Electronic Supplementary Information

Nanowarming using Ferromagnetic CoFe Nanowires

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Fig. S1. Segmented nanowire fabrication and coating Fig. S2. **Additional SEM images CoFe nanowires Fig. S3**. X-ray diffraction spectra from CoFe nanowires Fig. S4. Temperature curves for CoFe, Co, Ni nanowires **Fig. S5.** Magnetic nanowire alignment apparatus Fig. S6. Additional nanowarming temperature curves **Fig. S7.** Parallel minor loops for Ni, Co, Fe nanowires, perpendicular minor loops for **CoFe nanowires Fig. S8.** Iron concentration measurements by T_1 relaxation **Fig. S9.** Table S2. Effect of coating of segmented CoFe nanowires on relaxivity values Table S1. **Electrodeposition parameters** Table S2. Hysteresis Parameters for CoFe, Fe, Co and Ni nanowires Appendix Iron concentrations and suspension effects of coatings



Figure S1. Multistep fabrication process for magnetic nanowires. *Note that CoFe segment was replaced with Fe, Co, Ni for comparing different *M_s* nanowires.



Figure S2. Cross-sectional SEM images of (a) 4 μ m and (b) 10 μ m CoFe nanowires aligned in AAO.



Figure S3. X-ray diffraction spectra of CoFe nanowires with Au-tips.



Figure S4. Temperature curves for 8 μ m CoFe, Co, and Ni nanowires in glycerol at different concentrations. SAR values for different length CoFe nanowires in glycerol at various concentrations



Figure S5. Picture of the Helmholtz coil and DC power supply used to magnetically align the nanowires prior to SAR or nanowarming measurements.



Figure S6. Nanowarming temperature curves for three different 8 μ m CoFe nanowire samples which were aligned parallel with the AMF prior to being vitrified.



Figure S7. Minor loops for 8 μ m (a) Ni, (b) Co, and (c) Fe nanowires aligned in AAO parallel with the applied magnetic field. Also for (d) 8 μ m CoFe aligned in AAO perpendicular to the applied field. The reversal fields for the hysteresis loops were 20, 25, 30, 40, 50 and 60 kA/m (±0.25, ±0.31, ±0.38, ±0.5, ±0.63, and ±0.75 kOe).

Table S1. Table showing the electrolytic concentration, pH, and reduction potentials for Au, Ni, Co, Fe, and CoFe nanowires (NWs). All reduction potentials are vs. a saturated Ag/AgCl reference electrode.

Comment	Chemical	Concentration	рН	Reduction
Pure Au NWs	KAu(CN) ₂	10 g/L	6.0	-0.6 V
Supporting electrolyte	K ₂ PO ₄	120 g/L	6.0	
Supporting electrolyte	KH ₂ PO ₄	30 g/L	6.0	
Magnetic NWs				
Supporting electrolyte	H ₃ BO ₃	0.4 M	3.0	
Supporting electrolyte	NH ₄ Cl	0.3 M	3.0	
Supporting electrolyte	Malonic acid	0.001 M	3.0	
Wetting agent	SDS	0.0001 M	3.0	
Ni NWs	NiSO ₄	0.2 M	3.0	-0.9 V
Co NWs	CoSO ₄	0.2 M	3.0	-0.9 V
Fe NWs	FeSO ₄	0.2 M	3.0	-1.1 V
CoFe NWs	CoSO ₄ , FeSO ₄	0.1 M, 0.2 M	3.0	-1.1 V

The electrolyte solution was adjusted to pH 3.0 by adding H₂SO₄ or NaOH as needed. Pulsed potential deposition with time-on 2.5 s at -1.1V/SCE and time-off 1 s -0.7 V/SCE.

Table S2. Hc and Hk from full hysteresis loops for the nanowires in AAO were:

	Hk (Oe)	Hc (Oe)	
CoFe	1680	170	
Fe	1800	180	
Со	2500	150	
Ni	750	170	

It is important to recall that nanowire interactions will shear loops for nanowires in AAO compared to in a suspension because the nanowire density is greater. However, the M_s and anisotropy *comparisons* are important and are most practical in these aligned nanowire arrays.

Appendix. Iron concentration measurements by T₁ relaxation

Longitudinal (T_1) and transverse (T_2) relaxation times of the nanoparticles in DI water were measured using a Bruker Minispec mq60 NMR Analyzer at 1.5 T (60 MHz) and 25°C using the inversion recovery sequence and the Carr-Purcell-Meiboom-Gill sequence, respectively. For each probe, the longitudinal (r_1) and transverse (r_2) relaxivities were determined by fitting to Equation S1, below. Refer to ESI S3 for details of how the iron concentration, [Fe], of each sample was quantified

$$r_i[\text{Fe}] = \frac{1}{T_{i,\text{obs}}} - \frac{1}{T_{i,\text{H2O}}}$$
 where $i = 1 \text{ or } 2$ (S1)

The concentration of Fe in each sample was quantified using a calibration curve of FeCl₃ solutions of known concentrations. After measuring the relaxation times of the nanowire samples in DI water, an equal volume of HNO₃ (aq) was added to each sample and they were stored at room temperature overnight. This treatment decomposes the nanowires into metal aqua species. The concentration of Fe in the final media was determined by measuring T_1 of each sample using a calibration plot obtained from standard solutions of FeCl₃ in 1:1 HNO₃:DI water (same media as that of the decomposed nanowires). Note that the aqua Au species does not contribute to T_1 , so this method enables rapid determination of only the Fe concentration in each sample. The total concentration of Fe, [Fe], in each sample was calculated using Equation S2, below.

$$r_{1,\text{FeCl3}}[\text{Fe}] = \frac{1}{T_{1,\text{obs}}} - \frac{1}{T_{1,\text{H2O}}}$$
 (S2)

References

- 1. E. A. Weitz, C. Lewandowski, E. D. Smolensky, M. Marjanska and V. C. Pierre, ACS Nano, 2013, 7, 5842-5849.
- 2. E. D. Smolensky, M. Marjanska and V. C. Pierre, *Dalton Trans.*, 2012, 41, 8039-8046.

Table S3. Effect of coating of segmented CoFe nanowires on relaxivity values

Au-tip	CoFe	r ₁	r ₂	r ₂ / r ₁	Coating
(nm)	nanowires	(mM ⁻¹ s ⁻¹)	(mM ⁻¹ s ⁻¹)		
	(nm)				
200	200	0.015	0.11	7.33	Non-coated
200	200	0.03	1.06	35.3	HS-PEG-COOH
200	200	0.31	13.4	43.2	HS-PEG-COOH
					+ Dopamide-PEG

Daniel Shore, Sylvie L. Pailloux, Jinjin Zhang, Tom Gage, David J. Flannigan, Michael Garwood, Valérie C. Pierre, and Bethanie J.H. Stadler, "Electrodeposited Fe and Fe-Au Nanowires as MRI Contrast Agents," *Chemical Communications* **52** 12634-7 (2016). <u>doi:10.1039/C6CC06991F</u>