Supporting Information

Dual-Mode Crystal-Bound and X-Type Passivation of Quantum Dots

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Experimental procedures:

Materials:

Cadmium myristate and dodecyl-3-mercaptopropinoate (D3MP) were prepared following literature procedures (details below). Selenium dioxide (99.8%), 1,2-hexadecanediol (90%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OLAM, 70%), trioctylphosphine (TOP, 90%), zinc diethyldithiocarbamate (Zn(ddtc)₂, 97%), dodecanethiol (DDT, >98%), trioctylamine (TOA, 98%), mercaptopropionic acid (MPA,

>99%) tetramethylammonium hydroxide pentahydrate (TMAH, >97%), myristic acid (\geq 98%),1-dodecanol (98%), and potassium hydroxide (85%) were obtained from Sigma Aldrich. Zinc acetate dihydrate (Zn(OAc)₂ \Box 2H₂O), 97%) was obtained from Alfa Aesar. Cadmium nitrate tetrahydrate (98%) was obtained from Strem. All chemicals were used as obtained and standard Schlenk techniques were used during the syntheses.

Cadmium Selenide Synthesis:

CdSe was prepared following a modified literature procedure.¹ Briefly, Cd(myristate)₂ (0.5 mmol) was combined with SeO₂ (0.5 mmol) and 1,2-hexadecanediol (0.5 mmol) in 10 mL of ODE. The solution was purged by vacuum and the vessel was filled with N₂. The flask was then heated quickly to 240°C and reacted for 1 min at that temperature. The solution was cooled to RT and particles were isolated. First by precipitation by the addition of acetone and centrifugation at 8700 rpm for 5 min. The particles were then washed 3x using chloroform and acetone, then stored in the dark dispersed in chloroform.

Zinc Sulfide Shells with Surface-Bound Ligands:

The ZnS shell was prepared following a modified literature procedure.² The concentration of the CdSe stock solution was determined by the absorbance at the first exciton peak.³ 500 nmol of CdSe seeds were combined with $Zn(ddtc)_2$ (118 mg, enough for 2 monolayers (ML), calculated following a literature procedure⁴), OLAM (3 mL), TOP (3 mL), and ODE (10 mL). The solution was placed under vacuum for 1 h at room temperature to remove the CHCl₃. The solution was then heated at a rate of 80°C/h to 120°C and reacted for 1 h at that temperature. The particles were then cooled to RT and precipitated by the addition of acetone and centrifuged at 8700 rpm for 5 min. The particles were washed with acetone and chloroform until no unbound ligands were observed by ¹H NMR, typically 4×. Particles were stored in the dark in CHCl₃.

Surface-Bound Thiol Ligand Exchange:

To exchange DDT onto the surface of CdSe@ZnS, 100 mg of TMAH \Box 5H₂O was dissolved in 1 mL of CHCl₃ with 100 µL of DDT. The solution was stirred for 15 min and a phase separation was observed. The bottom CHCl₃ layer was collected, added to a CHCl₃ solution containing 50 nmol of CdSe@ZnS and stirred for 1 h at room temperature in the dark. The particles were then precipitated by the addition of ethanol and washed with chloroform and ethanol until no unbound ligands were observed by ¹H NMR, typically 5×. MPA exchange was similar except that the particles were washed using only ethanol, then dispersed in a pH 7 phosphate buffer.

Zinc Sulfide Shells with Crystal-Bound Ligands:

The concentration of the CdSe@ZnS with surface-bound ligands seeds stock solution was determined by the absorbance at the first exciton peak.³ A CHCl₃ solution containing 50 nmol of CdSe@ZnS was combined with 1 mL of TOA and placed under vacuum for 1 h to remove the CHCl₃. In a separate flask, $Zn(OAc)_2 \Box 2H_2O$ (15 mg, enough for 2 ML of ZnS), 2.5 mL of OA, and 2.5 mL TOA was combined and placed under vacuum at 105°C for 1 h to remove H₂O. The Zn containing solution was then heated to 150°C under N₂ at 150°C. CdSe@ZnS solution and 100 µL of DDT were injected simultaneously into the hot Zn containing solution. The resulting solution was reacted at 150°C for 1 h. Finally, the reaction was cooled to RT and the particles were

precipitated by the addition of acetone and centrifuged at 8700 rpm for 5 min. The particles were then washed with acetone and chloroform until no unbound ligands were observed by ¹H NMR, typically 4x. Particles were stored in the dark in CHCl₃. For D3MP capped particles, DDT was replaced with an equimolar amount of D3MP.

Base Treatment of Dodecanethiol capped CdSe@ZnS:

A CHCl₃ solution containing 10 nmol of CdSe@ZnS with DDT capping ligands was dissolved in 2 mL of THF and treated with 100 μ L of 2M KOH in H₂O followed by 10 s of sonication. The particles were obtained by centrifuging at 4400 rpm for 5 min; no additional solvent was need for surface-bound DDT while crystal-bound DDT needed methanol to precipitate. The particles were then washed 2× with ethanol to remove any excess base.

Hydrolysis of Dodecyl-3-Mercaptopropionate Capped CdSe@ZnS:

10 nmol of D3MP capped CdSe@ZnS was dissolved in 2 mL of THF and treated with 100 μ L of 2M KOH in H₂O followed by 10 min of sonication. To precipitate the particles, hexanes was added to the solution and centrifuged at 4400 rpm for 5 min. The particles were then washed 2× with ethanol then dissolved in a pH 7 phosphate buffer.

Photocatalytic Degradation of Methylene Blue:

A CdSe@ZnS solution was prepared by dissolving the water soluble QDs in a pH 7 phosphate buffer with the first excitation peak having an absorbance of 0.1. In a quartz cuvette sealed with a septum, 0.500 mL of CdSe@ZnS solution, 0.100 mL of 0.177 mM methylene blue solution in deionized water (Millipore, 18 m Ω), and 1.00 mL of pH 7 buffer was combined and bubbled with N₂ for 30 min. After the N₂ purge, 0.500 mL of ethanol that had been purged separately by freeze-pump-thaw was added to the solution. The solution was then exposed to light from a 13 W blue-colored compact fluorescent light (FEIT electric BPESL13T/B). The absorbance of methylene blue was monitored at 666 nm, every 10 min for 1 h. For the control experiment without QDs, the 0.500 mL of CdSe@ZnS solution was replaced with 0.500 mL of buffer solution. The solution is triplicate and the average of the runs reported.

Synthesis of Dodecyl-3-Mercaptopropionate:

Dodecyl-3-mercaptopropionate was prepared following a literature procedure.⁵ Briefly, 1dodecanol (44.0 g, 0.240 mol, 1.33 equiv.) and 3-mercaptopropionic acid (15.0 mL, 0.1800 mol, 1 equiv.) were dissolved in 30.0 mL of toluene with 6 drops of concentrated H₂SO₄. The flask was fitted with a Dean-Stark trap filled with a saturated aqueous KCI solution. The reagents were heated to reflux and reacted for 1 h. The resulting product was washed 2× with 20 mL of brine followed by 20 mL of DI water. The organic layer was then dried over MgSO₄. The product was purified by vacuum distillation (140°C at 400 mTorr). Yield 35 g (71%). $\delta_{\rm H}$ (400 MHz, CDCl₃) 4.09 (t, *J* = 6.76 Hz 2H, -CO₂CH₂-), 2.75 (q, *J* = 6 Hz, 2H, -CH₂SH), 2.61 (t, *J* = 6.5 Hz, 2H, -CH₂CO₂-), 1.62 (m, 3H, -CO₂CH₂CH₂-, -SH), 1.27-1.23 (m, 18H, -CH₂-x9), 0.87 (t, *J* = 7 Hz, 3H, -CH₃).

Synthesis of Cadmium Myristate:

Cadmium myristate was prepared following a literature procedure.¹ Briefly, two solutions were prepared, one of 1.54 g of cadmium nitrate tetrahydrate (5 mmol) in 50 mL of

ethanol and the other of 3.42 g of myristic acid (15 mmol) and 0.60 g of sodium hydroxide (15 mmol) in 500 mL of ethanol. The solution of cadmium nitrate was then added dropwise to the sodium myristate solution. The resulting precipitate was filtered and washed with methanol $3\times$. The product was then dried over night at 60°C under vacuum.

Quantum yield:

Quantum yields were determined by comparison of the emission of the nanocrystals to a standard of Rhodamine B in methanol (excitation at 348 nm gives a quantum yield, $\phi_{std} = 70\%$).⁶ The concentrations of the nanoparticles were adjusted so that the absorbance at 348 nm was 0.1 abs for all samples to assure reabsorption is not a problem. To calculate the photoluminescence quantum yield of the sample (ϕ_x), the following equation was used:

$$\phi_x = \frac{F_x a_{std} n_x^2}{F_{std} a_x n_{std}^2} \phi_{std}$$

Where F is the integrated intensity of the fluorescence, a is the absorbance at the excitation wavelength (348 nm), and n is the refractive index of solvent.

Density Functional Theory Calculations:

DFT calculations were performed using the PBE version of the exchange-correlation functional,⁷ PAW potentials,⁸ and a plane-wave basis as implemented in the VASP code.⁹ The plane-wave energy cutoff was set at 353 eV and a 5x3x1 k-point sampling was used. In all the slab models, the ligands from the periodic images of the slabs were separated by at least 19 Å, ensuring no artificial interactions between the images.

Instrumentation:

Transmission electron microscopy images were acquired using a FEI Tecnai Osiris operating at 200 keV. Samples were drop casted from solution onto a carbon coated Cu mesh grid. Absorbance spectra were obtained using a Jasco V-670 UV-Vis-NIR spectrophotometer. Fluorescence Spectra were obtained using a JASCO FP 8300 Fluorimeter. Infrared spectroscopy was obtained using a Bruker Tensor FTIR, where samples were pressed into a KBr pellet. ¹H NMR spectra were acquired using a 11.7 T magnet equipped with a Bruker DRX console operating at 500.13 MHz. Chemical shifts were referenced internally to CDCl₃ (7.26 ppm) or D₈-THF (3.58 and 1.73 ppm) depending on the solvent used. For XPS the nanocrystals were drop casted from a suspension in CHCl₃ onto a silicon wafer. XPS spectra were collected using a Physical Electronics (PHI) VersaProbe 5000, using Al K_a X-rays (1486 eV), a take-off angle of 45°, and a spot size of 100 μ m. Spectra were analyzed using CasaXPS software, calibrated to the lowest energy C 1s peak at 284.8 eV.

Determination of ligand density:

Using QDs with a known surface area determined by sizing the particles using TEM images and assuming a spherical particle. A NMR tube was filled with 700 μ L of a QD stock solution in CDCl₃ with a known concentration determined by UV-Vis and 10 μ L of a 0.12 mM solution of 1,2-dibromoethane. The number of bound ligands was determined by the 4:3 ratio of the integration of the 1,2-dibromoethane at 3.65 ppm to the terminal - CH₃ at 0.88 ppm. The number of ligands/particles was then determined by dividing the number of bound ligands to the number of particles in the sample. The ligand density is obtained by comparing the number of ligands/particle to the total surface area.



SI Figure A: ¹H NMR of CdSe@ZnS with crystal-bound DDT. 1,2-dibromoethane was added as an internal standard, ligand density was found to be 3.9 ligands/nm² for crystal-bound DDT. There are there are no resonances for the protons associated with the double bond of oleic acid despite being a reagent during the synthesis, indicating no oleic acid passivation.



SI Figure B: ¹H NMR of CdSe@ZnS with surface-bound DDT. 1,2-dibromoethane was added as an internal standard, ligand density was found to be 3.6 ligands/nm² for the surface-bound DDT.

Additional Figures:



SI Figure C: Absorbance (solid line) and fluorescence (dashed line) spectra of CdSe seeds (black) (in SI figure B), CdSe@ZnS with surface-bound ligands (red) (SI figure C), CdSe@ZnS with crystal-bound DDT (blue) (Figure 1 A in manuscript).



SI Figure D: TEM image of CdSe seeds (2.8 ± 0.2 nm n=125)



SI Figure E: TEM image of CdSe@ZnS with surface-bound ligands (3.2±0.2 nm n=127).



SI Figure F: Evidence that the particle growth seen when adding a crystal-bound ZnS shell is not simply from ripening processes. (A and Black) TEM and absorbance spectra of CdSe seeds (2.90 ± 0.17 nm n=150) used in the following controls: (B and Red) CdSe@ZnS with crystal-bound DDT with no initial shelling of ZnS (3.83 ± 0.27 nm n=129). The growth of the particles is similar in magnitude to particles that have an intermediate ZnS shell and undergo the addition of a crystal bound ZnS shell. (See manuscript) (C and Blue) CdSe seeds having undergone a crystal-bound shelling procedure with no zinc added. Some ripening was observed (3.24 ± 0.49 n=137) but is

smaller than what was seen for a normal shelling procedure. (See manuscript and part B above).



SI figure G: Detailed discussion of figure 1C. Ligand stability of the crystal-bound dodecanethiol (top spectra) compared to surface-bound dodecanethiol (bottom spectra) capping ligands shown by ¹H NMR. ¹H NMR was taken of D₈-THF solutions of QDs with crystal-bound and surface-bound DDT. 20 µL of 0.1 M KOH in D₂O was added to the tube and another NMR spectra was immediately taken (red). The samples were then sonicated for 10 s and another NMR was taken (blue). In both samples the raising pH of the solution shifted the peak position of -CH₂- and the -CH₃ resonances up-field. In free dodecanethiol ratio of integrations of the -CH₃ peak at 0.9 ppm and the -CH₂- at 1.3 ppm should be 3:18. For both the surface-bound and crystal-bound thiols the quadipolar interactions from the core nanocrystal broaden out the resonances of the protons near the core. This lowers the observed ratio to around 3:14 for the bound samples. Upon the addition of base, this ratio remains relatively constant for the crystal-bound sample, indicating the ligands remain bound to the surface. In contrast, the surface-bound sample sees a rise in the observed -CH₂- resonances, and the integrations even reaching the ideal ratio of 3:18 following sonication. This indicates that the ligands are largely removed from the nanocrystal surface.



SI figure H: Picture of the NMR tubes for the experiment described in SI figure G 1 h after the experiment. The left NMR tube contains the surface-bound DDT capped nanocrystals and the right NMR tube contains the crystal-bound DDT capped nanocrystals. The nanocrystals in the surface-bound sample loose colloidal stability because the ligands are removed in the base treatment. The crystal-bound stable remains colloidally stable in D₈-THF because the long chain thiol ligands are not removed by base treatment.



SI Figure I: S2p XPS of CdSe@ZnS with crystal-bound (black spectra) and surfacebound (red) thiols. Both DDT (solid line) and MPA (dashed) capped particles are shown. The presence of higher binding energy species in the surface-bound samples can be attributed to the presence of thiolate coordination to the surface which is missing in the crystal-bound case.⁸ Overlapping signal from the Se 3p in this region prevented detailed fittings of the spectra.



SI figure J: Infrared spectra of CdSe@ZnS with crystal-bound D3MP before (black) and after (red) hydrolysis. Evidence of the hydrolysis is observed by the loss of the ester C=O stretching mode at 1700 cm⁻¹ after the hydrolysis.



SI Figure K: Fluorescence spectra of 2.65 nm CdSe@ZnS shell with crystal-bound D3MP, before (black) and after (red) hydrolysis.



SI Figure L: Fluorescence spectra of 4.06 nm CdSe@ZnS shell with crystal-bound D3MP, before (black) and after (red) hydrolysis.



SI Figure M: Fluorescence spectra of 4.06 nm CdSe@ZnS with surface-bound native ligands (black) and after ligand exchange with MPA (red).



SI Figure N: Fluorescence spectra of 3.04 nm CdSe@ZnS with surface-bound native ligands (black) and after ligand exchange with MPA (red).



SI Figure O: High-resolution TEM images of CdSe@ZnS with crystal-bound D3MP before (A) and after (B) hydrolysis. (C) and (D) are plots of the intensity profiles along the marked lines in the TEM images. Distances between lattice planes are noted. The observed d-spacing of 0.35 nm is consistent with the d-spacing of the (111) of zinc

blende CdSe. The d-spacing of (111) zinc blende ZnS is 0.30 nm. From this we infer that the CdSe core dominates the lattice parameters and the ZnS shell is strained.



SI Figure P: (A) Absorbance spectra of methylene blue (blue), CdSe@ZnS with crystalbound MPA and methylene blue (black) and CdSe@ZnS with crystal-bound MPA and methylene blue after 1 h of exposure to blue light (red). (B) Absorbance spectra of methylene blue (blue), CdSe@ZnS with surface-bound MPA and methylene blue (black) and CdSe@ZnS with surface-bound MPA and methylene blue after 1 h of exposure to blue light (red). (C) Absorbance spectra of methylene blue (black) and methylene blue after 1 h exposure to blue light (red). Absorbance at wavelengths below 550 nm is attributed to the QDs. No change in the absorbance in this region is observed during the catalysis, suggesting no degradation of the QDs.

References:

1. Chen, O.; Chen, X.; Yang, Y. A.; Lynch, J.; Wu, H. M.; Zhuang, J. Q.; Cao, Y. C. "Synthesis of Metal-Selenide Nanocrystals Using Selenium Dioxide as the Selenium Precursor" *Angew. Chem. Int. Edit.* **2008**, 47, 8638-8641.

2. Dethlefsen, J. R.; Dossing, A. "Preparation of a Zns Shell on Cdse Quantum Dots Using a Single-Molecular Zns Precursor" *Nano Lett.* **2011**, 11, 1964-1969.

3. Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G. "Experimental Determination of the Extinction Coefficient of Cdte, Cdse, and Cds Nanocrystals" *Chem. Mater.* **2003**, 15, 2854-2860.

4. Chen, D. A.; Zhao, F.; Qi, H.; Rutherford, M.; Peng, X. G. "Bright and Stable Purple/Blue Emitting Cds/Zns Core/Shell Nanocrystals Grown by Thermal Cycling Using a Single-Source Precursor" *Chem. Mater.* **2010**, 22, 1437-1444.

5. Turo, M. J.; Macdonald, J. E. "Crystal-Bound Vs Surface-Bound Thiols on Nano Crystals" *ACS Nano* **2014**, 8, 10205-10213.

6. Brouwer, A. M. "Standards for Photoluminescence Quantum Yield Measurements in Solution (IUPAC Technical Report)" *Pure Appl. Chem.* **2011**, 83, 2213-2228.

7. Perdew, J. P.; Burke, K.; Ernzerhof, M. "Generalized Gradient Approximation Made Simple" *Phys. Rev. Lett.* **1996**, 77, 3865-3868.

8. Kresse, G.; Joubert, D. "From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method" *Phys. Rev. B* **1999**, 59, 1758-1775.

9. Kresse, G.; Furthmuller, J. "Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set" *Phys. Rev. B* **1996**, 54, 11169-11186.