

Supporting Information:

Heteroaggregation Approach for Depositing Magnetite Nanoparticles onto Silica-Overcoated Gold Nanorods

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Synthesis of Silica-Overcoated Au Nanorods (SiO₂-GNRs) and Magnetite Nanoparticles (Fe₃O₄ NPs)

Chemicals for Nanoparticle Synthesis, Purification, and Heteroaggregation. HAuCl₄·xH₂O (Alfa Aesar, 99.999%, where x was estimated as 3), cetyltrimethylammonium bromide (CTAB, Amresco, 99%), AgNO₃ (Alfa Aesar, 99.9995%), ascorbic acid (JT Baker, 99.5%), KBr (Alfa Aesar, ACS, 99% min), deionized water (Ricca, ACS Reagent grade, ASTM Type I, ASTM Type II), NaBH₄ (Sigma-Aldrich, 99%, 213462), tetraethyl orthosilicate (TEOS, Alfa Aesar, 99.9%), anhydrous methanol for diluting TEOS (EMD, DriSolv), methanol for SiO₂-GNR purification (Macron, Ultimar), NaOH (Sigma-Aldrich, 99%), anhydrous ethanol (Koptec, 99.5%), oleylamine (Sigma-Aldrich, 98% primary amine), hexanes (EMD, ACS, 98.5%), toluene (JT Baker, CMOS), benzyl ether (Acros, 99%), Fe(acac)₃ (Strem, 99%), and tetrahydrofuran (THF, EMD, OmniSolv, Non-UV) were used for synthesizing, purifying, and conducting heteroaggregation of SiO₂-GNRs and Fe₃O₄ NPs and for dispersing the product, Fe₃O₄-SiO₂-GNRs.

Synthesis of SiO₂-GNRs. CTAB-stabilized gold nanorods (GNRs) were synthesized using a seed-mediated approach.¹ This method produced 1 L of aqueous GNRs containing 0.1 M CTAB and 190 mg of GNRs. A secondary injection of ascorbic acid was used to reduce and deposit the residual Au precursor onto the surface of the GNRs. To prepare the GNRs for overcoating with SiO₂,² 100 mL of the unpurified product was warmed to 28 °C and then centrifuged twice at 14,000 g (IEC Centra MP4 with 854 rotor). By following the established purification procedure, the final GNR concentration was increased 10-fold in a final volume of 10 mL, and the CTAB concentration was ~1 mM.²

The concentrated GNRs were heated to 30 °C in a water bath, and the pH was increased to 10.4 by slowly adding 0.1 M NaOH. 250 µL of 20 v% TEOS in anhydrous methanol was then injected into the GNRs by syringe pump at a rate to 50 µL/min, while stirring at 150 rpm. After completing the injection, the stir rate was adjusted to 30 rpm for 30 min. The mixture was then left unstirred for 20 hours. Upon completing the reaction, the mixture was immediately divided equally among four 40-mL centrifuge tubes. The contents of each tube were diluted to 40 mL with methanol and centrifuged at 8,500 g for 10 min. This dilution and centrifugation process was repeated five times, with removal of the supernatant, redispersion of the SiO₂-GNRs in fresh methanol, and sonication between runs. The final product was stored in methanol at a concentration of 3.8 mg/mL by dilution to a final volume of 5 mL with methanol.

Synthesis of Fe₃O₄ NPs. Oleylamine-stabilized Fe₃O₄ NPs with an average diameter of 7 nm were synthesized by scaling up a heat-up method.³ 3.12 g of Fe(acac)₃ was mixed with 45 mL of benzyl ether and 45 mL of oleylamine in a 250-mL, three-necked, round-bottomed flask equipped with a condenser, thermocouple, and rubber septum. The condenser was then connected to a vacuum and inert gas manifold, and the flask was placed under vacuum for 1 hour at room temperature, followed by heating to 90 °C, backfilling with N₂, and then heating to 120 °C for 1 hour. The temperature was then ramped (at a rate of ~15 °C/min) to 290 °C and held for 1 hour. Upon cooling to room temperature, the product was purified by centrifugation by adding an equal volume of ethanol and centrifuging at 2,500 g, followed by redispersion in hexanes for storage.

Synthesis and Purification of PEG-Catechol

Chemicals for Synthesis of PEG-Catechol. Methoxypoly(ethylene glycol) acetic acid (mPEG-CM, Laysan Bio, Inc., MW = 2 kDa), dopamine hydrochloride (Sigma-Aldrich), *N,N,N',N'*-tetramethyl-*O*-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU, Sigma-Aldrich, $\geq 98.0\%$), 1-hydroxybenzotriazole hydrate (HOBt, Sigma-Aldrich, 97%), triethylamine (TEA, Sigma-Aldrich, $\geq 99\%$), dichloromethane (DCM, Sigma-Aldrich, anhydrous, $\geq 99.8\%$), *N,N*-dimethylformamide (DMF, Sigma-Aldrich, anhydrous, 99.8%), diethyl ether (Et₂O, Sigma-Aldrich, anhydrous, $\geq 99.7\%$), chloroform (CHCl₃, Sigma-Aldrich, $\geq 99.5\%$), sodium sulfate (Na₂SO₄, Sigma-Aldrich, $\geq 99.0\%$, anhydrous), and hydrochloric acid (HCl, Sigma-Aldrich, 37%) were used for the synthesis and purification of PEG-catechol.

Synthesis and Purification of PEG-Catechol. PEG-catechol was synthesized by modifying a commercially available PEG-COOH.⁴ Briefly, 500 mg (0.25 mmol) of mPEG-CM was dissolved in 6 mL of a 2:1 (v/v) solution of DCM and DMF. 72 mg (0.38 mmol) of dopamine hydrochloride and 90 mg (0.67 mmol) of HOBt were then added, and N₂ was bubbled through the mixture for 15 min. 153 mg (0.40 mmol) of HBTU and 100 μ L (0.72 mmol) of TEA were added, and the mixture was stirred under N₂ atmosphere at room temperature overnight. The solution volume was reduced by rotary evaporation, followed by acidification by adding 10 mL of 1 M HCl with mixing. The aqueous solution was extracted with 10 mL of CHCl₃ three times. The organic phase was then collected and dried with Na₂SO₄. After the solution was concentrated to <2 mL by rotary evaporation, it was precipitated with 30 mL of cold Et₂O at $-20\text{ }^{\circ}\text{C}$. The crude product (white precipitate) was purified by redissolving in ~ 2 mL of DCM and precipitation in 30 mL of cold Et₂O at $-20\text{ }^{\circ}\text{C}$ two more times. The precipitate was finally redissolved in water and lyophilized. The final, purified PEG-catechol was obtained as a white solid powder and stored at $-20\text{ }^{\circ}\text{C}$ until needed. ¹H NMR (D₂O) δ (ppm): 6.7–6.8 (m, 3H, aromatic), 3.3–4.0 (m, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.4 (t, 2H, CH₂ adjacent to aromatic ring), 2.7 (t, 2H, $-\text{CH}_2-\text{NH}-\text{CO}-$).

Unnormalized Optical Absorbance Spectra

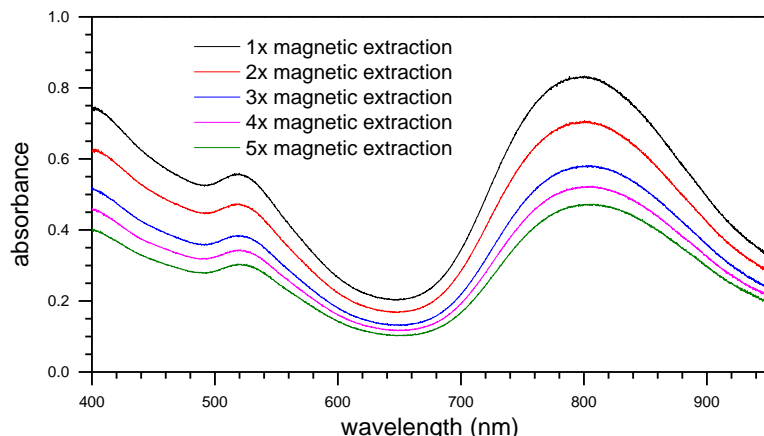


Figure S1. Unnormalized optical absorbance spectra of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-GNRs}$ during five rounds of purification through magnetic extraction. The normalized version of these spectra is provided in the main text, Figure 4.

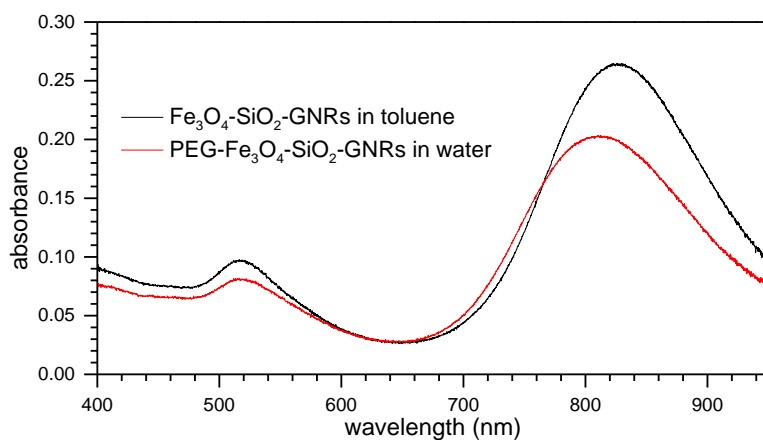


Figure S2. Unnormalized optical absorbance spectra of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-GNRs}$ in toluene and $\text{PEG-Fe}_3\text{O}_4\text{-SiO}_2\text{-GNRs}$ in water. The normalized version of these spectra is provided in the main text, Figure 5.

References

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