

## Electronic Supplementary Information

### Electrodeposited Fe and Fe-Au Nanowires as MRI Contrast

#### Agents

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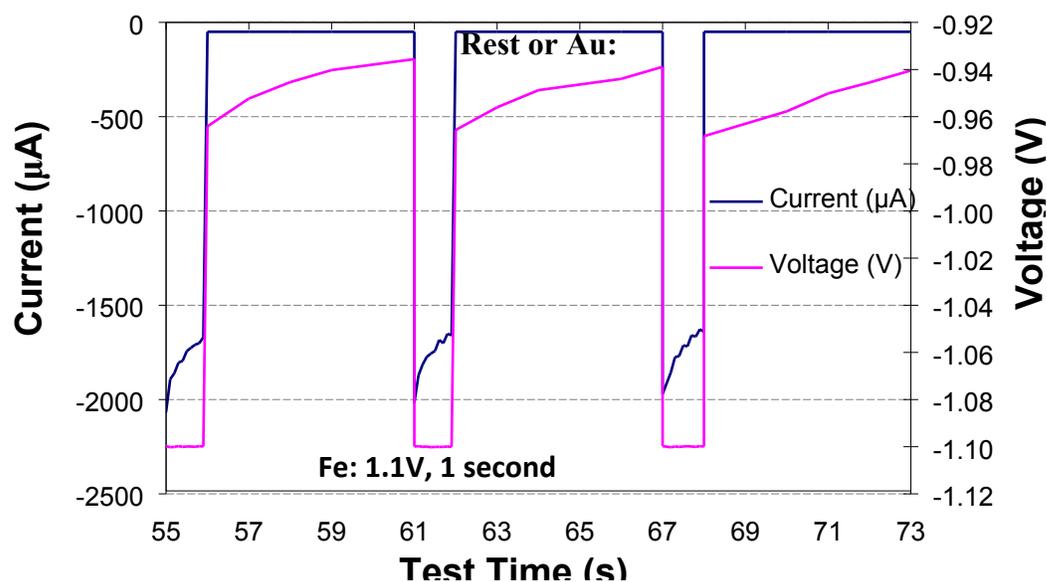
## **S1. Nanowire Fabrication**

Nanoporous anodic aluminum oxide (AAO) membranes (1 cm<sup>2</sup>) with 35 nm, 55 nm, and 100 nm pore diameters (Synkera Technologies, Inc.) were sputter-coated on one side with 20 nm W and 300 nm Cu for electrical contact. After sealing the contact side of the AAO, an Au seed layer was electrodeposited (Arbin Instruments) inside the bottom of the nanopores, -100  $\mu$ A, 1, 2, or 3 min, depending on pore diameter. Next, the Fe nanowires were synthesized using pulsed electrodeposition, -1.1 V for 1 or 2 secs, and -50  $\mu$ A for 5 or 10 secs, depending on the membrane pore diameter (see Table S1). The number of cycles and total deposition time determined the nanowire length. Figure S1 shows a plot of a typical current and voltage output over time during pulsed deposition. The Fe electrolyte contained 0.4 M H<sub>3</sub>BO<sub>3</sub>, 0.3 M NH<sub>4</sub>Cl (adjusted to pH 3 with 1 M NaOH) with 0.02 M FeSO<sub>4</sub>. For the Fe-Au nanowires, 0.002 M KAu(CN)<sub>2</sub> was added to the electrolyte before deposition, so that Au-rich segments were synthesized during -50  $\mu$ A pulses. A platinum mesh counter electrode (Technic Inc.) and Ag/AgCl reference electrode (BASi) were used in a standard three-electrode cell.

The growth electrode was removed by first dissolving the Cu layer for 10 min using a copper etchant containing 5.2 g of cupric tetrafluoroborate in 85 mL of ethylene glycol, 10 mL 2-butene-1,4-diol and 10 mL triethylorthoformate. Next the W layer was dissolved in 30% H<sub>2</sub>O<sub>2</sub> for ~1 min. The AAO membrane was etched in 1 M NaOH for 1 h. An ultrasonicator bath (33 kHz) was used once every 20 min for 3 min in order to free wires into solution. Using a magnetic stand, the nanowires were collected on the walls of the 2 mL microcentrifuge tube where they were washed 3 times with deionized (DI) water.

**Table S1.** Example electrode position parameters for different size pore diameter membranes. The number of pulse cycles was adjusted based on desired nanowire length.

Sample	NW Length ( $\mu$ m)	NW Diameter (nm)	Au seed layer	Pulsed deposition cycle		Cycles
				Fe layer	Rest or Au layer	
Fe 1	0.5 $\pm$ 0.24	35 $\pm$ 2	-100 $\mu$ A, 1 min	-1.1 V, 1 sec	-50 $\mu$ A, 5 secs	50
Fe 2	1.0 $\pm$ 0.15	35 $\pm$ 2	-100 $\mu$ A, 1 min	-1.1 V, 1 sec	-50 $\mu$ A, 5 secs	75
Fe 3	1.8 $\pm$ 0.17	35 $\pm$ 2	-100 $\mu$ A, 1 min	-1.1 V, 1 sec	-50 $\mu$ A, 5 secs	100
Fe 4	2.3 $\pm$ 0.29	35 $\pm$ 2	-100 $\mu$ A, 1 min	-1.1 V, 1 sec	-50 $\mu$ A, 5 secs	200
Fe 5	1.0 $\pm$ 0.18	50 $\pm$ 8	-100 $\mu$ A, 2 mins	-1.1 V, 1 sec	-50 $\mu$ A, 5 secs	100
Fe 6	0.7 $\pm$ 0.16	110 $\pm$ 20	-100 $\mu$ A, 3 mins	-1.1 V, 2 secs	-50 $\mu$ A, 10 secs	100
Fe-Au 1	1.0 $\pm$ 0.29	32.8 $\pm$ 4.3	-100 $\mu$ A, 1 min	-1.1 V, 1 sec	-50 $\mu$ A, 5 secs	75
Fe-Au 2	2.66 $\pm$ 0.78	28.8 $\pm$ 3.3	-100 $\mu$ A, 1 min	-1.1 V, 1 sec	-50 $\mu$ A, 5 secs	200



**Figure S1.** Plot of current and potential versus time for an example pulsed electrodeposition regime. Voltage is measured versus Ag/AgCl reference electrode and negative current indicates reduction.

## **S2. Nanowire Characterization**

Fe and Fe-Au nanowires were deposited onto Quantifoil TEM grids and imaged using FEI Tecnai G<sup>2</sup> F30 and FEI Tecnai Femto TEMs in thermionic mode. A Princeton vibrating sample magnetometer (VSM) was used to measure the hysteresis loops of the nanowires, ( $\pm 5\text{kOe}$ ,  $25\text{ Oe/s}$ ,  $25^\circ\text{C}$ ), while they were still inside the AAO, aligned parallel to the applied field.

## **S3. Nanowire Functionalization**

The surfaces of the iron nanowires were coated with Dopamide-PEG (Dop-PEG) molecules (average MW = 2,000 g). Dop-PEG was synthesized as previously reported, described below in S4.<sup>1, 2</sup> The iron surfaces of the Fe-Au nanowires were coated with Dop-PEG while the Au surfaces were coated with thiol and carboxylic acid functionalized poly(ethyleneglycol), SH-PEG-COOH in this work, (2-mercaptoethyl ether acetic acid, Aldrich, average MW=1,000 g).

Separate solutions of SH-PEG-COOH, 1 mM, and Dop-PEG, 1 mM, were prepared in pH 7.0 phosphate buffered saline. 1 mL of the Dop-PEG solution (1 mM) was added to 0.5 mg of iron nanowires and 1 mL each of the SH-PEG-COOH (1 mM) and Dop-PEG (1

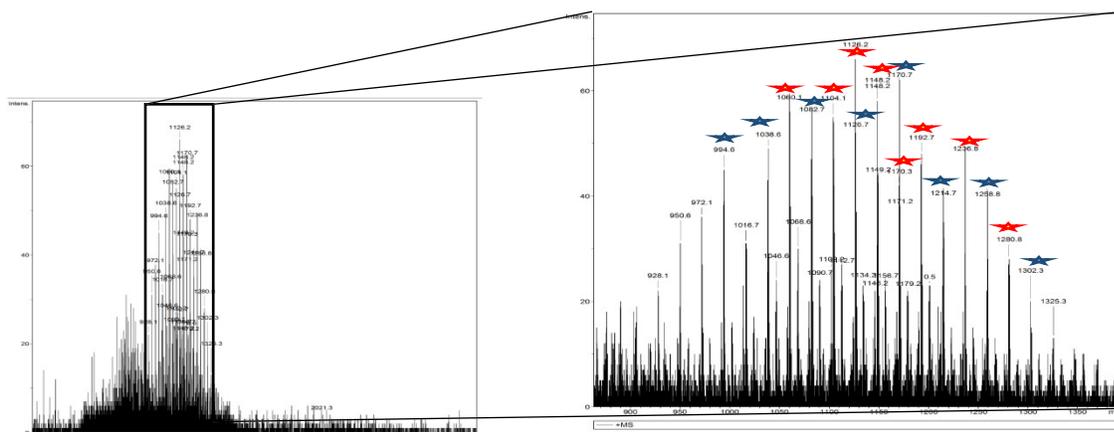
mM) were added to 0.5 mg of Fe-Au nanowires to functionalize them. Each nanowire sample was well-mixed and stored 12 hours to attach the PEG molecules.

## **S4. Dopamide-PEG Synthesis**

Dop-PEG was synthesized as follows: a solution of dopamine (16.0 mg, 0.068 mM) in DMA (dimethylacetamide, 4.0 mL) was added to a solution of PEG-NHS-2000 (100 mg, 0.050 mM) in chloroform. DIPEA (diisopropylethylamine, 19.0 mg, 0.150 mM) was added to the reaction mixture which was stirred overnight at room temperature. The solvent was removed under reduced pressure. The oily residue was diluted in 2.5 ml of water and purified using a NAP5 column. The UV active fraction was collected from the column in 10 mL tornado tubes. Water was removed by lyophilisation, yielding the product as a white solid (72.0 mg, 71%). Structure was confirmed by NMR and Mass spectrometry.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ = 6.82 (d, 1H,  $J$  = 12 Hz), 6.75 (d, 1H,  $J$  = 4 Hz), 6.58 (dd, 1H,  $J$  = 12 Hz,  $J$  = 4 Hz), 3.96 (s, 2H) 3.64 (m, 141H), 3.38 (s, 3H), 3.30 (m, 2H), 2.72 (t, 2H,  $J$  = 8 Hz)

ESI-MS for main peak ( $m/z$ ) = 1126 value comparable to the reported value for the amine analogue<sup>2</sup>



★ Z=2 difference of 0.5 between two isotopic peaks  
Loss of 22 between two peaks consistent with one PEG unit ( $\text{CH}_2\text{-CH}_2\text{-O}$ )

## **S5. Relaxivity Measurements**

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

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

The concentration of Fe in each sample was quantified using a calibration curve of FeCl<sub>3</sub> solutions of known concentrations. After measuring the relaxation times of the nanowire samples in DI water, an equal volume of HNO<sub>3</sub> (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 FeCl<sub>3</sub> in 1:1 HNO<sub>3</sub>: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.

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

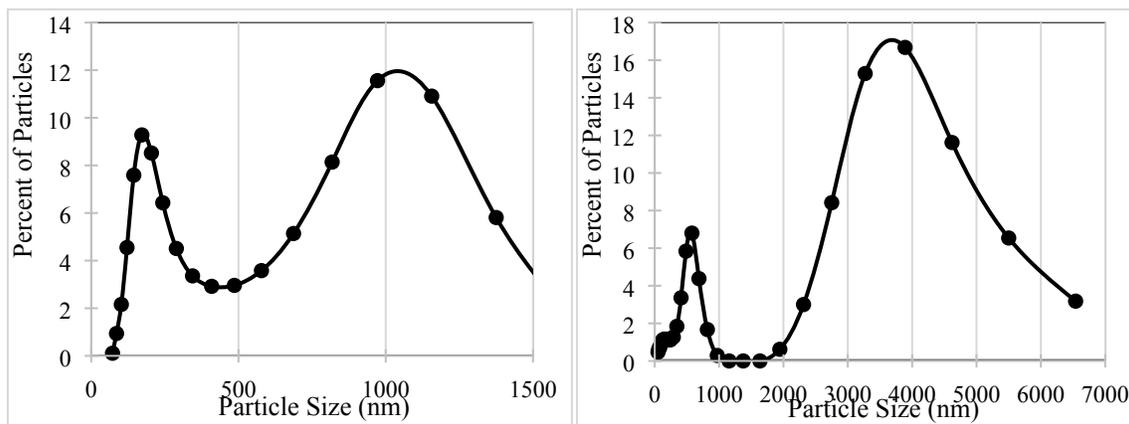
## **S6. MR Imaging**

A 9.4 T magnet equipped with a DirectDrive spectrometer with a volume transmit/receive coil (Agilent Technologies) was used for MR imaging. A conventional gradient echo sequence was applied with the following settings: repetition time = 4.9 ms, echo time = 2.5 ms, flip angle = 10°, band width = 100 kHz, and field of view = 50 × 50 × 150 mm<sup>3</sup>.

## **S7. Dynamic Light Scattering Data**

Nanowire samples Fe 4 and Fe-Au 1\* were analyzed using a Microtrac NanoFlex Dynamic Light Scatter (DLS) Particle Analyzer. Sample Fe 4 was coated with Dop-PEG and sample Fe-Au 1\* was coated with Dop-PEG and SH-PEG-COOH. Both samples were suspended in DI water during imaging. The plots in Figure S2 show the DLS data for Fe-Au 1\* (top) and Fe 4 (bottom). For the Fe-Au 1\* sample there is one peak at 173 nm and another at 879 nm, representing the nanowires' diameters and lengths, respectively. For the Fe 4 sample there is one peak at 486 nm and another at 3900 nm, for the diameters and lengths, respectively. From Table 1 in the text, Fe-Au 1\* are 32.8 ± 4.3 nm in diameter and 1.0 ± 0.29 μm long, as determined by TEM. The Fe 4 nanowires are 35 ± 2 nm in diameter and 2.3 ± 0.29 μm long. When comparing the apparent lengths and diameters from the DLS data to the actual values measured in TEM images it is important to note that DLS is optimal for determining the size of small (sub-micron), spherical or

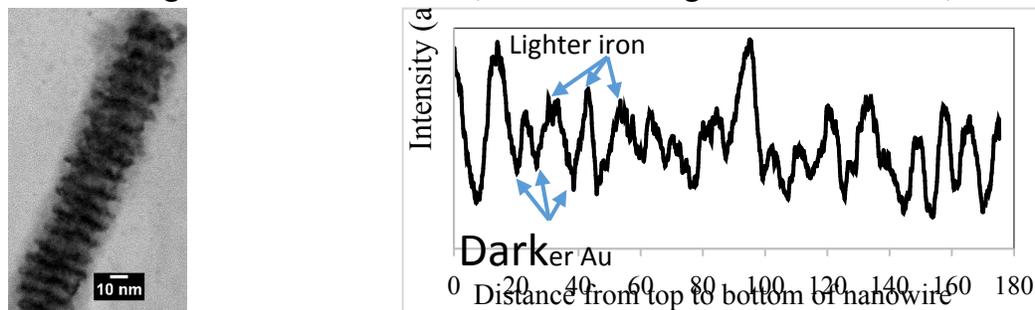
low aspect ratio particles rather than long, high aspect ratio nanowires. This may explain why some of the nanowires appear to have larger diameters and shorter lengths in the DLS plots than in the TEM images. The lengths of these nanowire samples. If the nanowire is oriented at an angle to the DLS emitter-detector the diameter. If two nanowires are nearby or overlapping they may appear as one longer nanowire to the DLS detector.

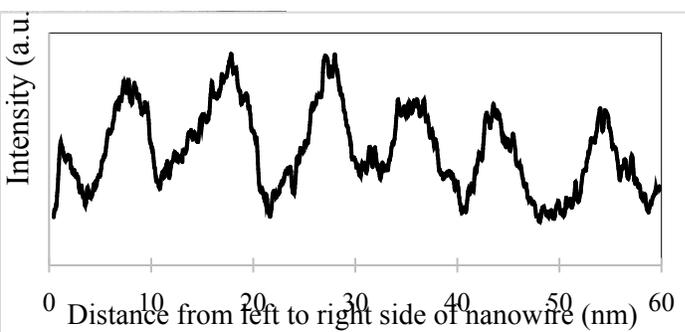


**Figure S2. DLS data showing the percent of particles at different particle sizes. Nanowires Fe-Au 1\* (left) and Fe 4 (right) which are representative of the Fe-Au and Fe nanowire samples.**

### **S8. Additional TEM images and analysis of Fe-Au Nanowires**

ImageJ software was used to analyse the high-resolution TEM images and plot the measured intensity vs. distance along the center of the nanowires to illustrate the thickness and periodicity of the iron and Au layers. The peak intensities indicate lighter, iron-rich regions of the nanowires, while the troughs indicate darker, Au-rich regions.





**Figure S3. TEM images of Fe-Au 1\* nanowires (left column) and plots showing grey value vs. distance along the center of the nanowire (right side).**

#### 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.