**Supporting Information for**

# Band Gap Engineering of Quaternary Alloyed ZnCdSSe Quantum Dots via a Facile Phosphine-Free Colloidal Method

*Zhengtao Deng, Hao Yan, Yan Liu*

The Biodesign Institute & Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, 85287

## Experimental Section

***Chemicals:*** Zinc oxide (ZnO, 99.9%, powder < 5 micron), Cadmium oxide (CdO, 99.99+%, powder), sulfur (S, 99.998% powder), Selenium powder (Se, , 99.99%, powder, <100 mesh), oleic acid (90%), 2-ethylhexanoic acid (EHA, $CH_3(CH_2)_3CH(C_2H_5)COOH$, 99+%), paraffin liquid (for IR spectroscopy), 1-pentanol (≥99%), methanol (≥99.5%), hexane (≥95%), Coumarin 480 (λem=467), Rhodamine 110 (λem=520 nm), Rhodamine 6G (λem=547 nm), and Rhodamine 101 (λem=589 nm), were purchased from Sigma-Aldrich and used without further purification. No phosphine such as trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), or tributhylphosphine (TBP) were used.

### *Experimental details:*

In a typical synthesis of $Zn_{0.6}Cd_{0.4}S_{0.5}Se_{0.5}$ quantum dots (QDs), Zn/Cd -complex precursor solution was prepared by adding 4.5 mmol of ZnO and 3.0 mmol CdO into a 100 mL flask containing 10 mL paraffin liquid, 10 mL oleic acid, and 5 mL 2-ethylhexanoic acid. The mixture were heated to 100$^{o}$C, degassed under 100 mtorr pressure for 30 minutes, filled with $N_2$, and further heated to 200$^{o}$C to form a clear mixture solution of Zn/Cd precursor. Then, S/Se precursor solution was prepared in a separate

flask, where 0.15 mmol of S and 0.15 mmol of Se were mixed with 15 mL paraffin liquid, degassed for 30 minutes, filled with $N_2$, and heated to 280$^o$C. At this temperature, 1 mL Cd/Zn precursor solution was quickly injected to the flask containing the above mixture. The new mixture was then maintained at 280$^o$C with continuous stirring. A number of aliquots (each 1 mL) can be collected in test tubes containing 2 mL cold hexane to quench further QQD growth at different intervals such as 3, 6, 9, 12, 15 and 20 minutes. The samples were purified by centrifugation (13,000 rpm for 30 minutes) several times after being precipitated with pentanol and methanol. The final products were dispersed in hexane. The synthesis of other types of QQDs was similar to that of $Zn_{0.6}Cd_{0.4}S_{0.5}Se_{0.5}$. For the growth a series of QQDs samples shown in Figure 2, use total 0.30 mmol of ZnO and CdO powder mixture, and total 0.30 mmol of sulfur and selenium powder mixture, with their corresponding ZnO:CdO:S:Se molar ratio of 9:1:9:1, 8:2:7:3, 7:3:6:4, 4:6:4:6, 2.5:7.5:2.5:7.5; 1:9:1:9, respectively.

***Characterization methods:***

High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM 2010F electron microscope operating at 200 kV. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded at room temperature with a CARY-300 spectrophotometer. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at room temperature using a PTI fluorescence spectrometer (814 photomultiplier detection system and LPS-220B power supply).

We used a cross-calibrated method to measure the quantum yield of the as-obtained quantum dots.[S1] The PL quantum yield for blue emission (400-500 nm) QQDs was obtained by referencing to coumarin 480 as a dye standard (99% QY in ethanol). For green emission (500-550 nm) QQD, the PL quantum yield was obtained by referencing to a standard Rhodamine 110 (QY = 91% in ethanol). For orange and red emission QQDs, their PL quantum yields were obtained by referencing to a standard Rhodamine 101 (QY = 100% in ethanol + 0.01 HCl). All these standard dye were cross-calibrated by referencing to Rhodamine 6G (QY = 95% in ethanol). The PL quantum yield was calculated using the following equation:

$$\varphi = \varphi' \times \left(\frac{I}{I'}\right) \times \left(\frac{A'}{A}\right) \times \left(\frac{n}{n'}\right)^2 \quad (1)$$

where $\varphi$ and $\varphi'$ are the PL QY for the sample and standard, respectively; I (sample) and I′ (standard) are the integrated emission peak areas at a given wavelength; A (sample) and A′ (standard) are the absorption intensities at the same wavelength used for PL excitation; n (sample) and n′ (standard) are the refractive indices of the solvents.

Powder X-ray diffraction (XRD) measurements employed a using a PANalytical X'Pert Pro Materials Research X-ray Diffractometer with Cu Kα radiation (λ=1.5418 Å) and scanned at a rate of 0.025 deg/s. The lattice constant of the alloyed materials could be calculated using Vegard's law.[S2] According to Vegard's law, the lattice quaternary alloyed $Zn_xCd_{1-x}S_ySe_{1-y}$ quantum dots can be expressed as:

$$a\ (Zn_xCd_{1-x}S_ySe_{1-y}) = xya_{ZnS} + x(1-y)\ a_{ZnSe} + (1-x)y\ a_{CdS} + (1-x)(1-y)\ a_{CdSe} \quad (2)$$

Where, $a_{ZnS}$ = 5.345 Å (JCPDS file No. 80-0020); $a_{ZnSe}$ = 5.618 Å (JCPDS card No. 80-0021); $a_{CdS}$ = 5.811 Å (JCPDS file No. 80-0019); $a_{CdSe}$ = 6.077Å (JCPDS file No. 19-0191).

REFERENCES

(S1) http://www.horiba.com/us/en/scientific/products/fluorescence-spectroscopy/application-notes/quantum-yields/

(S2) Razeghi, M. *Fundamentals of Solid State Engineering,* 2nd ed. Springer-Verlag, New York, LLC. **2005**.

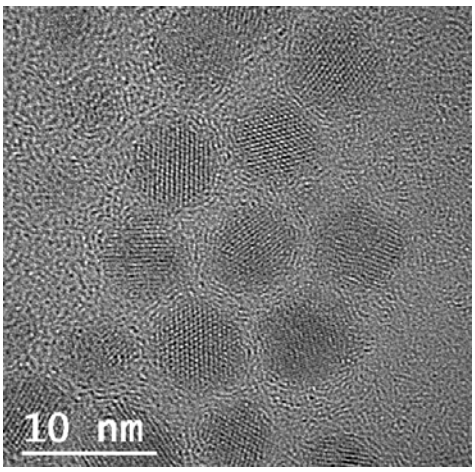



**Figure S1**. High resolution TEM image of the ~6 nm $Zn_{0.6}Cd_{0.4}S_{0.5}Se_{0.5}$ QD ensembles.

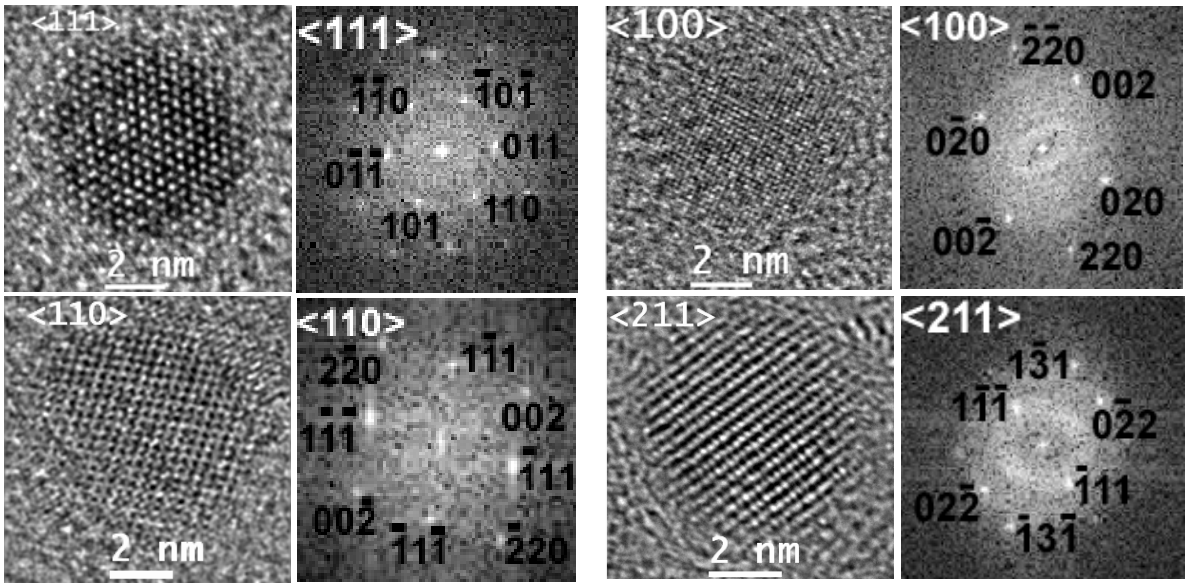



**Figure S2**. High resolution TEM image and their corresponding indexed fast Fourier transforms of the single 6 nm $Zn_{0.6}Cd_{0.4}S_{0.5}Se_{0.5}$ QQD projected in the <111>, <100>, <110>, and <211> directions.

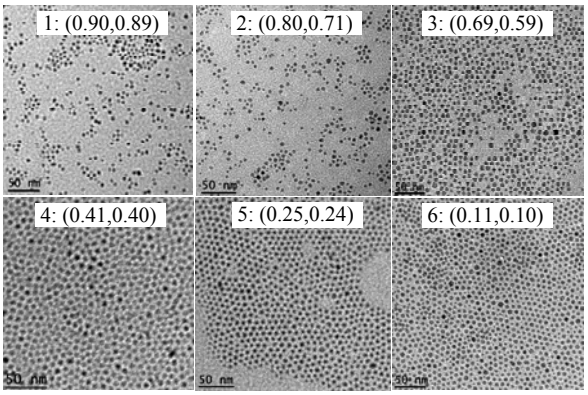
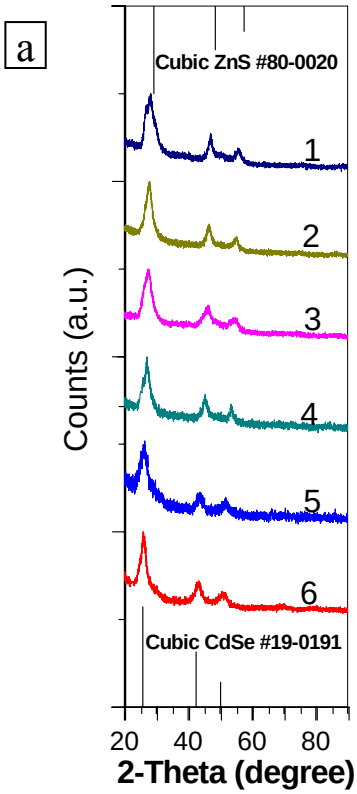



**Figure S3**. TEM images of a series of ~6 nm $Zn_xCd_{1-x}S_ySe_{1-y}$ QQDs; the labeled composition ($x$, $y$) is determined by TEM-EDS on ensembles of quantum dots as shown in Figure 2.




b

| *Sample No.* | *x* | *y* | *a (from XRD)* | *a (from Vegard's law)* |
|---|---|---|---|---|
| 1 | 0.90 | 0.89 | 5.44 | 5.42 |
| 2 | 0.80 | 0.71 | 5.51 | 5.52 |
| 3 | 0.69 | 0.59 | 5.58 | 5.60 |
| 4 | 0.41 | 0.40 | 5.75 | 5.78 |
| 5 | 0.25 | 0.24 | 5.88 | 5.90 |
| 6 | 0.11 | 0.10 | 5.96 | 6.00 |

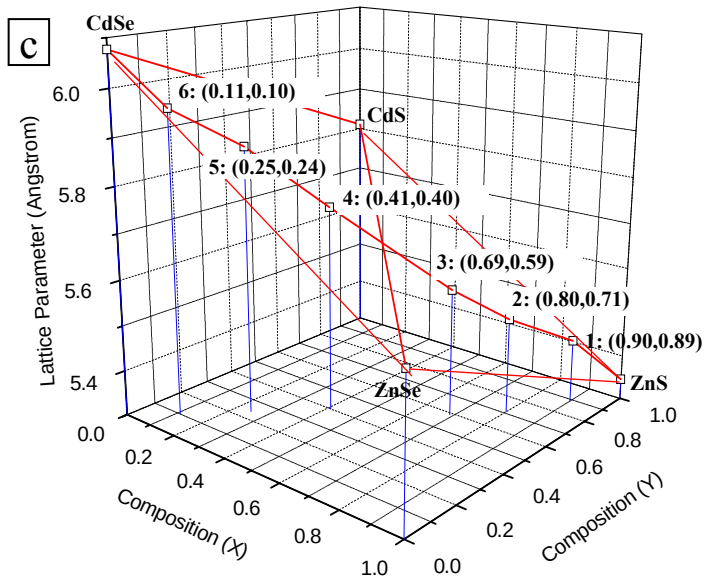



**Figure S4**. (a) XRD patterns of a series of $Zn_xCd_{1-x}S_ySe_{1-y}$ QQD samples; (b) Table for comparison of the lattice constants *a* derived from XRD diffraction peaks and derived from the Vegard's law. (c) Lattice constants *a* derived from XRD diffraction peaks plotted as functions of *x and y*; standard cubic ZnS, ZnSe, CdS, and CdSe also plotted for comparison.

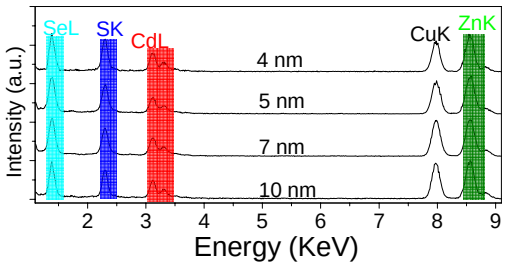



**Figure S5**. TEM-EDS spectra of the $Zn_{0.6}Cd_{0.4}S_{0.5}Se_{0.5}$ QQD samples with varying size.