Supporting Information

Pulsed laser deposition of CdSe quantum dots on Zn_2SnO_4 nanowires and their photovoltaic applications

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1. SEM and TEM images of Zn_2SnO_4 nanowires

Figure S1(a) is the SEM image of a typical axially periodic Zn_2SnO_4 nanowire. Figure S1(b) shows the schematic of a Zn_2SnO_4 nanowire formed by periodic rhombohedral crystals that are enclosed by {111} equivalent facets. Figure S1(c) is the TEM image of a Zn_2SnO_4 nanowire, and the growth direction is along $[1\bar{1}1]$. Figure S1(d)-(f) are enlarged images of the corresponding areas in (c), exhibiting the single crystal structure of the nanowire.

2. Pulsed Laser Deposition System

Figure S2(a) shows the schematic of the pulsed laser deposition system. Adjustable growth parameters include laser fluence, chamber pressure, substrate temperature, and deposition time. Figure S2(b) shows the dependence of our Nd:YAG laser output energy on the pumping energy. The lowest laser fluence in our experiment (6.4 J/cm^2) was achieved using a pumping energy of 28 J, which was close to the onset of output energy generation in our system.

3. Lattice parameter calculation

Figure S3(a) shows the calculation results of lattice parameters of CdSe QDs on Zn_2SnO_4 nanowire and amorphous carbon film after SAED measurement. Figure S3(b) shows the calculation results of lattice parameters of Zn_2SnO_4 nanowire after SAED measurement.

4. PLD-coated QD size distribution

Figure S4(a) & (b) are the TEM image and corresponding size distribution of the QDs deposited using a low laser fluence of 6.4 J/cm^2, while 3(c) & (d) are the results from a high laser fluence of 12.6 J/cm^2. The Gaussian fittings for the size distributions are given by solid lines.

5. QDSSC fabrication flow

Figure S5 shows the fabrication process flow of QDSSCs based on PLD-coated quantum dots.

6. Calculation of the driving force

The driving force can be calculated using the following equation:[1]

$$\begin{aligned}\Delta G &= \Delta G_{\text{electronic}} + \Delta G_{\text{coulomb}} + \Delta G_{\text{charging}} \\ &= E_{\text{MO}} - E_{1\text{Se}} + (1+C)\frac{e^2}{\varepsilon_{\text{QD}} R_{\text{QD}}} + \frac{e^2}{2R_{\text{QD}}}\left(\frac{1}{\varepsilon_{EL}} + \frac{C}{\varepsilon_{\text{QD}}}\right) - \frac{e^2}{4\varepsilon_{EL}\left(R_{\text{QD}} + h\right)}\frac{\varepsilon_{\text{MO}} - \varepsilon_{EL}}{\varepsilon_{\text{MO}} + \varepsilon_{EL}}, \\ &\approx E_{\text{MO}} - E_{1\text{Se}} + 2.2\frac{e^2}{\varepsilon_{\text{QD}} R_{\text{QD}}}\end{aligned}$$

where $\Delta G_{\text{electronic}}$, $\Delta G_{\text{coulomb}}$, and $\Delta G_{\text{charging}}$ represent the electronic energy, coulomb interaction, and electron charging contributions to the total driving force, respectively; E_{MO} and $E_{1\text{Se}}$ are electron energies at the conduction band edges of the metal oxide and QD, respectively; C is a constant and is equal to 0.786; ε_{MO}, ε_{QD} and ε_{EL} are the dielectric constants of the metal oxide, QD, and the polysulfide electrolyte, respectively; R_{QD} is the radius of the QD; and h is the separation distance. Since the water-based electrolyte has a much higher dielectric constant than

those of the metal oxide and QD, the equation is simplified accordingly.[2] To utilize this model for our structures, we first needed to find out the energy band alignment between the PLD-coated QDs and the Zn_2SnO_4 nanowire. From the TEM structural analysis, the QD size actually did not show significant difference at different laser fluences; however, the onset of the IPCE spectra indicated a bandgap decrease for the QDs prepared using higher laser fluences. This observation could be explained by the formation of interconnecting QDs that caused a decrease in the effective energy bandgaps of the CdSe QD films. Using the onset photon energies in the IPCE spectra as the effective bandgaps of the CdSe QD films, we could outline the energy band alignment and estimate the driving force accordingly. The onset energy was defined as the lowest photon energy where the IPCE efficiency was larger than 3 times of the standard deviation of the background noise. Figure S6 shows the band alignment between Zn_2SnO_4 nanowire and CdSe QDs coated with laser fluences of 6.4, 7.6, and 9.6 J/cm^2. Since in CdSe the effective mass of the hole is much larger than that of the electron, the bandgap increase was mainly manifested by the upward shift of the conduction band edge.[1,3] Under these assumptions the driving force for the QDs deposited using laser fluences of 6.4, 7.6, and 9.6 J/cm^2 was calculated to be 0.47, 0.32, and 0.25 eV, respectively, which showed a decrease for the samples prepared with increasing laser fluences.

References:

(1) Tvrdy, K.; Frantsuzov, P. A.; Kamat, P. V. *PNAS* **2011**, *108*, 29–34.

(2) Wang, P.; Anderko, A. *Fluid Phase Equilibria* **2001**, *186*, 103–122.

(3) Tvrdy, K. Electron Transfer Reactions in Quantum Dot Sensitized Solar Cells. Ph.D. Dissertation, University of Notre Dame: United States - Indiana, 2011.

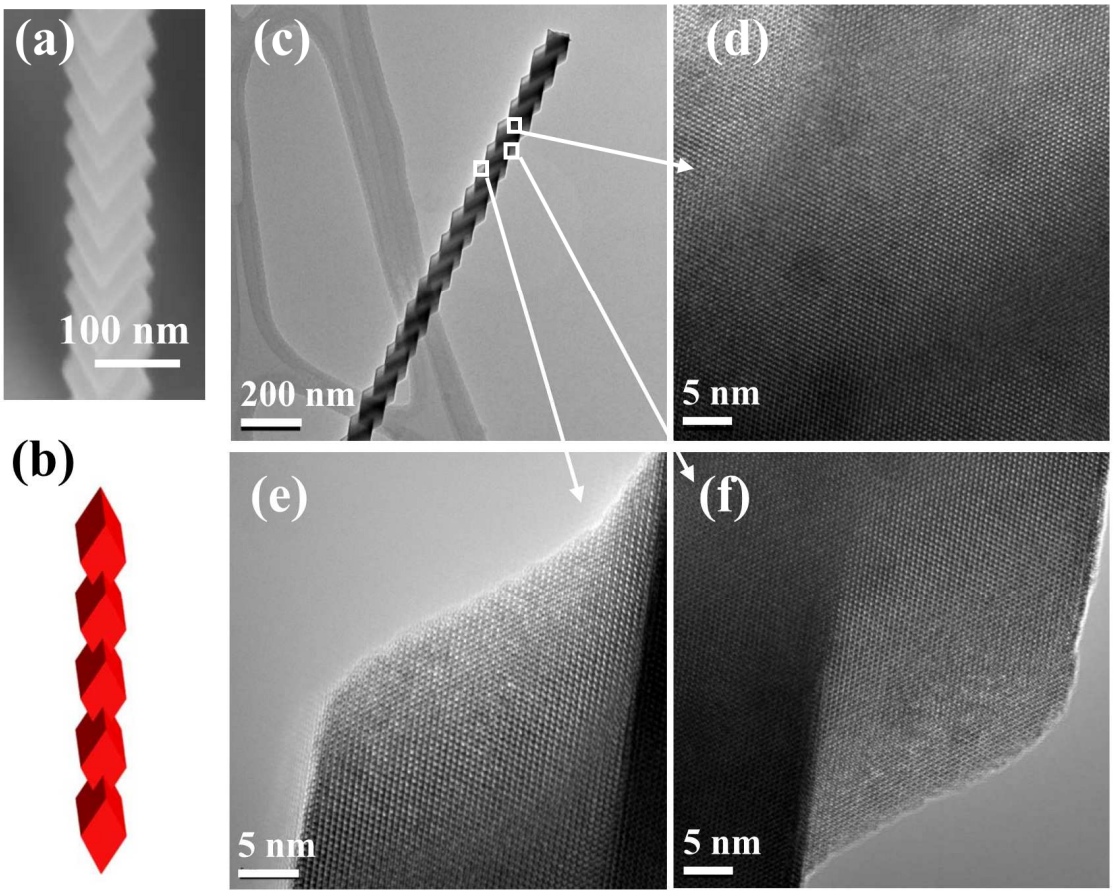
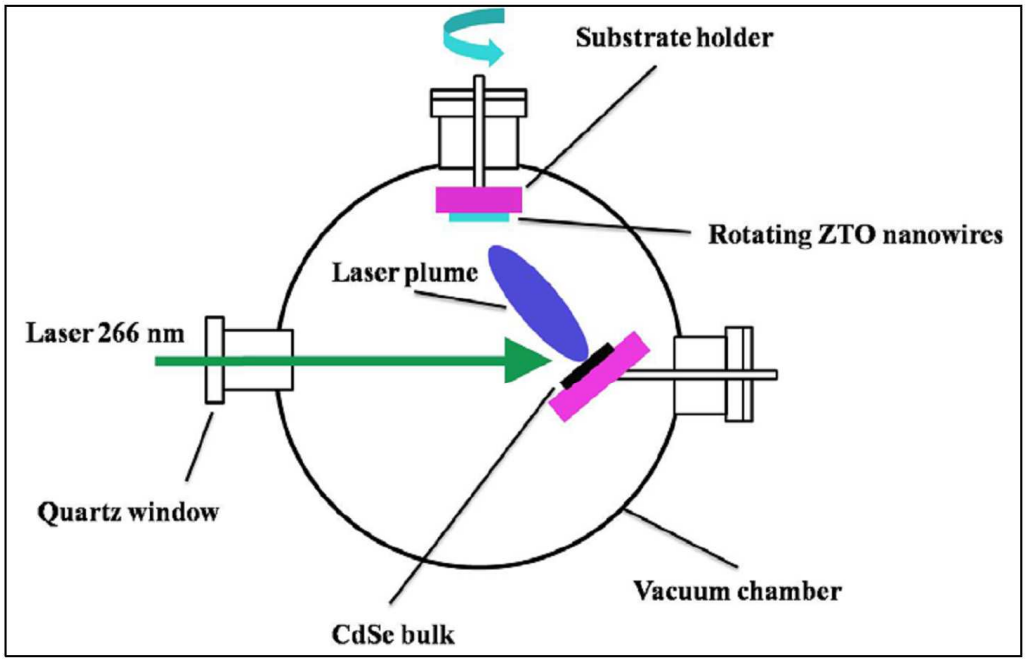


Figure S1

(a)


Substrate holder
Rotating ZTO nanowires
Laser plume
Laser 266 nm
Quartz window
Vacuum chamber
CdSe bulk

(b)

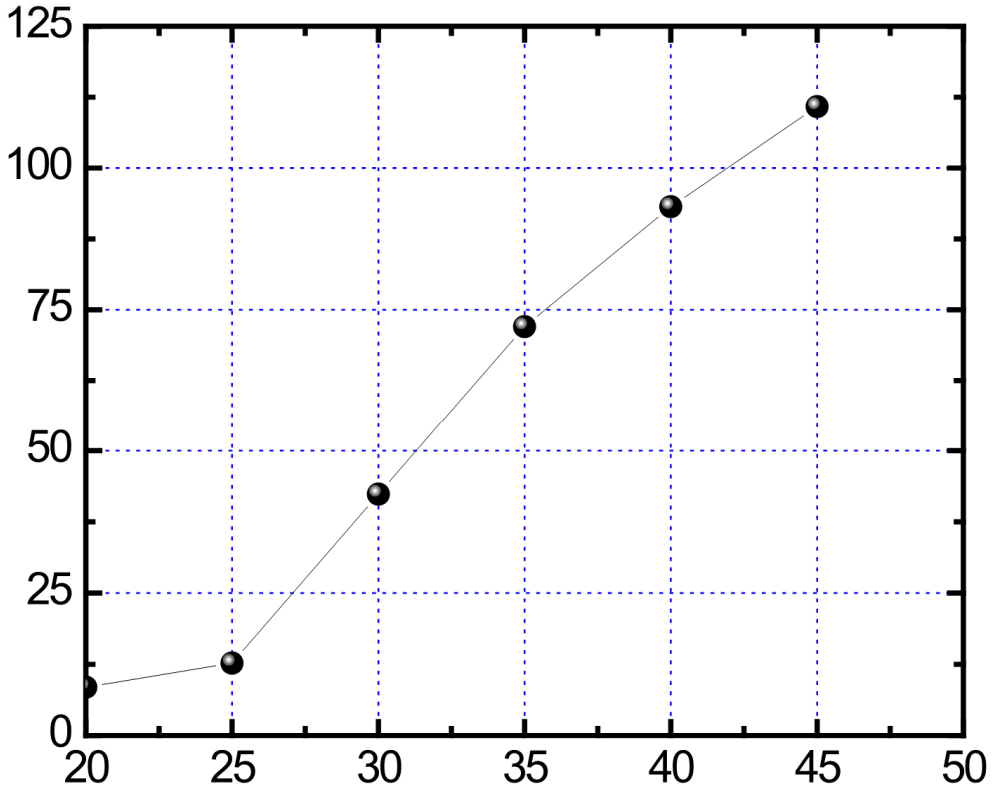

125
100
75
50
25
0
20
25
30
35
40
45
50

Figure S2

(a)

hkl	R_{hkl} (mm)	$\left(R_{hkl}/R_{111}\right)^2$ Measured	$\left(R_{hkl}/R_{111}\right)^2$ Theoretical	*a* (Å)
CdSe QDs on Zn_2SnO_4 nanowire				
111	6.745	1	1	6.091
220	11.016	2.666	2.667	6.090
311	12.945	3.682	3.667	6.077
CdSe QDs on amorphous carbon film				
111	6.728	1	1	6.086
220	11.060	2.702	2.667	6.066
311	12.592	3.503	3.667	6.074

(b)

hkl	R_{hkl} (mm)	$\left(R_{hkl}/R_{111}\right)^2$ Measured	$\left(R_{hkl}/R_{111}\right)^2$ Theoretical	*a* (Å)
111	4.734	1	1	8.678
200	5.477	1.339	1.333	8.662
220	7.786	2.705	2.667	8.616
311	9.115	3.707	3.667	8.631
331	11.945	6.367	6.333	8.655

Figure S3

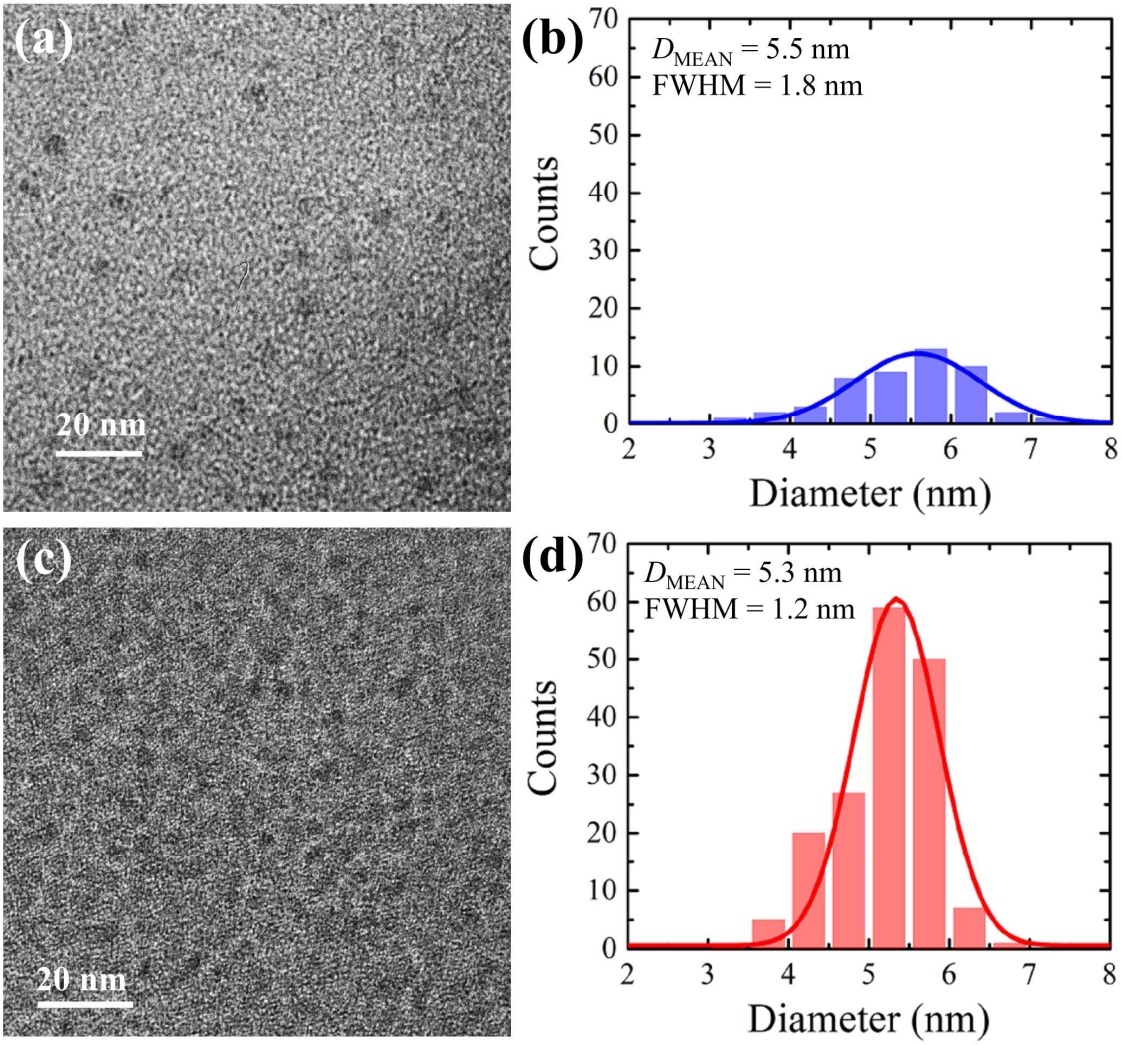

(a)
20 nm
(b)
D_{MEAN} = 5.5 nm
FWHM = 1.8 nm
Counts
Diameter (nm)
(c)
20 nm
(d)
D_{MEAN} = 5.3 nm
FWHM = 1.2 nm
Counts
Diameter (nm)

Figure S4

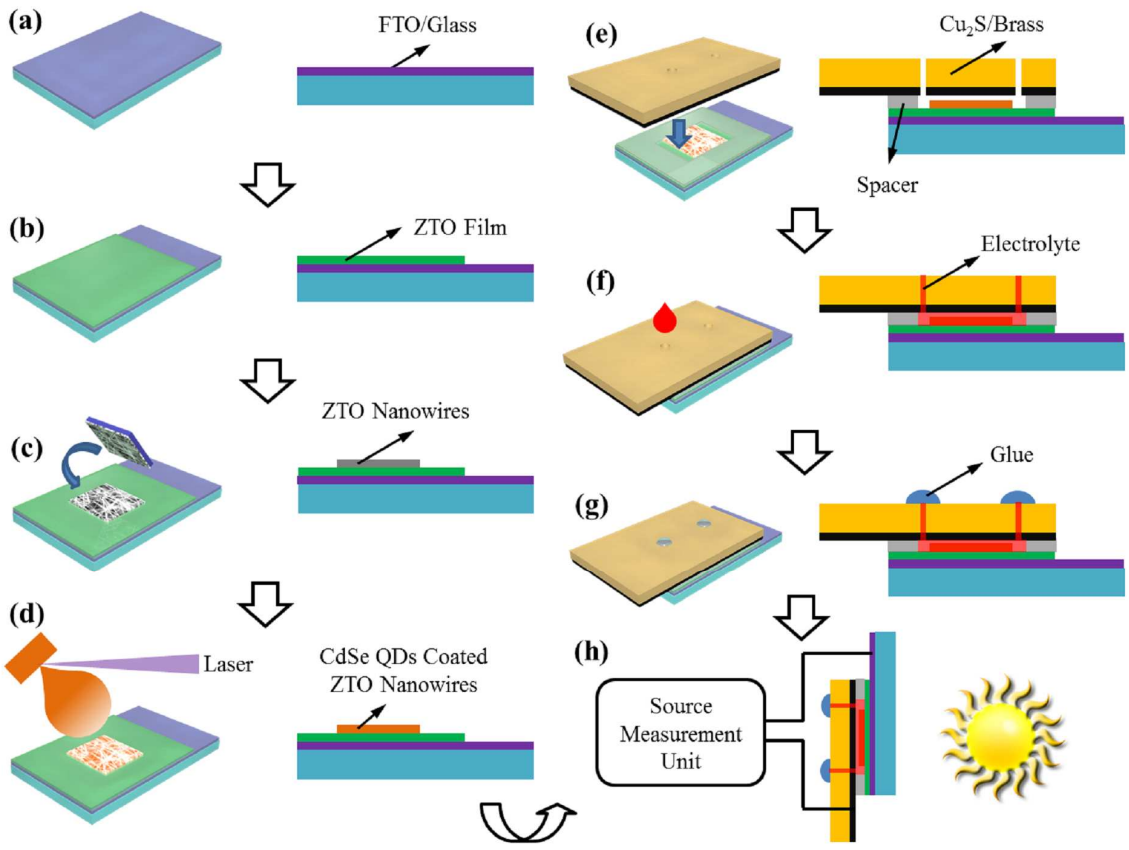

(a)
FTO/Glass
(b)
ZTO Film
(c)
ZTO Nanowires
(d)
Laser
CdSe QDs Coated
ZTO Nanowires
(e)
Cu2S/Brass
Spacer
(f)
Electrolyte
(g)
Glue
(h)
Source
Measurement
Unit

Figure S5

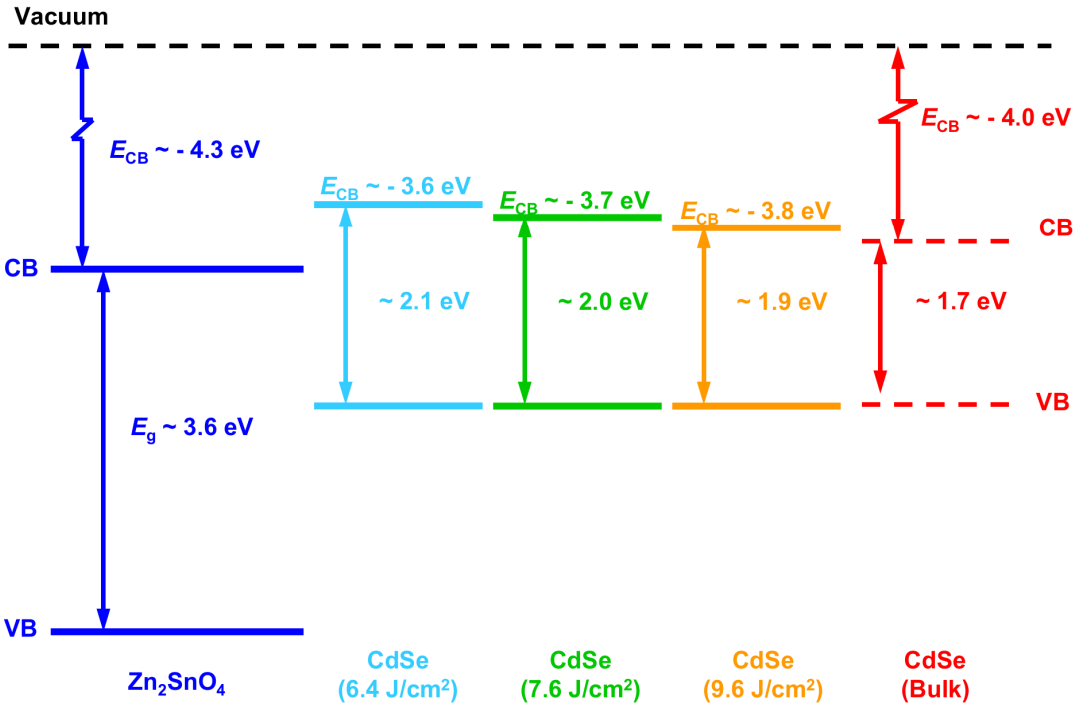

Vacuum
E_{CB} ~ - 4.3 eV
CB
E_g ~ 3.6 eV
VB
Zn_2SnO_4
E_{CB} ~ - 3.6 eV
~ 2.1 eV
CdSe
(6.4 J/cm²)
E_{CB} ~ - 3.7 eV
~ 2.0 eV
CdSe
(7.6 J/cm²)
E_{CB} ~ - 3.8 eV
~ 1.9 eV
CdSe
(9.6 J/cm²)
E_{CB} ~ - 4.0 eV
CB
~ 1.7 eV
VB
CdSe
(Bulk)

Figure S6