

Electronic Supplementary Information

Reversible phase transfer of quantum dots and metal nanoparticles

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Experimental

Materials and Instruments. Gold (III) chloride (99%), silver nitrate (99%), lead (II) acetate trihydrate ($\text{Pb}(\text{OAc})_2$, 99%), oleylamine (OLA) (technical grade, 70%), cadmium oxide (99.99+%), trioctylamine (98%), selenium and sulfur powders (99.5+%), trioctylphosphine (TOP, technical grade, 90%), OA (technical grade, 90%), glutathione (GSH) (99+%), decanoic acid (99+%), methanol (98%), toluene (97%), chloroform (98%) and acetone (98%) from Aldrich; octadecylphosphonic acid (ODPA) from PolyCarbon Industries Inc.; zinc acetate dihydrate (98+%) from Alfa Aesar; cadmium acetate dihydrate (97+%) and tetramethylammonium hydroxide pentahydrate (TMAH, 95.0+%) from Fluka; and CTAB (98%) from Lancaster were used as received. De-ionized (DI) water was obtained using a Milli-Q water purification system. All glassware and Teflon-coated magnetic stirring bars were cleaned with *aqua regia*, followed by copious washing with DI water before drying in an oven.

A FEI Tecnai G² F20 electron microscope operated at 200 kV with the software package for automated electron tomography was used to obtain TEM images of the nanoparticles. A drop of the nanoparticle solution was dispensed onto a 3-mm copper grid covered with a continuous carbon film. Excess solution was removed with an absorbent paper, and the sample was dried under vacuum at room temperature.

FTIR, UV-Vis and emission spectra were recorded on DigiLab FTS 7000 FTIR spectrometer equipped with Varian PAC 300 photoacoustic accessory, Agilent 8453 UV-Vis spectrometer and Jobin Yvon Horiba Fluorolog fluorescence spectrometer, respectively. For FTIR characterization, the materials were precipitated with methanol or acetone, washed twice with acetone, and dried in vacuum for 2 days.

Synthesis of Au and Ag Nanoparticles. AuCl_3 (300 mg, 1 mmol) or AgNO_3 (170

mg, 1 mmol) and 20 mL of OLA were placed in a two-neck round-bottom flask under Ar flow and stirred at 60°C until the AuCl_3 or AgNO_3 completely dissolved. The mixture was then heated to 150°C with stirring, and kept at that temperature for 2 h, followed by cooling down to room temperature. The Au or Ag nanoparticles thus formed were precipitated, washed twice with methanol, and re-dispersed in 20 mL of toluene.

Synthesis of CdSe@CdZnS QDs. CdSe@CdZnS QDs were synthesized according to a published method.¹ In a typical synthesis of the CdSe cores, CdO (130 mg, 1 mmol), 800 mg of ODPa and 50 mL of trioctylamine were first placed in a four-neck round-bottom flask under Ar flow, and stirred at 300°C until the CdO completely dissolved. Se powder (400 mg, 50 mmol) was dissolved in 5 mL of TOP. The TOPSe solution was then injected into the Cd solution with rapid stirring, and kept at 300°C for 2 min, followed by cooling down to room temperature. 50 mL of chloroform and 100 mL of methanol were added to precipitate the CdSe nanocrystals. The product was then washed twice with copious methanol, re-dispersed in 20 mL of toluene, and centrifuged to remove the sludge. Next, the CdSe cores were precipitated with methanol, and re-dispersed in 5 mL of toluene for subsequent injection.

To synthesize the CdZnS shell, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (220 mg, 1 mmol), $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (17 mg, 0.06 mmol), 2 mL of OA and 50 mL of trioctylamine were placed in a four-neck round-bottom flask under Ar flow, and stirred at 300°C until the Cd and Zn salts were completely dissolved. S powder (60 mg, 2 mmol) was dissolved in 5 mL of TOP. The toluene solution of CdSe cores was injected with rapid stirring, followed by the dropwise addition of the TOPS solution. The mixture was kept at 300°C for another 2 h, followed by cooling down to room temperature. The products were precipitated, washed twice with methanol, and re-dispersed in 20 mL of toluene.

Synthesis of PbS QDs. 379 mg of $\text{Pb}(\text{OAc})_2$, 10 mL of OLA and 10 mL of OA were introduced to a two-neck round-bottom flask, and heated to 160°C under Ar flow until they were completely dissolved. S powder (32 mg, 1 mmol) was dissolved in 2 mL of OLA. The S solution in OLA was then injected into the lead(II) solution with rapid stirring, and kept at 160°C for 5 min, followed by cooling down to room temperature. 10 mL of toluene and 60 mL of methanol were added to precipitate the PbS nanocrystals. The product was then washed twice with copious methanol, and re-dispersed in 20 mL of toluene.

Synthesis of CdS Rods. CdS rods were synthesized following an established

protocol.² In brief, a S injection solution containing 72 mg of S (2.25 mmol) was prepared by dissolving S powder in 2 mL of TOP. 100 mg of CdO (0.78 mmol) and 456.5 mg of tetradecylphosphonic acid (TDPA) (1.64 mmol) were loaded into a 50-mL three-neck flask, and heated to 200°C under Ar flow. After the CdO was completely dissolved, the Cd-TDPA complex was allowed to cool to room temperature. Subsequently, 1350 mg of trioctylphosphine oxide (TOPO) was added to the flask, and the temperature was raised to 320°C to produce an optically clear solution. After S injection into a 320°C mixture containing Cd-TDPA complex and TOPO, the temperature of the reaction system was decreased to 280°C. The reaction lasted for 5 min to allow for the growth of CdS rods, and was then terminated by quenching the reaction to 40°C. Subsequently, 5 mL of toluene was introduced to dissolve the reaction mixture, and a yellow precipitate was obtained by adding 15 mL of methanol, followed by centrifugation at 3000 rpm. The precipitate was washed twice using methanol, and re-dispersed in 20 mL of toluene.

Ligand Exchange Based Phase Transfer from Organic to Aqueous Phase (GTMA Coating). GSH (300 mg, 1 mmol) and TMAH (540 mg, 3 mmol) were dissolved in 10 mL of methanol to form the GTMA salt (100 mM). 1 mL of toluene solution of QDs or metal nanoparticles was dissolved in 5 mL of chloroform. With rapid stirring, 0.5 mL of GTMA solution was added dropwise. The QDs or metal nanoparticles first precipitated due to ligand exchange of the original stabilizer (OA for QD or OLA for Au) for GTMA, and then re-dissolved as more of the methanolic solution was added. 4.5 mL of water was then added. The mixture was left to stand, and the upper (aqueous) phase was collected (nominally 10 mM of Cd or Au).

Electrostatic Interaction Based Reversible Phase Transfer Between Aqueous and Organic Phases. Aqueous to organic phase transfer: CTAB (3.6 g, 10 mmol) was dissolved in 100 mL of methanol in advance. With rapid stirring, 5 mL of the CTAB solution (100 mM) was added to 5 mL of GTMA-stabilized nanoparticle solution, followed by the introduction of 5 mL of toluene. The mixture was left to stand, and the upper (toluene) phase was collected.

Organic to aqueous phase transfer: Decanoic acid (DA, 1.7 g, 10 mmol) and TMAH (1.8 g, 10 mmol) were dissolved in 100 mL of methanol to form TMAD (100 mM). 5 mL of chloroform and 5 mL of water were added to 5 mL of toluene solution of CTAB-stabilized nanoparticles. Next, 5 mL of TMAD solution were added to the mixture with rapid stirring. The mixture was left to stand and the upper (aqueous) phase was collected.

References

1. S. Jun, E. Jang, J. E. Lim, *Nanotechnology*, 2006, **17**, 3892.
2. C.-C. Kang, C.-W. Lai, H.-C. Peng, J.-J. Shyue, P.-T. Chou, *Small*, 2007, **3**, 1882.

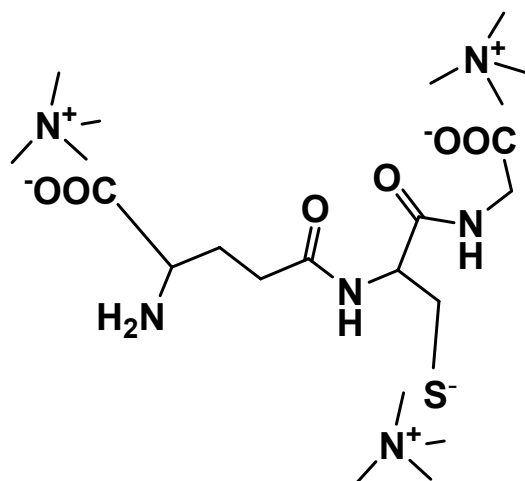


Fig. S1. Chemical structure of glutathione tetramethylammonium salt (GTMA).

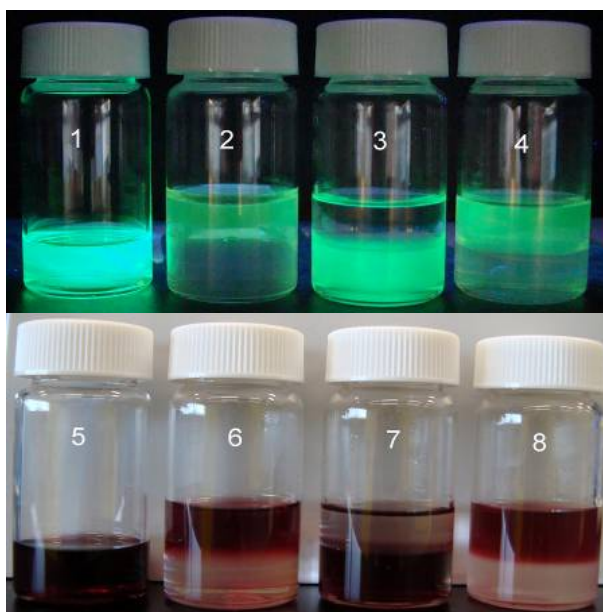


Fig. S2 Photographs under of (1–4) CdSe@CdZnS QDs under UV irradiation and (5–8) Au nanoparticles under ambient light: (1, 5) in chloroform solutions, (2, 6) transferred from chloroform to aqueous phase based on ligand exchange with GTMA, (3, 7) transferred back to chloroform upon the addition of CTAB, and (4, 8) transferred back to aqueous phase upon the addition of TMAD.

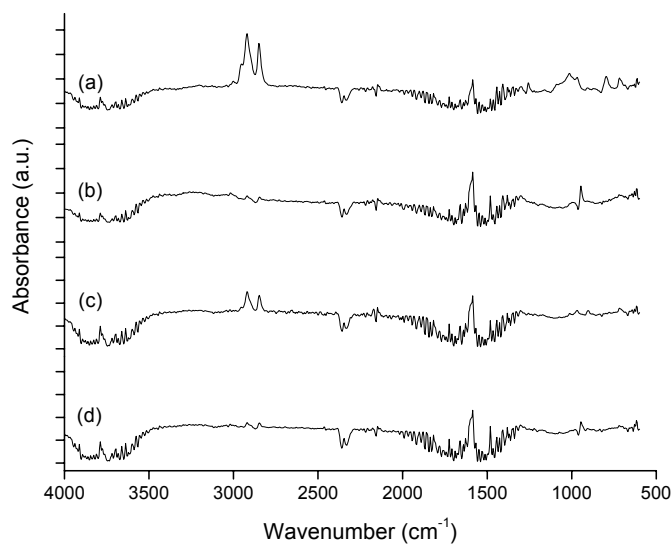


Fig. S3. Photoacoustic FTIR spectra of CdSe@CdZnS QDs with (a) OA, (b) GTMA, (c) CTAB, and (d) TMAD.

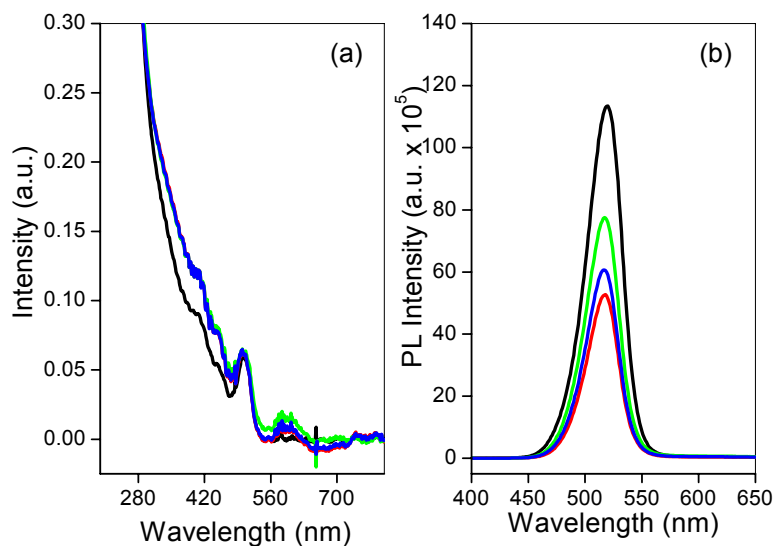


Fig. S4 Room-temperature (a) UV-Vis and (b) PL spectra of CdSe@CdZnS: (—) as prepared, (—) transferred to aqueous phase using GTMA, (—) transferred back to chloroform using CTAB, and (—) transferred back to water using TMAD.

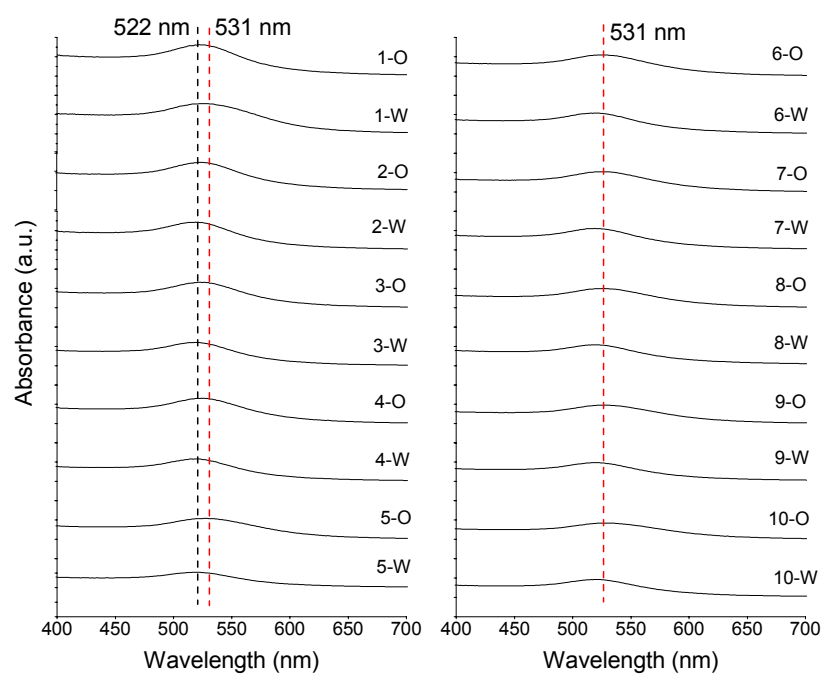


Fig. S5. UV-Vis spectra of Au nanoparticles as prepared (1-O) and after x rounds of transfer between organic phase (x -O) and aqueous phase (x -W).