in keeping with a mixture of $\gamma$-$Fe_2O_3$ and $Fe_3O_4$ in nanoparticulate form [1,2,3].

Table SM1: Summary of the hyperfine parameters for the Fe-sites from Mössbauer spectra collected at room temperature.

| **Sample** | **Site** | **Γ (mm/s)** | **δ (mm/s)** | **$B_{hf}$ (T)** | **Δ (mm/s)** | **Relative Area (%)** |
|---|---|---|---|---|---|---|
| **3 nm Fe-oxide** | I | 0.396(3) | 0.457(8) | 0 | 0.673(7) | 100 |
| **3 nm Fe-oxide/$SiO_2$** | I | 0.323(3) | 0.488(3) | 0 | 0.649(6) | 100 |
| **10 nm Fe-oxide** | I | 0.37(2) | 0.517(7) | 43.73(8) | 0 | 46 |
|  | II | 0.24(2) | 0.336(9) | 47.15(7) | -0.03(2) | 20 |
|  | III | 0.58(5) | 0.48(2) | 38.8(3) | 0 | 34 |
| **10 nm Fe-oxide/$SiO_2$** | I | 0.34(3) | 0.59(1) | 43.94(9) | -0.05(2) | 41 |
|  | II | 0.26(2) | 0.38(1) | 47.13(8) | -0.05(2) | 24 |
|  | III | 0.60(6) | 0.52(3) | 38.9(3) | 0 | 35 |

## REFERENCES

[1] C. L. Dennis et al., Adv. Funct. Mater. **2015**, *25*, 4300.

[2] V. Yathindranath et al., Adv. Funct. Mater. **2011**, 21, 1457.

[3] C. L. Dennis et al., Nanotechnology, **2009**, *20*, 395103.