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Supporting Information

Band Alignment by Ternary Crystalline Potential-Tuning Interlayer for Efficient Electron Injection in Quantum Dot-Sensitized Solar Cells

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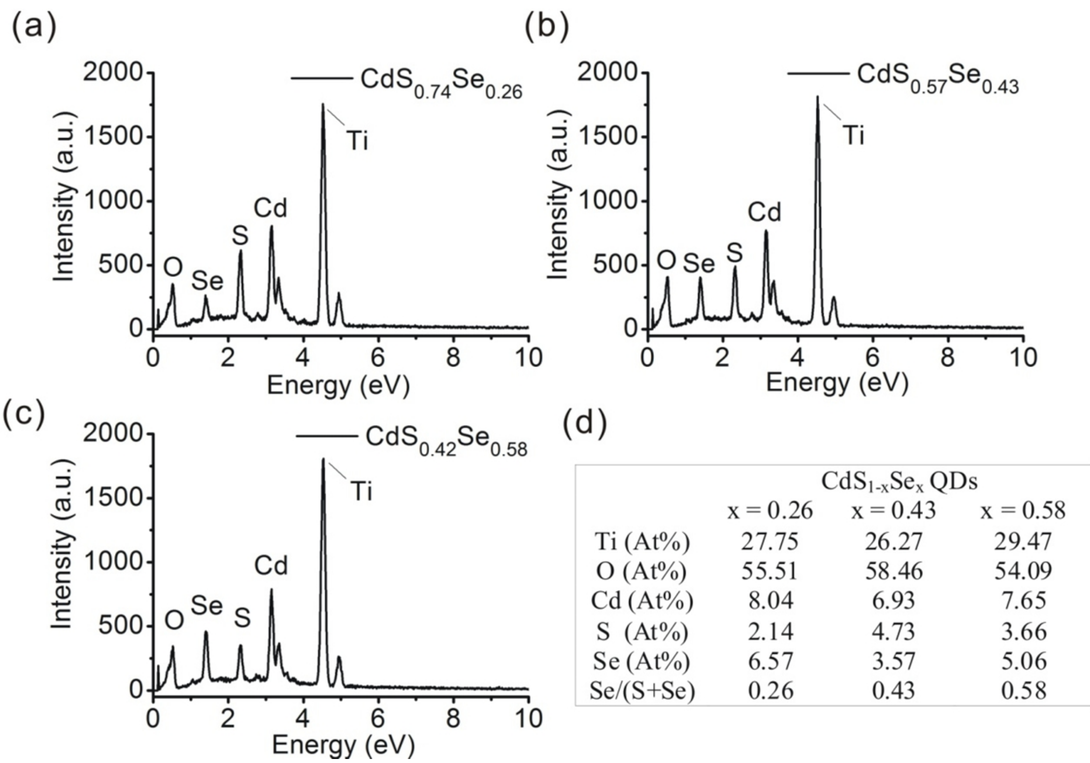

	CdS$_{1-x}$Se$_x$ QDs		
	x = 0.26	x = 0.43	x = 0.58
Ti (At%)	27.75	26.27	29.47
O (At%)	55.51	58.46	54.09
Cd (At%)	8.04	6.93	7.65
S (At%)	2.14	4.73	3.66
Se (At%)	6.57	3.57	5.06
Se/(S+Se)	0.26	0.43	0.58

Fig. S1 EDX spectrum of ternary $CdS_{0.74}Se_{0.26}$ QDs (Figure S1a), $CdS_{0.57}Se_{0.43}$ QDs (Figure S1b), and $CdS_{0.42}Se_{0.58}$ QDs (Figure S1c), with specific elemental peaks. These peaks are as follows: Titanium K_α=4.51 keV and K_β=4.93 keV, Oxygen K_α=0.52 keV, Cadmium L_α=3.13 keV and L_β=3.31 keV, Surful K_α=2.37 keV and Selenium L_α=1.37 keV. The detailed composition of elements in $CdS_{1-x}Se_x$ QDs have been listed in Figure S1d.

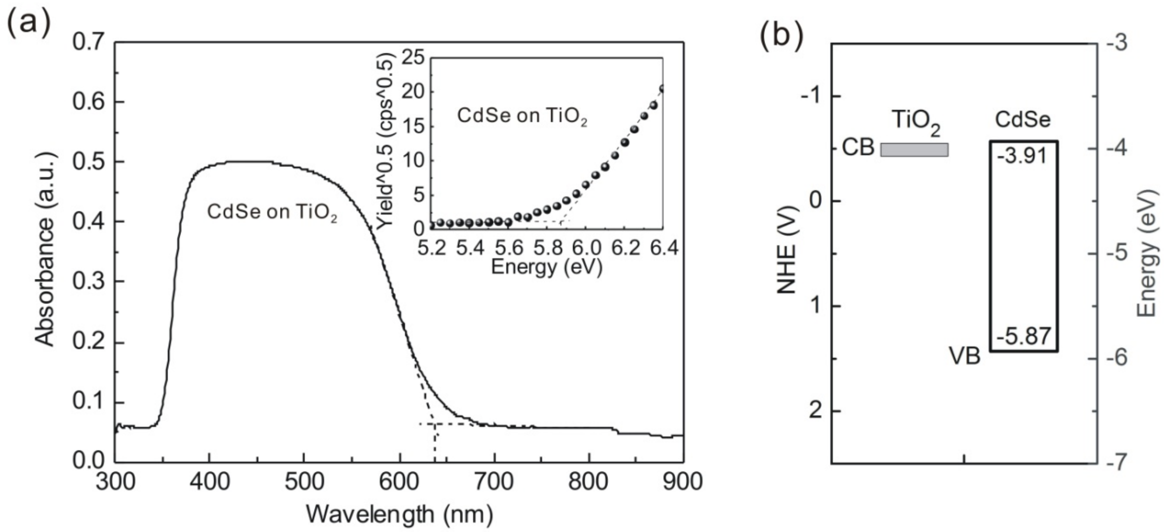

Fig. S2 (a) Absorbance spectrum of CdSe QDs decorated TiO_2 nanoparticles by SILAR process (7 cycles). The inset is its corresponding ionization spectra. (b) Band diagram at the TiO_2/CdSe interface.

Fig. S3a shows scanning electron micrographs of bare TiO_2 nanoparticles (upper part) and TiO_2 nanoparticles decorated with $CdS_{0.57}Se_{0.43}$/CdSe QDs (lower part). The transparent TiO_2 nanoparticles we prepared had an average diameter of 25 nm with a pore size of 25.0 ± 4 nm, as determined by the Brunauer–Emmett–Teller method. After coverage with the $CdS_{0.57}Se_{0.43}$/CdSe QDs, the surface of the TiO_2 nanoparticles was rough and the pore size became smaller. The double-layer $CdS_{0.57}Se_{0.43}$/CdSe QDs were effectively loaded onto the TiO_2 film, as demonstrated in the cross-sectional scanning electron micrograph shown in Fig. S3b. Cross-sectional mapping of Cd, S, and Se indicates that these elements were uniformly distributed throughout the photoanode.

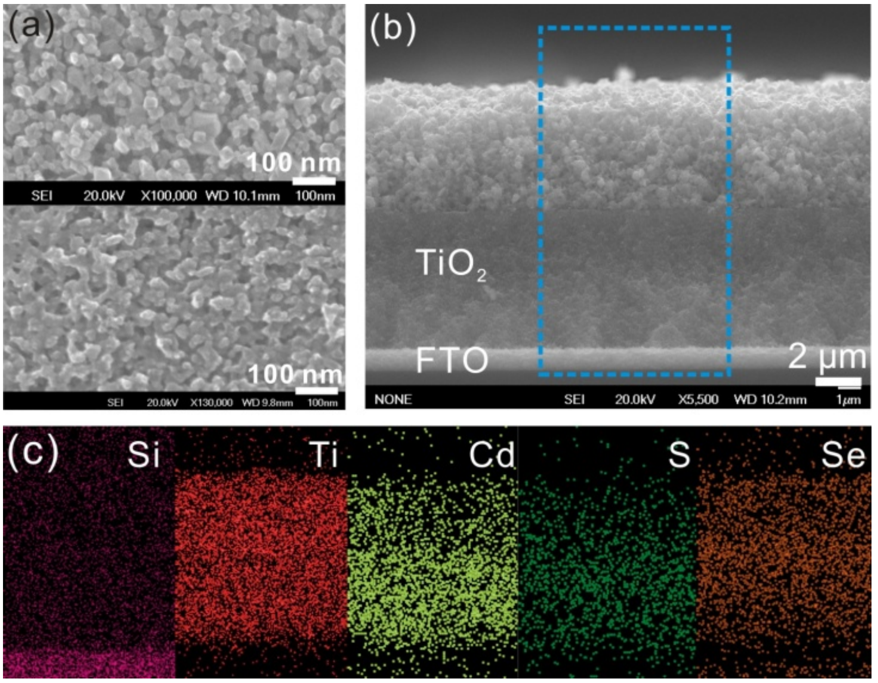

Fig. S3 (a) Scanning electron micrographs of bare TiO_2 nanoparticles (upper image) and $CdS_{0.57}Se_{0.43}$/CdSe QD–decorated TiO_2 nanoparticles (lower image). (b) Cross-section scanning electron micrograph of the mesoporous TiO_2 substrate consisting of a 5-µm-thick, dense, transparent layer of TiO_2 nanoparticles (diameter ~25 nm) and a 5-µm-thick scattering layer (diameter ~400 nm). (c) Elemental mapping of Si, Ti, Cd, S, and Se in a QD-sensitized TiO_2 film.

We determined the LHEs of the CdS/CdSe QDs and three types of $CdS_{1-x}Se_x$ QDs/CdSe QDs (x = 0.26, 0.43, and 0.58) on a thin cover glass (0.14 mm) to avoid scattered light leaks from the glass substrate side. The transmittance and reflectance spectra of bare TiO_2 film are shown in Fig. S4a. The light collection obtained by adding the transmittance and reflectance spectra approached 100% above 400 nm. Fig. S4b shows the LHE of QD-sensitized films; light harvesting below 400 nm was assigned to absorption by the TiO_2 film. The band edge of the LHE spectra in Fig. 4b was kept at 710 nm for the different double-layer QDs. The LHEs of the QDs approached 90% at 550 nm owing to the high extinction coefficient of semiconductor QDs, the concentration of QDs, and the thickness of the absorbing layer we used.

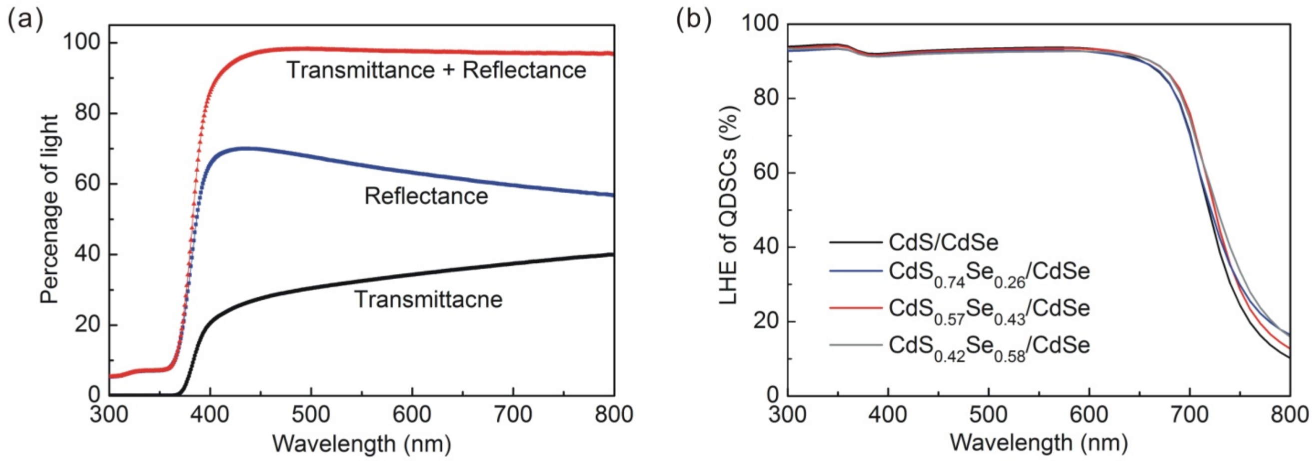

Fig. S4 (a) Reflectance, transmittance spectrum and the sum of them for bare TiO_2 film. The construction of this measurement is composed by thin cover glass, deposited bare TiO_2 film and the other thin cover glass with aqueous solution, to model electrolyte in real solar cells. [28] (b) LHE of QDSCs vs. wavelength calculated for both CdS/CdSe and $CdS_{1-x}Se_x$/CdSe QDSCs (x=0.26, 0.43, 0.58).

The τ_{sc} values can be calculated as $\tau_{sc} = 1/\omega_{min,sc} = 1/2\pi f_{min,sc}$, where $f_{min,sc}$ is the frequency of the lowest imaginary number in the IMPS plot. The τ_{oc} values can be calculated as $\tau_{oc} = 1/\omega_{min,oc} = 1/2\pi f_{min,oc}$, where $f_{min,oc}$ is the frequency of the lowest imaginary number in the IMVS plot.

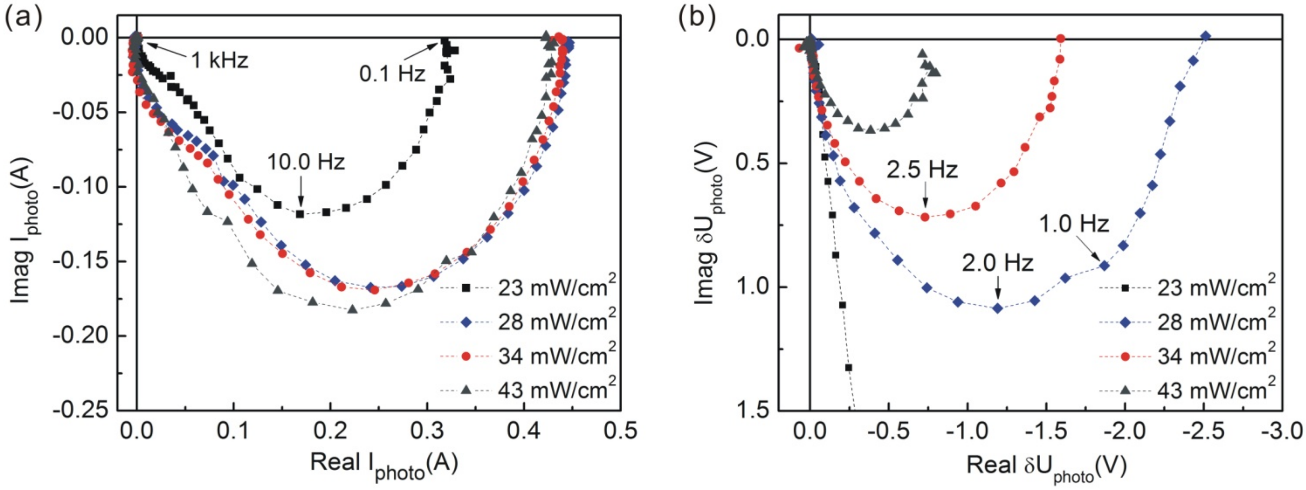

Fig. S5 (a) IMPS and (b) IMVS spectra of $CdS_{0.57}Se_{0.43}$/CdSe QDSCs measured under varying level of laser intensities (λ=446 nm). The τ_{sc} can be obtained from the frequency of the lowest imaginary in the IMPS plot while τ_{oc} can be calculated from the frequency of the lowest imaginary in the IMVS plot.

Table S1 Values of τ_{oc}, τ_{sc}, and η_{coll} for QDSCs under varying light intensities (λ = 446 nm) calculated from IMVS and IMPS measurements.

	Intensity (W/m^2)	τ_{oc} (ms)	τ_{sc} (ms)	η_{coll} (%)
CdS/CdSe	24.1	503.3	31.8	93.7
	30.3	63.4	5.0	92.1
	37.5	50.3	2.5	95.0
	46.6	25.2	1.6	93.7
$CdS_{0.74}Se_{0.26}$/CdSe	24.1	797.6	25.2	96.8
	30.3	110.4	4.0	96.0
	37.5	50.3	2.5	95.0
	46.6	31.8	1.6	95.0
$CdS_{0.57}Se_{0.43}$/CdSe	24.1	633.6	15.9	97.5
	30.3	79.8	3.2	96.0
	37.5	63.4	2.0	96.8
	46.6	50.3	1.3	97.5
$CdS_{0.42}Se_{0.58}$/CdSe	24.1	633.6	20.0	96.8
	30.3	100.4	4.0	96.0
	37.5	63.4	2.5	96.0
	46.6	40.0	2.0	95.0

Table S2 Calculated J_{sc}, V_{oc}, FF, η, series (R_S) and shunt (R_{SH}) resistance values for Zn-doped CdS/CdSe, Se-doped CdS/CdSe and ternary $CdS_{0.57}Se_{0.43}$/CdSe QDSCs under 1-sun illumination (100 mW/cm^2).

	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)	R_S (ohm)	R_{SH} (ohm)
Zn-doped CdS/CdSe	11.98	517.7	51.5	3.19	61.9	1810.4
Se-doped CdS/CdSe	12.08	548.5	54.2	3.42	41.5	3150.0
$CdS_{0.57}Se_{0.43}$/CdSe	14.22	566.8	55.3	4.46	35.2	5554.6

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