

Supporting Information for

Differential Magnetic Catch and Release: Experimental Parameters for Controlled Separation of Magnetic Nanoparticles

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Synthesis of Au Nanoparticles. The synthesis of Au nanoparticles was carried out following a previously reported method.^{S1} In a 3 neck round bottom flask, 10 mL of oleylamine (~30.3 mmol), 10 mL of tetralin, and 0.1 g H₂AuCl₄·nH₂O were stirred at 32° C under a flow of nitrogen for 10 minutes. A solution of 1 mL tetralin, 1 mL oleylamine, and 0.0435 g borane tert-butylamine (0.5 mmol) was sonicated and injected into the flask, immediately turning the reaction black/purple, and the stirring was continued for 1 hour at 32° C. Au nanoparticles were isolated by multiple precipitations with ethanol, centrifugation, and re-suspension in hexane. In a diagnostic UV-Vis absorbance spectrum, the resulting Au nanoparticles exhibited a characteristic surface plasmon peak at 522 nm, Figure S2, and were stored in hexane.

Synthesis of Cobalt Ferrite Nanoparticles. Synthesis of CoFe₂O₄ nanoparticles were carried out via slightly modified literature methods.^{S2} Briefly, CoFe₂O₄ nanoparticles were synthesized by combination of 0.706 g Fe(acac)₃ (2 mmol), 0.356 g Co(acac)₂ (1 mmol), 2.304 g 1,2-tetradecanediol (10 mmol), 1.69 g oleic acid (6 mmol), 1.60 g oleylamine (6 mmol), and 20 mL benzyl ether, which were mixed and stirred in a round bottom flask. The flask was evacuated and purged with N₂ three times, then under a

N₂ flow the solution was rapidly heated (~17° C/min) to 200° C for 2 hours, and the temperature was then increased at a rate of ~3° C/min to reflux. After 1 hour the heat was removed and the mixture cooled to room temperature. The nanoparticles were precipitated by addition of ethanol and isolated via centrifugation. After decanting the supernatant, the precipitate was re-dispersed in hexane in the presence of oleic acid (~0.05 mL) and oleylamine (~0.05 mL). The solution was again centrifuged to remove particle aggregates or insoluble particles, the soluble particles were precipitated with ethanol, centrifuged, and re-dispersed in hexane three times. The final particle sample was re-dispersed and stored in hexane. Larger CoFe₂O₄ nanoparticles were synthesized using smaller nanoparticles as ‘seeds’ using standard literature methods.^{S2b} The seeded growth particles were isolated from the reaction matrix by precipitation and centrifugation as described above.

Table S1: Relative Magnetic Flux and Gradients used in the Magnetic Nanoparticle Catch and Release Experiments.

Magnetic Flux Density_{center} (T)^a	Magnetic Flux Density_{edge} (T)^b	Magnetic Flux Density Gradient (T/m)^c
0.000	0.000	0.000
0.250	0.238	57.500
0.500	0.476	115.000
0.750	0.714	172.500
1.000	0.951	230.000
1.250	1.189	287.500
1.500	1.427	345.000
1.750	1.665	402.500
2.000	1.903	460.000

^a Magnetic flux density at the center of the electromagnet poles, measured with a gaussmeter. ^b Calculated flux density at the outer edge of the electromagnet pole ^c Magnetic flux gradient across the capillary, determined using Comsol Multiphysics model.

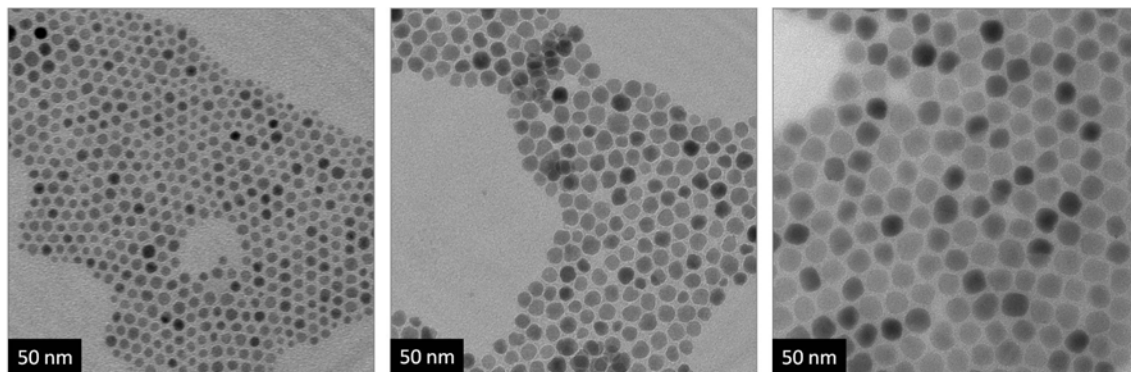


Figure S1 Transmission electron microscopy images of the CoFe_2O_4 nanoparticles used in this work are determined to have diameters of (A) 6.9 ± 1.1 ; (B) 10.6 ± 1.4 ; and (C) 16.6 ± 1.2 nm

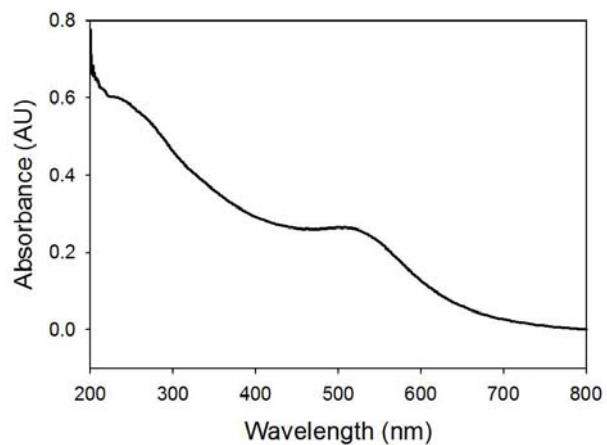


Figure S2 UV Vis absorbance spectra of ~ 4 nm diameter Au nanoparticles in hexane.

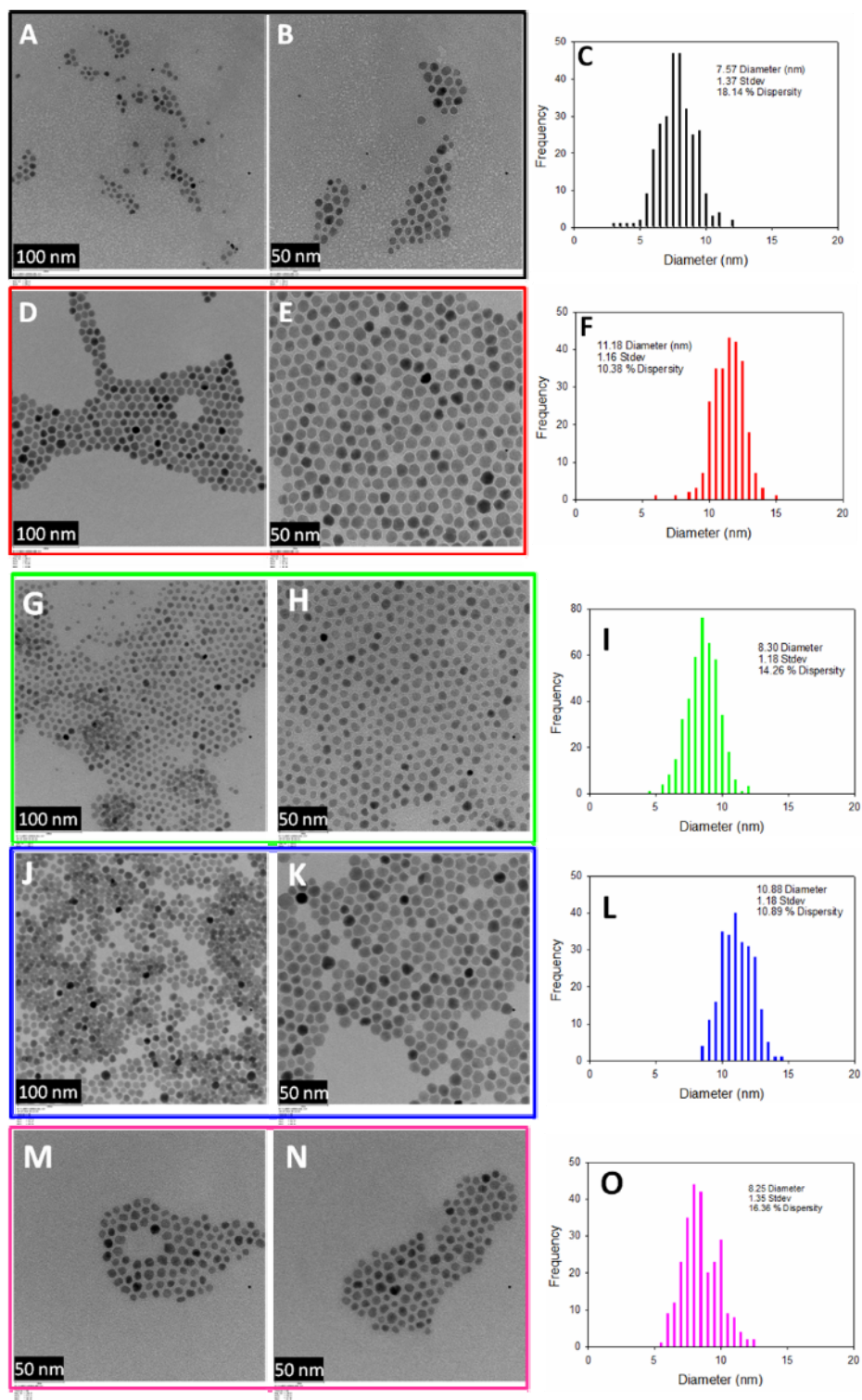


Figure S3 Transmission electron microscopy images and corresponding size distribution histograms of the particles from Figure 1: (A, B and C) void peak; (D, E, F) and trapped peak for the 3 mg/mL sample. (G, H, I) void peak; and (J, K, L) trapped peak for the 250 mg/mL sample. (M, N, O) TEM images and histogram of the tailing region (600 – 800 sec) of the 250 mg/mL sample.

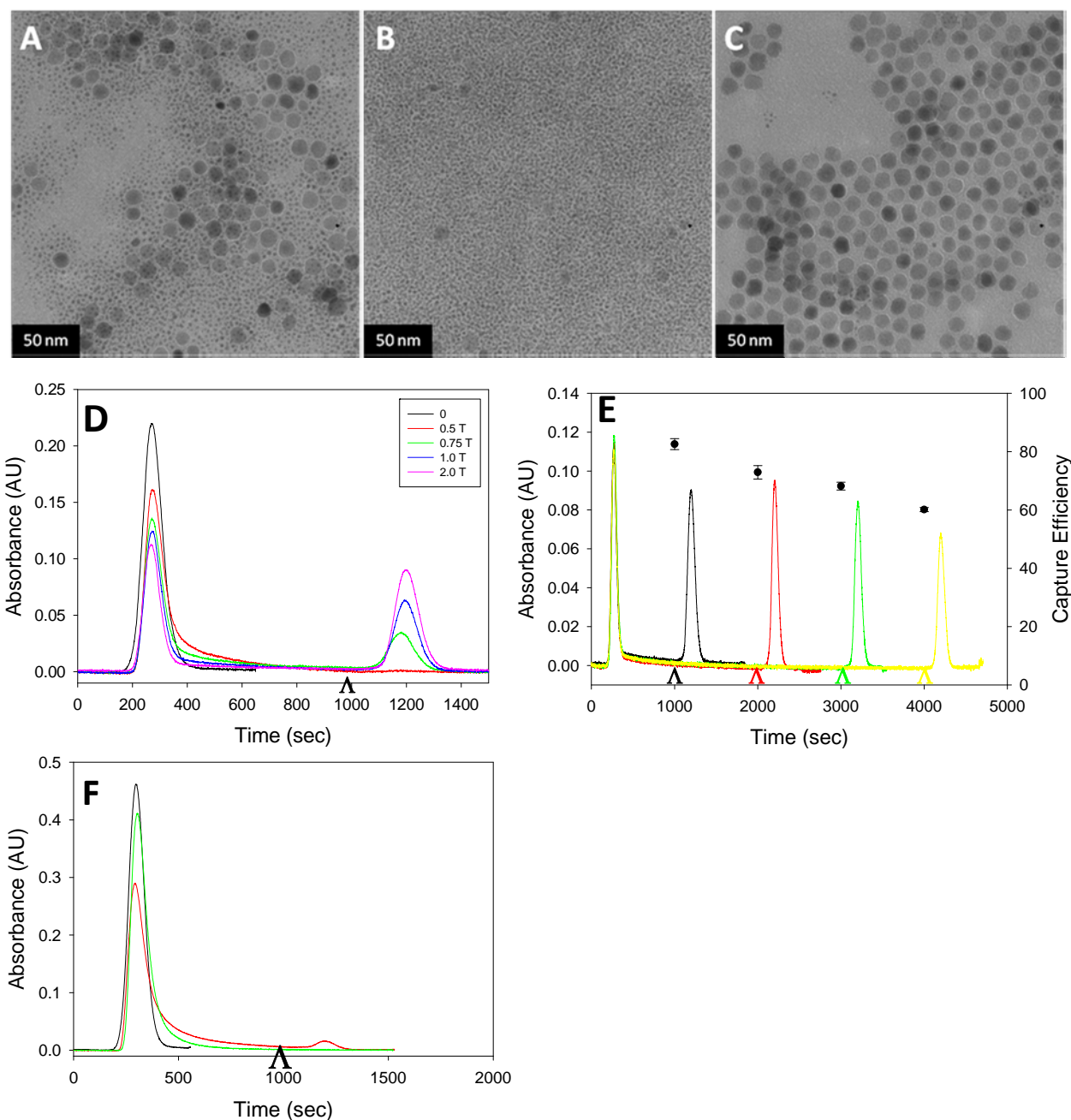


Figure S4. TEM images of the (A) mixture of the 4 nm Au and 10 nm CoFe₂O₄ nanoparticles eluting from the column under no magnetic field at a 10 μL/min flow rate; (B) void peak of 4 nm Au nanoparticles; (C) particles trapped at 2 T and released after 1000 seconds. (D) At a constant release time (1000 sec), chromatograms of a solution containing 3 ppm each 10 nm diameter CoFe₂O₄ and 4 nm diameter Au nanoparticle obtained with a flow rate of 10 μL/min, a 1.3 μL injection volume, and the indicated initial applied magnetic fluxes. (E) Chromatograms and capture efficiencies (●) obtained for this mixture under the same conditions using constant magnetic flux (2 T) and various release times. Release time (B = 0) indicated with Λ: 1000 (black line); 2000 (red line); 3000 (green line) and 4000 (yellow line) seconds. (F) 3 ppm 7 nm diameter CoFe₂O₄ nanoparticles at a flow rate of 10 μL/min using hexane as the mobile phase. Black line (0 T), red line (2 T), and green line (1 T). Λ indicates times when the magnetic field is removed.

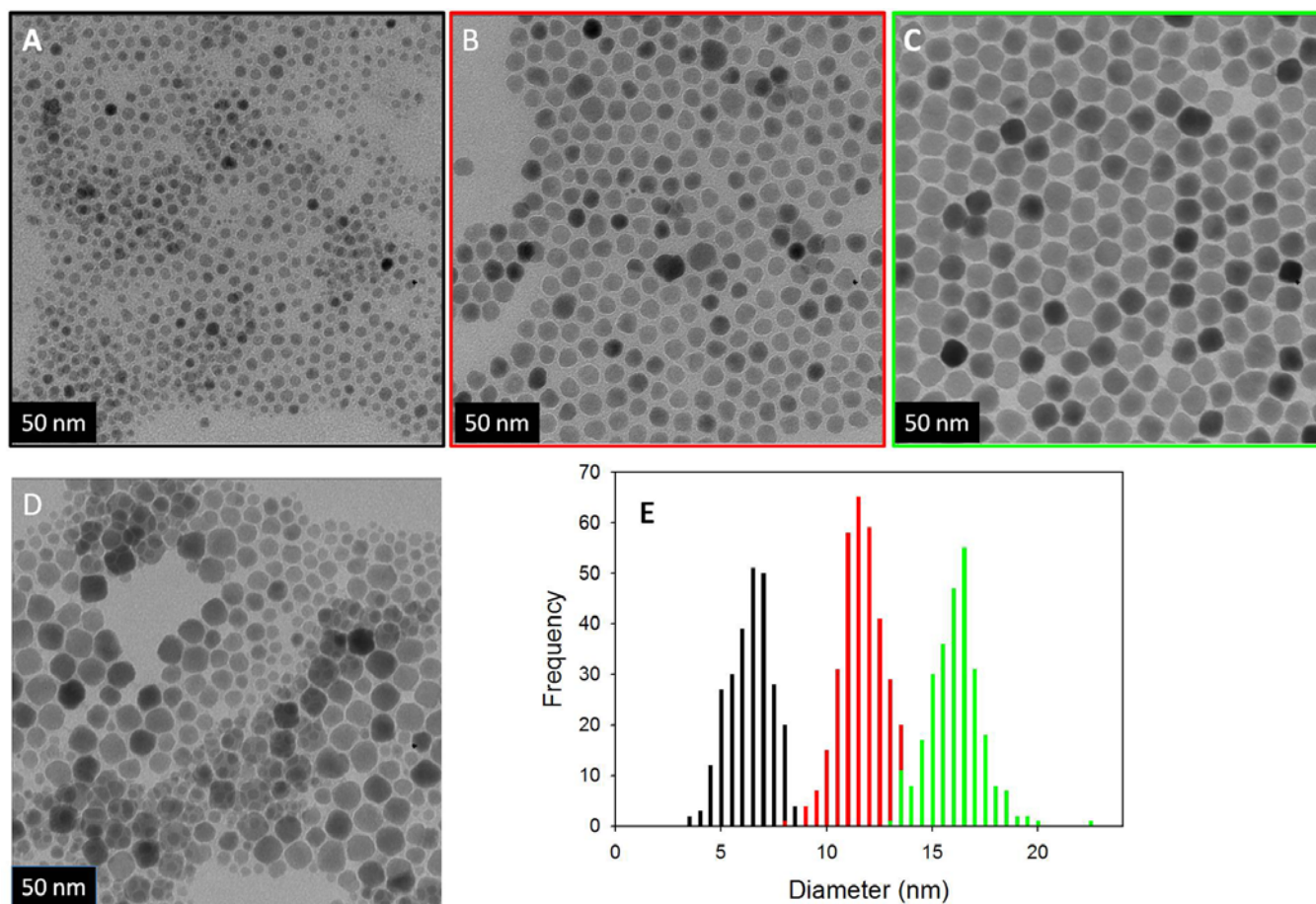


Figure S5. TEM images of fractions collected during the separation of 7, 10, and 16 nm CoFe₂O₄ nanoparticles for the peaks (A) eluted under a 2 T magnetic field, 6.2 ± 1.3 nm diameter; (B) released when the magnetic field was turned to 0.5 T, 11.6 ± 1.3 nm diameter; (C) released when the magnetic field was turned off, 15.8 ± 1.3 nm diameter. (D) TEM image of the original (pre-separation) mixture of 7, 10, and 16 nm diameter CoFe₂O₄. (E) Histograms of the particles size distributions corresponding to panels (A), (B), and (C).

Table 1: Peak area ratios for the separation of three diameters of CoFe₂O₄ nanoparticles shown in Figure 5 (main text).

	Chromatograph I	Chromatograph II	Chromatograph III
Peak 1	1.00	1.00	1.00
Peak 2	1.04	0.94	1.04
Peak 3	2.06	1.45	1.39

References.

- S1. Peng, S.; Lee, Y.; Wang, C.; Yin, H.; Dai, S.; Sun, S. *Nano Res.* **2008**, *1*, 229-234
- S2. (a) Lattauda, M; Hatton, T. A. *Langmuir* **2007**, *23*, 2158-2168. (b) Sun, S.; Zheng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G. *J. Am. Chem. Soc.* **2004**, *126*, 273 – 279.