

Supporting Information

Rational Design, Fabrication and Performance of Monolithic Superparamagnetic Iron

Oxide/Silica Nanocomposite Inductors

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Experimental Section

Sample Synthesis and Preparation

The core/shell iron-oxide/silica nanoparticles were synthesized by ammonium hydroxide-driven oxygen substitution onto iron chloride salts followed by a modified Stober process to deposit the silica shells. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (4.44 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.65 g) were dissolved in H_2O (190 mL). Ammonium hydroxide (~28%, 10 mL) was then added dropwise to the vigorously stirred reaction. The product was collected and washed with 2M nitric acid, and then H_2O . The nanoparticles were next dispersed in H_2O (200 mL), and the pH was raised to 7 using additional ammonium hydroxide. Triethylamine (5.5 mL) was introduced to the suspension and allowed to fully mix. Tetraethyl orthosilicate (TEOS) (see Table 1 for TEOS versus silica shell thickness data) in ethanol (123 mL) was added to this nanoparticle suspension, and stirred for 15 minutes. The silica-coated iron-oxide nanoparticles were precipitated from solution by lowering the pH to between 7 and 8 using 2M nitric acid. The precipitated core/shell nanoparticle product was collected and washed with ethanol. The dried nanoparticles were finally consolidated using a hot press (Thermal Technologies) at 415 °C and 80 MPa for 20 minutes under an argon atmosphere.

Measurement and Characterization

Analysis was conducted on the nanoparticle powder and sintered monolithic nanocomposite using SEM-EDS (HD2000, Hitachi), TEM (H7600T, Hitachi), XRD (Brüker D8 Da-Vinci), and SQUID magnetometry and susceptometry (Quantum Design MPMS XL5). Magnetometry experiments were done on samples that were 50 kOe field-cooled from 400 K to 10 K before hysteresis loops were collected. Transmission Mössbauer spectra were collected at 10 K using a Janis SHI-850 closed cycle refrigeration system and a WissEl constant acceleration spectrometer with a 10 GBq $^{57}\text{CoRh}$ source. The source drive velocity was calibrated using a 6 μm thick $\alpha\text{-Fe}$ foil at room temperature. Q factors were calculated using the following equation:

$$Q \text{ Factor} = \frac{2\pi(\text{Frequency})(\text{Inductance})}{(\text{Resistance})}$$

Table S1) Correlation between volume of TEOS used during synthesis for the silica shells and the resulting shell thickness determined from transmission electron microscopy (TEM) images.

TEOS used in synthesis (mL)	Nanoparticle's silica shell thickness (nm)
1.4	3.6 ± 1.4
2.8	4.6 ± 1.8
4.2	5.2 ± 2.5

Table S2) Results of fits to the AC susceptibility data for the nanoparticles to the Vogel-Fulcher law (as described in the text). $\nu_0 = 1 - 3 \times 10^{12}$ Hz.

TEM measurement of nanoparticle system		AC susceptibility data	
Fe-oxide core diameter (nm)	SiO ₂ shell thickness (nm)	K (erg/cm ³)	T_0 (K)
4.6	3.6	$4.3 \pm 0.3 \times 10^6$	153 ± 13

4.9	4.6	$4.5 \pm 0.2 \times 10^6$	148 ± 8
4.3	5.4	$5.1 \pm 0.4 \times 10^6$	125 ± 12

Table S3) Hyperfine parameters determined from fits to the Mössbauer spectra. Γ (FWHM) = 0.22 ± 0.01 mm/s (relative to $\Gamma_{\text{nat}} = 0.133 \pm 0.002$ mm/s for the source) that reflects an amount of chemical and structural disorder about the Fe-sites typical to nanoparticles. δ (mm/s) is the (chemical) isomer shift, Δ (mm/s) is the quadrupole shift (quadrupole splitting), and B_{hf} the hyperfine field.

Fe species in nanoparticle	δ (mm/s)	Δ (mm/s)	B_{hf} (T)
Fe ₃ O ₄ tetrahedral Fe ²⁺ A-site	0.483 ± 0.002	0	49.96 ± 0.07
Fe ₃ O ₄ octahedral Fe ^{3+/2+} B-site	0.595 ± 0.005	0	53.67 ± 0.09
γ -Fe ₂ O ₃ Tetrahedral Fe ³⁺ A-site	0.403 ± 0.009	0.56 ± 0.06	50.12 ± 0.03
γ -Fe ₂ O ₃ Octahedral Fe ³⁺ B-site	0.572 ± 0.003	-0.36 ± 0.03	53.74 ± 0.02
orthosilicate: Fe ^{2.5+}	0.403 ± 0.009	-0.03 ± 0.02	51.72 ± 0.05

Figure S1a) Reitveld refined^[1] x-ray diffraction pattern of the nanoparticles with a 4.6 nm diameter Fe-oxide core and 3.6 nm thick silica shell. The black line is the refinement, and the blue represents the residuals. Bragg markers identify the reflections for the spinel structure Fd-3m space group, with $a=b=c=0.8359(5)$ nm. Occupancies of the Fe $8a$ and $16d$ sites were fixed

at 1/8 and 1/2.^[2] The broad, diffuse reflection below 18 degrees 2-theta is consistent with an amorphous silica shell.^[3]

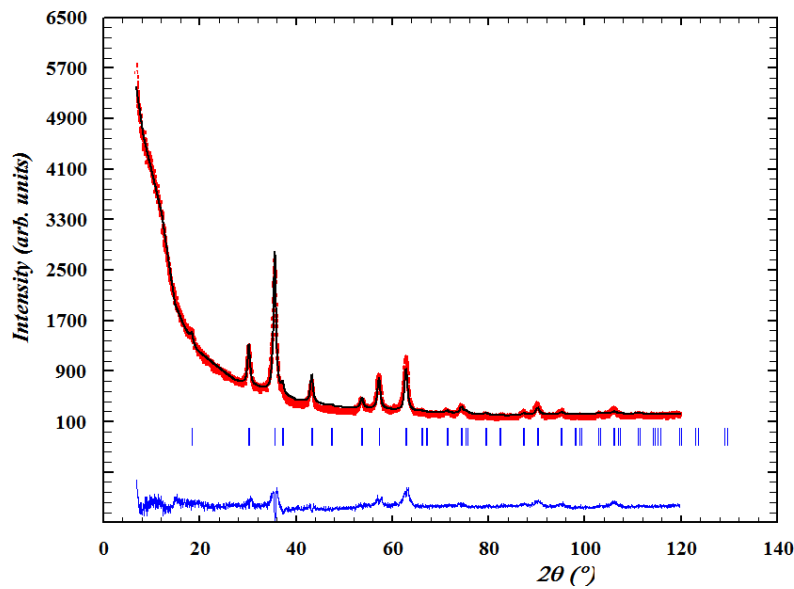


Figure S1b) Reitveld refined^[1] x-ray diffraction pattern of the nanoparticles with a 4.9 nm diameter Fe-oxide core and 4.6 nm thick silica shell. The black line is the refinement, and the blue represents the residuals. Blue Bragg markers identify the reflections for the spinel structure $Fd\text{-}3m$ space group, with $a=b=c=0.8370(2)$ nm. Occupancies of the Fe $8a$ and $16d$ sites were fixed at 1/8 and 1/2.^[2] Red Bragg markers incorporate an orthosilicate phase ($\text{Fe}_2[\text{SiO}_4]$) with reflections for the $Fd\text{-}3m$ space group, $a=b=c=0.8294(1)$ nm, and site occupancies for the Fe fixed at 1/8 and 1/2 for the $M=0.989 \text{ Fe}+0.011 \text{ Si}$ and $T=0.977 \text{ Si} + 0.023 \text{ Fe}$ $16d$ and $8a$ sites, respectively.^[2]

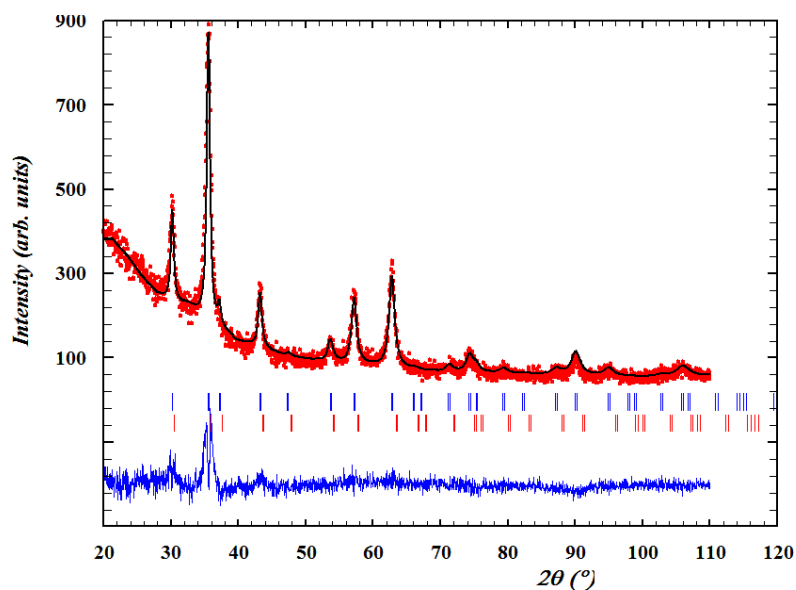


Figure S1c) Reitveld refined^[1] x-ray diffraction pattern of the nanoparticles with a 4.3 nm diameter Fe-oxide core and 4.4 nm thick silica shell. The black line is the refinement, and the blue represents the residuals. Bragg markers identify the reflections for the spinel structure Fd-3m space group, with $a=b=c=0.8363(3)$ nm. Occupancies of the Fe $8a$ and $16d$ sites were fixed at 1/8 and 1/2.^[2] The broad, diffuse reflection below 18 degrees 2-theta is consistent with an amorphous silica shell.^[3]

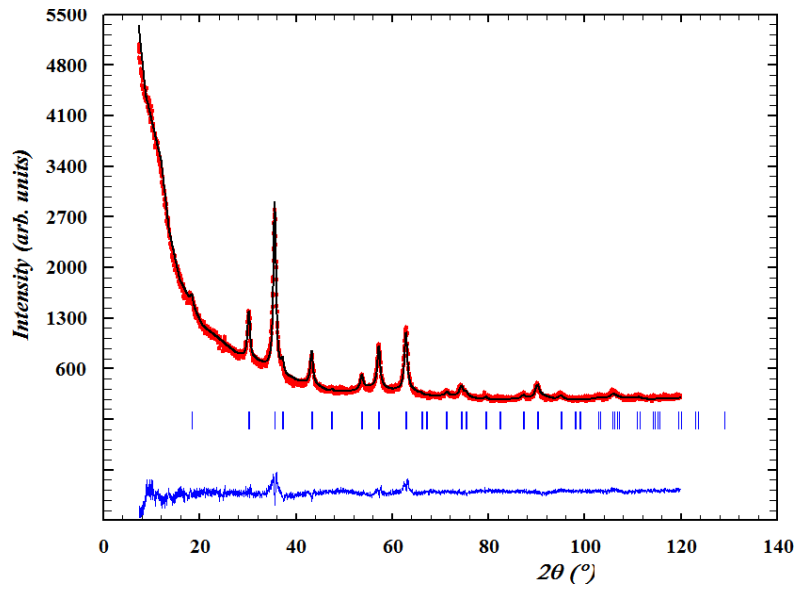


Figure S2) Left: Temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) 100 Oe magnetization (M) for the Fe-oxide/SiO₂ core/shell nanoparticles and the nanocomposite. The increasing broadening of $M_{ZFC}(T)$ is an indication of increasing interparticle interaction strength between systems. The divergence of $M_{ZFC}(T)$ and $M_{FC}(T)$ marks the superparamagnetic blocking temperature of the system. **Right:** Difference between the FC and ZFC magnetizations ($\Delta M = M_{FC} - M_{ZFC}$) as a function of temperature to more easily observe the identical T_B s between the as-prepared nanoparticle power systems despite increasing SiO₂ shell thickness (that should decrease the interparticle interactions).

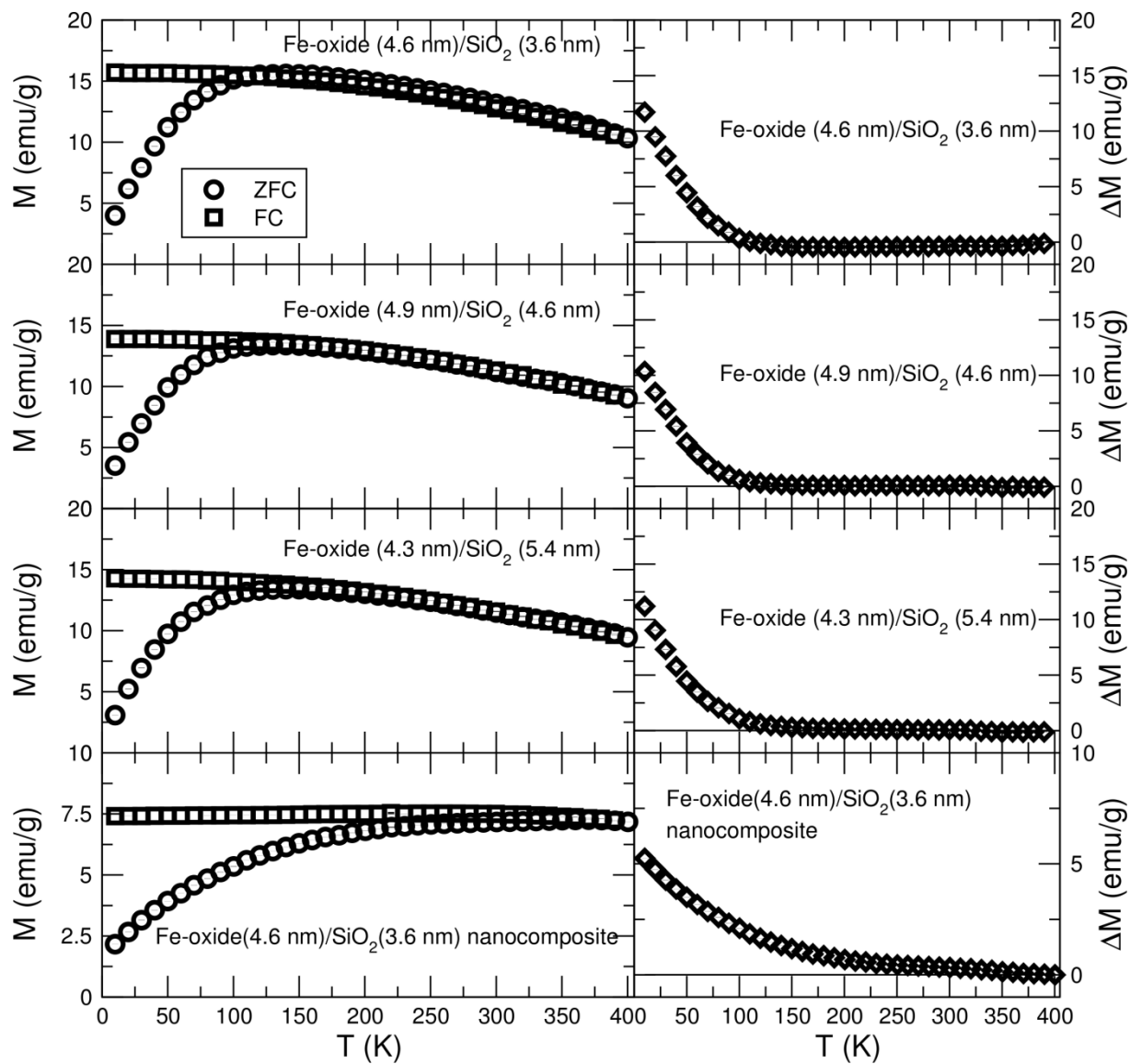
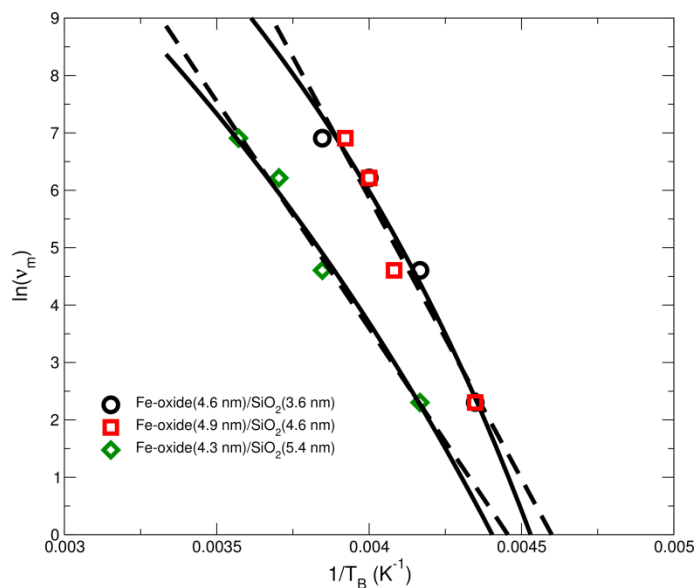


Figure S4) Inverse blocking temperature ($1/T_B$) determined from $\chi'_{AC}(T)$ scans as a function of the natural logarithm of the measuring frequency, ν_m , for the three as-prepared Fe-oxide/SiO₂ core/shell nanoparticle systems. The dashed lines represent a fit with the Néel-Brown model that yields unphysically large K ($2\text{--}3 \times 10^7$ erg/cm³) and attempt frequency, ν_0 (10^{20} Hz, frequencies much larger than the Larmour precession frequency of the atoms) values. The solid lines are a fits to the Vogel-Fulcher model that describe the slight curvature of $\ln(\nu_m)$ vs $1/T_B$ and provide reasonable K , ν_0 and T_0 values (see text).



Supporting Information References:

- _ [1] J. Rodriguez-Carvajal, Physica B, 25, 192 (1993)
- _ [2] P. Villars, K. Cenzual, Pearson's Crystal Data: Crystal Structure Database for Inorganic Compounds (on DVD), Release 2011/12, ASM International®, Materials Park, Ohio, USA
- _ [3] W. Vogel, S. Botti, S. martelli and E. Carlino, New J. Chem., 749 (1998)