Supporting Information

Materials

Hydrogen tetrachloroaurate(III) (99.99%, $HAuCl_4$), sodium borohydride (98%, $NaBH_4$), sodium citrate (ACS, 99.0% min.), sulfur (325 mesh, 99.5%), selenium (325 mesh, 99.5%), nonanoic acid (97%), dimethylformamide (99%, DMF), and nitrosonium tetrafluoroborate (98%, $NOBF_4$) were purchased from Alfa Aesar. Streptavidin−iron oxide particles from *Streptomyces avidinii* (in 0.85% NaCl, 0.01 M phosphate, pH 8.0, containing 0.1% bovine serum albumin, 0.1% sodium azide), cadmium oxide (99.99%, CdO), trioctylphosphine (97%, TOP), trioctylphosphine oxide (99%, TOPO), oleylamine (70%), and poly(ethylene glycol) methyl ether thiol (M_n = 5000, mPEG-SH) were purchased from Sigma Aldrich. Octadecylphosphonic acid (ODPA) was purchase from PCI Synthesis (Newburyport, CT). Sodium hydroxide pellets (NaOH), hydrochloric acid (HCl), and isopropyl alcohol (IPA) were purchased from EMD. Tris hydrochloride (99% assay, Tris) was purchased from VWR. Tween 20 was purchased from GE Healthcare. The custom peptide (AuST) was synthesized by the Core Research Facilities at The Milton S. Hershey Medical Center of the Pennsylvania State University. All chemicals were used as received without further purification. All water used was NANOpure, 18 MΩ water.

Synthesis of Au Nanoparticles

Au nanoparticles were synthesized using a pH-stabilized $NaBH_4$ reduction of $HAuCl_4$ in water.[1] A stock solution containing 50 mM $HAuCl_4$ and 50 mM HCl was prepared in a 15-mL conical tube. A second stock solution containing 50 mM $NaBH_4$ and 50 mM NaOH in water, was prepared in a 2 mL microcentrifuge tube. To 9.6 mL of water in a 15-mL conical tube, 100 µL of the $HAuCl_4$/HCl stock solution was added. While vigorously stirring, 400 µL of the $NaBH_4$/NaOH solution was added. The reaction was stopped after 5 min, and the pH was adjusted to 7. The reaction solution was left uncapped overnight before use of the nanoparticles. The Au nanoparticles are colloidally stable, but do not have any added surface stabilizers, according to ref. 1. The λ_{max} of the surface plasmon resonance for the Au nanoparticles (~525 nm) is consistent with ref. 1.

Synthesis of CdS Nanoparticles

The synthesis of CdS nanoparticles was based on published synthetic preparations.[2,3] To a 50-mL round-bottom flask, CdO (103 mg), ODPA (0.59 g) and TOPO (6 g) were added. The contents were held under vacuum at approximately 120 °C for 1 h prior to further heating. Following the introduction of argon to the flask and its contents, the reaction was heated to 320 °C for 30 min to form a Cd-ODPA complex, evident by the clear and colorless solution. The temperature of the flask was then decreased to 120 °C and vacuum was pulled on the contents for 1 h to remove water produced by the

condensation reaction of CdO to Cd-ODPA. Following this vacuum evacuation, the reaction flask was again heated to 320 °C under argon, where 1 mL of TOP was injected into the flask. Once the temperature was stabilized at 320 °C, a stoichiometric mixture (1:1:1 TOP:S:Cd) of TOP-S was introduced through rapid injection. A yellow color slowly started to develop. The temperature was held near 320 °C for 50 minutes. Cooling was achieved by removing the heating mantle from the base of the flask, and toluene was injected near 80 °C to prevent the solidification of the TOPO solvent. The reaction solution was transferred to centrifuge tubes where IPA was added (roughly 3:1 ratio of IPA:reaction solution). Following the first centrifugation run at 5000 rpm for 5 min, the yellow precipitate was resuspended in toluene with a small amount of nonanoic acid and oleylamine, flocculated with IPA, and centrifuged. This process was repeated three times. The samples were stored in toluene in a 20 mL scintillation vial.

Phase Transfer of Cadmium Sulfide

Phase transfer was carried out using a modification of a recently published protocol.[4] In an 8-mL borosilicate vial, 4 mL of DMF was stirred vigorously with 20 mg of $NOBF_4$; 1.5 mL of the cleaned CdS nanoparticle solution in toluene was added, and stirred vigorously for 5 min. The nanoparticles were collected by centrifugation at 14000 rpm for 5 min and washed twice with DMF, with collection by centrifugation. To the washed nanoparticles in DMF, 20 mg of sodium citrate was added, and the solution was shaken vigorously for 1 min. The nanoparticles were collected by centrifugation at 14000 rpm for 5 min and washed twice with water, with collection by centrifugation. The nanoparticles were resuspended in 1 mL of water for use in the magnetic separations.

Magnetic Separations

The magnetic separations were carried out in 8-mL borosilicate vials. Amounts of Au and CdS nanoparticles were chosen such that they produced similar absorbances by UV-Vis. For the magnetic separation of Au nanoparticles from solution, 1.75 µL of a 0.53 mM solution of the AuST peptide was incubated with 400 µL of Au nanoparticle solution in 1.6 mL of 10 mM Tris/1% Tween at pH 7.5 (“Tris/Tween”) in one vial for 1.5 hours with rolling. In a separate vial, 300 µL of the Fe_2O_3-streptavidin particles were washed twice with 3 mL of water, followed by once with 3 mL of Tris/Tween and once with 2 mL of Tris/Tween. Between washes, the particles were collected with a cylindrical benchtop neodymium iron boride permanent magnet against the side of the vial, and the remaining solution was removed with a disposable pipette. After the initial incubation period, the Au-AuST solution was added to the Fe_2O_3-streptavidin particles (the magnetic portion of the final wash). This solution was shaken for 30 s and then rolled for 2 h. After this incubation period, a benchtop magnet was placed next to the vial to collect the magnetic portion against the side of the vial. The remaining solution could be removed with a disposable pipette.

The magnetic separation of Au nanoparticles from a mixture of Au and CdS nanoparticles was carried out as above, except that incubation of the peptide with the nanoparticles was carried out with 1.75 µL of the 0.53 mM AuST peptide, 400 µL of Au nanoparticles, 200 µL of CdS nanoparticles, and 1.4 mL of water. In addition, control experiments were conducted with an identical procedure as above but with the following initial incubation reaction mixtures: (1) 400 µL Au nanoparticles in 1.6 mL Tris/Tween (no peptide), (2) 200 µL CdS nanoparticles and 1.75 µL 0.53 mM AuST peptide in 1.8 mL Tris/Tween.

Preliminary Recoverability Experiments

The magnetic portion of the above magnetic separation of Au nanoparticles from solution was resuspended in 2 mL of water. With vigorous stirring, 100 mg of mPEG-SH was added to this solution and stirred for 2 hours. The magnetic portion of the sample was collected against the side of the vial with a benchtop magnet.

Characterization

Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were collected using a JEOL JEM 1200 EXII microscope operating at 80 kV. Samples for TEM analysis were prepared by briefly sonicating the samples suspended in water and immediately drop casting 8 µL onto the surface of a formvar carbon coated nickel grid, allowing the sample to settle for 3-5 min, wicking away excess moisture with a torn piece of filter paper, then air drying. UV–Visible absorption spectra were collected using an Ocean Optics HR4000 spectrometer using a DH-2000-BAL light source and quartz cuvettes. Based on the ratio of the non-normalized absorption peak at 525 nm before and after sequestration of the Au-only sample (see Figure 1), we estimate a separation efficiency of approx. 89%. It is more difficult to provide a semi-quantitative estimate of the separation efficiency for the Au/CdS system because of the overlap of the CdS and Au absorption peaks, their overall weaker signal, and the persistence of non-zero absorption at 525 nm in the UV-Visible absorption spectrum for the CdS nanoparticles. As a preliminary rough estimate, the Au/CdS absorption spectra were normalized to the CdS-only absorption spectrum, the background at 525 nm due to the presence of CdS was subtracted, and the resulting values, approximating those of Au only, were compared. Based on this treatment, it was estimated that approx. 60% of the Au was removed and approx. 40% was recovered.

1. M. N. Martin, J. I. Basham, P. Chando, S. K. Eah, *Langmuir*, 2010, **26**, 7410-7417.

2. B. Sadtler, D. O. Demchenko, H. Zheng, S. M. Hughes, M. G. Merkle, U. Dahmen, L. W. Wang, A. P. Alivisatos, *J. Am. Chem. Soc.*, 2009, **131**, 5285-5293.
3. A. E. Saunders, I. Popov, U. Banin, *J. Phys. Chem. B*, 2006, **110**, 25421-25429.
4. A. G. Dong, X. C. Ye, J. Chen, Y. J. Kang, T. Gordon, J. M. Kikkawa, C. B. Murray, *J. Am. Chem. Soc.*, 2011, **133**, 998-1006.

Supplementary Figures

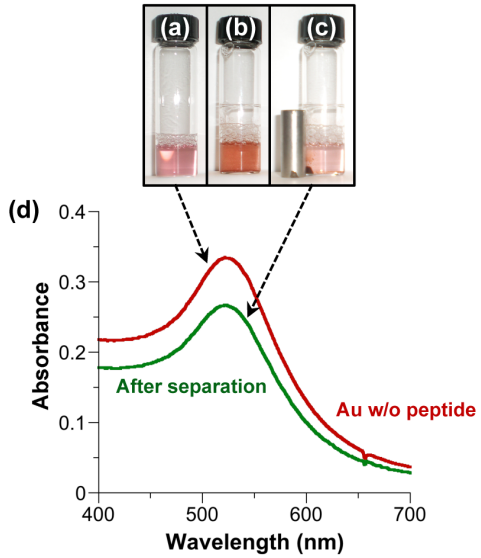

Figure S1. (a-c) Photographs of vials containing (a) Au nanoparticles with *no* AuST peptide, (b) the sample from (a) incubated with Fe_2O_3-strep, and (c) the sample from (b) after exposure to a benchtop magnet. (d) UV-Visible absorption spectra of the Au nanoparticles (red) and the supernatant after incubation with Fe_2O_3-strep (*without* AuST) and magnetic separation (green).

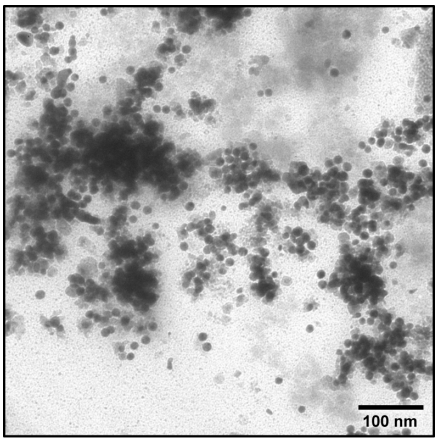

Figure S2. TEM image of the mixture of Au and CdS nanoparticles corresponding to the sample shown in Figure 3b.

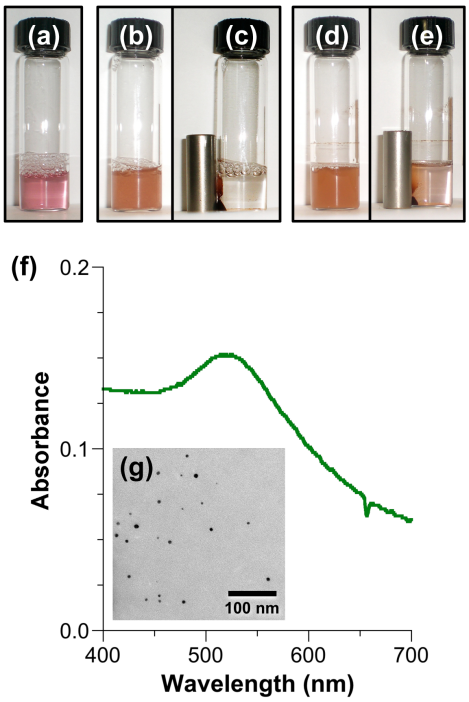

Figure S3. (a-c) Photographs of vials containing (a) Au nanoparticles incubated with AuST (same photograph as shown in Figure 1d, for reference), (b) Au-AuST incubated with Fe_2O_3-strep, and (c) the sample from (b) after exposure to a benchtop magnet. [Panels (b) and (c) are the same photographs shown in Figures 1e and 1f, respectively, for reference.] (d-e) Photographs of vials containing (d) Au-AuST/Fe_2O_3-strep with polyethylene glycol monomethyl ether thiol and (e) the sample from (d) after exposure to a benchtop magnet. (f) UV-Visible absorption spectrum and (g) TEM image of the Au nanoparticles released from Au-AuST/Fe_2O_3-strep after incubation with polyethylene glycol monomethyl ether thiol.

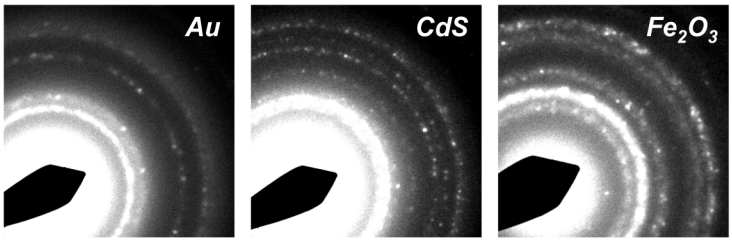

Figure S4. Representative SAED patterns for Au, CdS, and Fe_2O_3-strep nanoparticles.