

## Supporting information

### *Synthesis CdSe<sub>x</sub>S<sub>1-x</sub> Core/Shell Type Quantum Dots via One Injection Method*

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## 1. Experimentals

**Materials.** All of the chemicals are commercially available and were used as received. They are cadmium oxide (CdO, 99.99%, Alfa), oleic acid (OA, ACS grade, SHOWA), tri-*n*-butylphosphine (TBP, 93%, STREM), 1-octadecene (1-ODE, 90%, ACROS), selenium powder (Se, 99.99%, Alfa), sulfur powder (S, 99.999%, Alfa), methanol (MeOH, 99.9%, ACROS), hexane (99%, ACROS), acetone (99.9%, ACROS) and Rhodamine (R6G, Fluka)

**Synthesis procedure.** Typically, 41.9 mg of CdO, 0.45 mL of OA and 9 g of 1-ODE were heated to 300°C in a 25 mL three-neck round-bottom flask under argon. At 290°C, the solution turned colorless, indicating the formation of cadmium oleate. To produce various compositions of CdSe<sub>x</sub>S<sub>1-x</sub> QDs, a solution containing various molar ratios of Se and S in TBP/1-ODE was swiftly injection into the flask once it had reacted 300°C. Aliquots were taken at different time intervals, and UV/Vis and photoluminescence spectra were recorded for each aliquot. When the temperature was lowered to 260°C and the QDs were allowed to grow until the desired size has been achieved. Once synthesized, the unconsumed cadmium precursor was separated from QDs by the repeated extraction with MeOH/hexane by volume ratio of 2 to 1. The extraction process was monitored by a UV/Visible absorption spectrophotometer.

**Characteristics.** X-ray diffraction (XRD, Rigaku ATE-X, 18 kW Rotating Anode X-ray Generator) and transmission electron microscopy (TEM, Philips Tecnai G<sup>2</sup>, 200KV) measurement were also performed to analyze the crystallinity, size and size distribution of the resulting crystals. The size and its distribution were determined by TEM measurements and literature data on size versus the position of the first sorption peak.<sup>S1</sup> All the measurement were performed on the original aliquots without any size sorting. In order to analyze the optical properties of CdSe<sub>x</sub>S<sub>1-x</sub> QDs, PL emission peak position and PL quantum yield was characterized by standard procedure by comparing R6G dye.<sup>S2</sup>

## 2. X-ray Absorption Spectroscopy (XAS) measurement.

The X-ray absorption spectra were recorded at the beam line BL01C1 at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The electron storage ring of NSRRC was operated at 1.5 GeV. A double Si(111) crystal monochromator was employed for the energy selection with a resolution  $\Delta E/E$  better than  $1 \times 10^{-4}$  at both the Cd K-edge (26711 eV) and the Se K-edge (12658 eV). All the experiments for Tri-elemental nanoparticles were conducted in a homemade cell made with PTFE was used in both the edge measurements. One hole was covered with a PTFE rod and the position can be adjusted to get the better edge step. Before measuring the XAS, the sample was reduced with 5% H<sub>2</sub> for 30 min in order to remove the surface oxygen effect. All of the spectra were recorded at room temperature in a transmission mode. Higher harmonics were eliminated by detuning the double crystal Si (111) monochromator. Three gas-filled ionization chambers were used in series to measure the intensities of the incident beam ( $I_0$ ), the beam transmitted by the sample ( $I_t$ ), the beam subsequently transmitted by the reference foil ( $I_r$ ). The third ion chamber was used in conjunction with the reference sample, which was a Cd foil for Cd K-edge measurements and Se foil for Se K-edge measurements. The control of parameters for EXAFS measurements, data collection modes and calculation of errors were all done as per the guidelines set by International XAFS Society Standards and Criteria Committee.<sup>S3</sup>

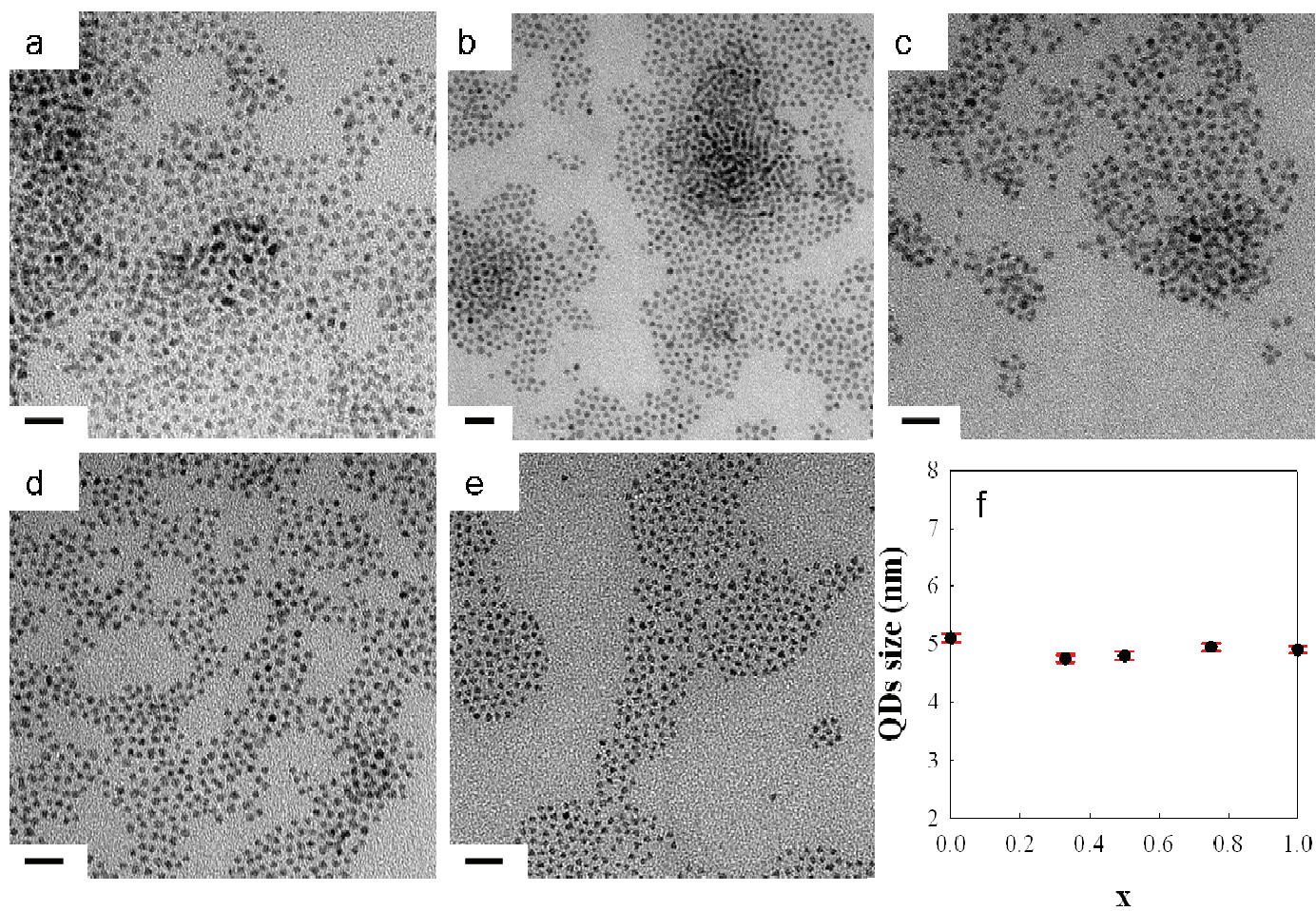
The extended X-ray absorption fine structure (EXAFS) data reduction was conducted utilizing standard procedures. The normalized  $\chi(E)$  was transformed from energy space to  $k$ -space, where ' $k$ ' is the photoelectron wave vector. The  $\chi(k)$  data were multiplied by  $k^2$  for Cd K-edge and  $k^3$  for Se K-edge to compensate the damping of EXAFS oscillations in the high  $k$ -region. Subsequently,  $\chi(k)$  data in the  $k$ -space ranging from 3.63 to 10.69 Å<sup>-1</sup> for the Cd K-edge, from 3.03 to 10.12 Å<sup>-1</sup> for the Se K-edge were Fourier transformed (FT) to  $r$ -space to separate the EXAFS contributions from the different coordination shells.

A nonlinear least-squares algorithm was applied to the curve fitting of an EXAFS with phase correlation in the  $r$ -space between 1.6 to 4.0 Å for both Cd and Se, depending on the bond to be fitted. For Cd–Se, Cd–S, and Se–S reference files, a suitable experimental reference compound was not available for calibration purposes. Hence, the effective scattering amplitude [ $f(k)$ ] and phase shift [ $\delta(k)$ ] for the Cd–Se, Cd–S, Cd–Cd, Se–Cd, Se–S, and Se–Se were generated by using FEFF7 code. Cd atoms were kept at (0, 0, 0), (0, 1/2, 1/2), (1/2, 0, 1/2), and (1/2, 1/2, 0) position in a cubic unit cell model. Se atoms were kept at (3/4, 3/4, 3/4) and (1/4, 3/4, 1/4) position. Furthermore, S atoms remained at (1/4, 1/4, 3/4) and (3/4, 1/4, 1/4) position. The lattice parameter  $a=5.5303$  Å was used in the FEFF7 calculation. All computer programs were implemented in the UWXAFS 3.0 package<sup>S4</sup> with

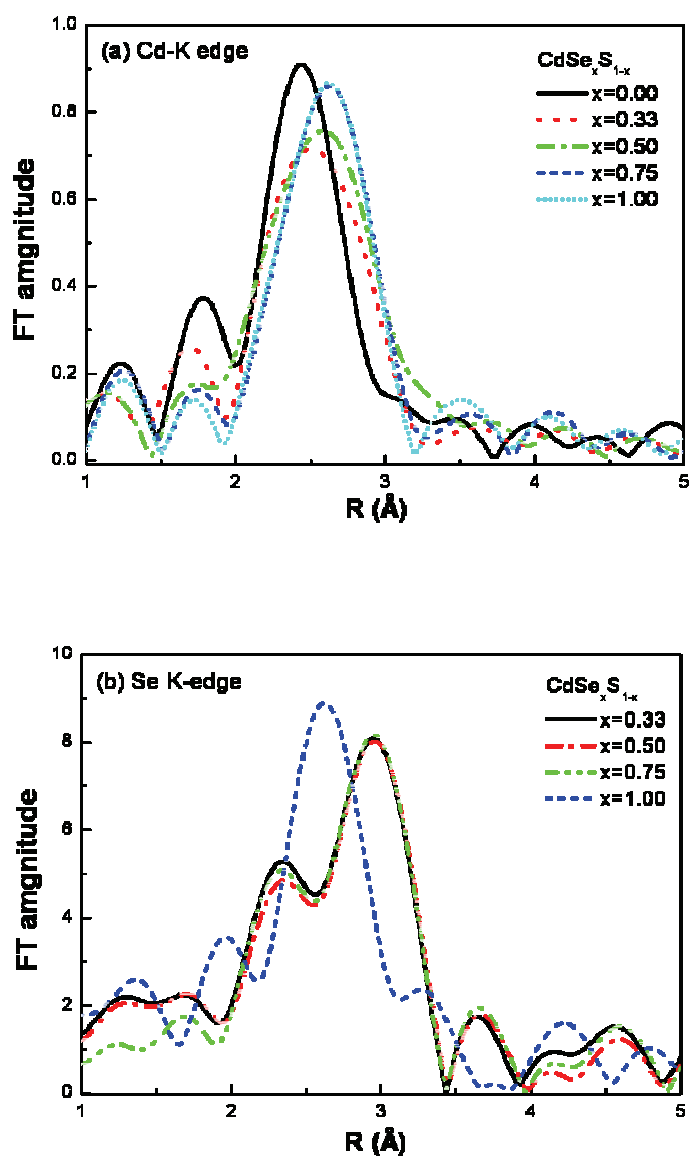
backscattering amplitude and phase shift for the specific atom pairs being theoretically calculated by using the FEFF7 code.<sup>S5</sup> Using the results, structural parameters like coordination numbers ( $N$ ) and bond distance ( $R$ ) were also calculated. The amplitude reduction factor ( $S_0^2$ ) values for Cd and Se, which accounted for energy loss due to multiple excitations, were obtained by analyzing the Cd foil and Se foil reference samples, respectively, and by fixing the coordination number in the FEFFIT input file. The  $S_0^2$  values were found to be 0.874 and 0.846 for Cd and Se, respectively.

## REFERENCES:

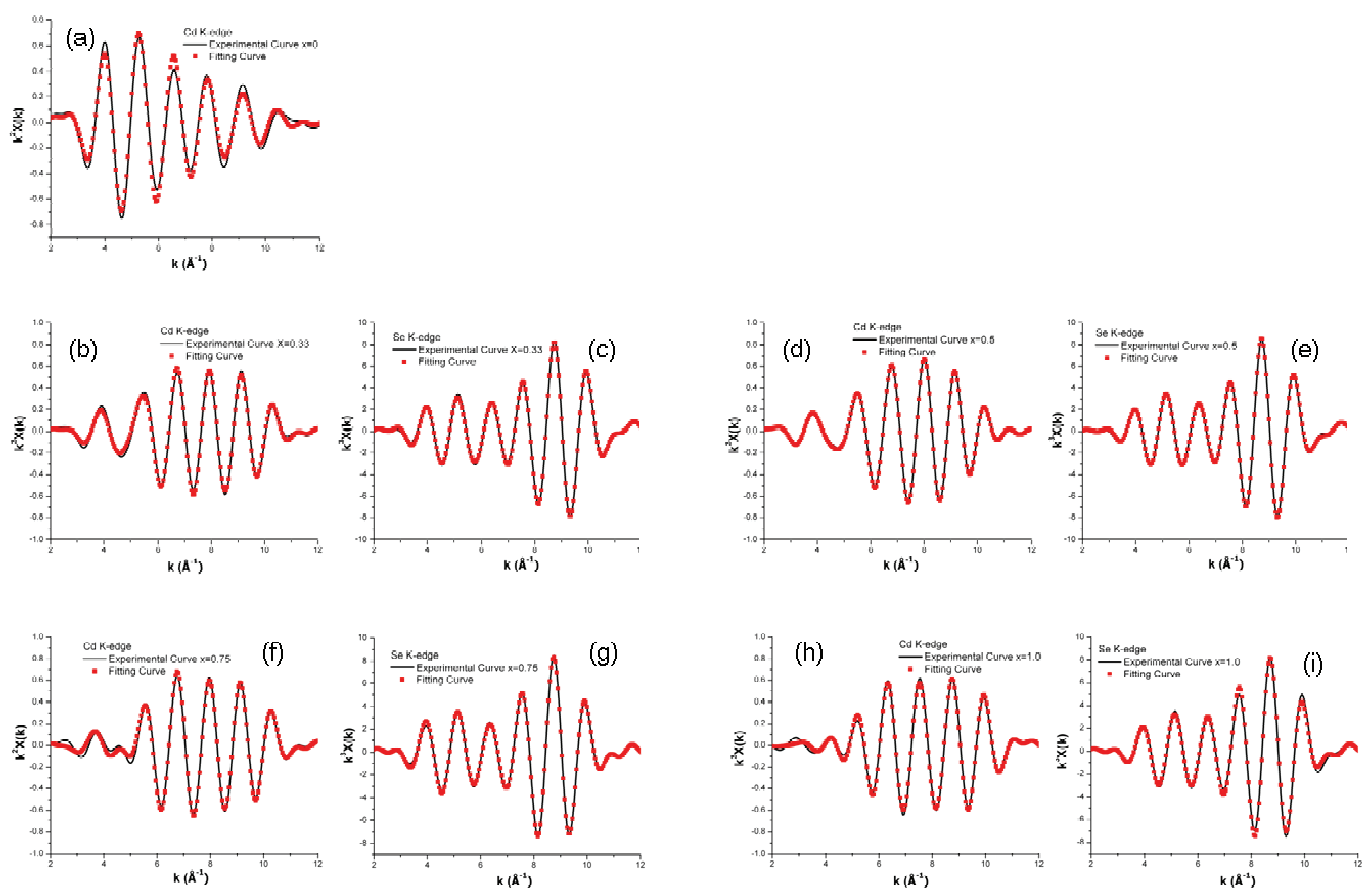
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**Fig S1.** TEM images of (a) CdSe, (b) CdSe<sub>0.75</sub>S<sub>0.25</sub>, (c) CdSe<sub>0.5</sub>S<sub>0.5</sub>, (d) CdSe<sub>0.25</sub>S<sub>0.75</sub>, (e) CdS QDs prepared with varied Se content of injection solution; (f) average sizes and size distribution of CdSe<sub>x</sub>S<sub>1-x</sub> QDs.



**Fig. S2** The Fourier transformed at (a)  $k^2$ -weighted EXAFS Cd K-edge spectrum and (b)  $k^3$ -weighted EXAFS Se K-edge for variable  $x$  of CdSe <sub>$x$</sub> S<sub>1- $x$</sub>  QDs.



**Fig. S3** Multi-shell fits with back-transformed experimental EXAFS data with both Cd K-edge and Se K-edge for variable  $x$  of  $\text{CdSe}_x\text{S}_{1-x}$  QDs. (a) CdS-QDs; (b)-(c)  $\text{CdSe}_{0.33}\text{S}_{0.67}$ -QDs; (d)-(e)  $\text{CdSe}_{0.5}\text{S}_{0.5}$ -QDs; (f)-(g)  $\text{CdSe}_{0.75}\text{S}_{0.25}$ -QDs; (h)-(i) CdSe-QDs.

**Table 1.** Structural parameters derived from the combination of EXAFS results at Cd K-edge and Se K-edge

| <b>CdSe<sub>x</sub>S<sub>1-x</sub></b> |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |  |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--|
| <b>x</b>                               | <b>1.00</b>     |                 | <b>0.75</b>     |                 | <b>0.50</b>     |                 | <b>0.33</b>     |                 | <b>0.00</b>     |                 |  |
| <b>r</b>                               | 0.001           |                 | 0.002           |                 | 0.002           |                 | 0.001           |                 | 0.001           |                 |  |
| <b>No</b>                              | N               | R               | N               | R               | N               | R               | N               | R               | N               | R               |  |
| <b>Cd-S</b>                            |                 |                 | 1.10<br>(0.050) | 2.49<br>(0.003) | 1.60<br>(0.070) | 2.50<br>(0.009) | 2.60<br>(0.090) | 2.43<br>(0.012) | 4.00<br>(0.090) | 2.35<br>(0.005) |  |
| <b>Cd-Se</b>                           | 3.50<br>(0.100) | 2.48<br>(0.009) | 2.70<br>(0.090) | 2.52<br>(0.003) | 1.60<br>(0.070) | 2.54<br>(0.009) | 1.20<br>(0.050) | 2.53<br>(0.009) |                 |                 |  |
| <b>Cd-Cd</b>                           | 3.70<br>(0.090) | 3.76<br>(0.004) | 3.60<br>(0.080) | 3.76<br>(0.003) | 3.70<br>(0.070) | 3.74<br>(0.009) | 3.60<br>(0.050) | 3.71<br>(0.007) | 3.90<br>(0.040) | 3.67<br>(0.006) |  |
| <b>Se-Cd</b>                           | 3.50<br>(0.060) | 2.48<br>(0.004) | 3.50<br>(0.090) | 2.52<br>(0.001) | 3.20<br>(0.080) | 2.54<br>(0.009) | 3.60<br>(0.060) | 2.53<br>(0.009) |                 |                 |  |
| <b>Se-S</b>                            |                 |                 | 0.40<br>(0.050) | 3.33<br>(0.006) | 0.60<br>(0.070) | 3.41<br>(0.008) | 0.60<br>(0.060) | 3.47<br>(0.006) |                 |                 |  |
| <b>Se-Se</b>                           | 3.60<br>(0.060) | 3.54<br>(0.005) | 3.50<br>(0.050) | 3.55<br>(0.005) | 3.40<br>(0.060) | 3.58<br>(0.005) | 3.40<br>(0.030) | 3.58<br>(0.008) |                 |                 |  |

N: Coordination number

R: Bonding distance (Å)

r: fitting residual factor