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Supporting Information for

Tuning band alignment by CdS layers using SILAR method to enhance TiO_2/CdS/CdSe quantum-dot solar-cell performance

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Experimental Section.

Solar cell assembly

To investigate the photovoltaic performance of CdS/CdSe-sensitized mesoscopic TiO_2 electrodes, sandwich type thin layer cells were fabricated with Pb/PbS as the counter electrode, and a polysulfide electrolyte as the hole transporter. TiO_2 films were prepared by coating commercial P-25 TiO_2 powders onto FTO using a doctor blade method and sintered at 450 °C for 30 min. The deposition of CdS buffer layer was prepared using the SILAR method described as below. For CdS deposition, TiO_2 films were immersed into a solution of $Cd(Ac)_2$ (0.1 M) for 1 min and then in 0.1 M Na_2S solution. Each immersion, the TiO_2 film was rinsed with ethanol and methanol respectively, and dried with N_2 gun. If the process was repeated x cycles, then the prepared electrodes are represented herein as $TiO_2/(CdS)_x$. To ensure the CdSe sensitizer has bulk properties to that of cascaded CdS/CdSe, CdSe were deposited by the chemical bath deposition (CBD) method based on slow release of selenide ions (Se^{2-}) from Na_2SeSO_3 in the presence of Cd^{2+} at 5 °C (16h) and 25 °C (72h). These as-prepared electrodes are represented herein as $TiO_2/(CdS)_x/CdSe$. PbS/Pb counter electrode, the polysulfide electrolyte and fabrication of the QDSSCs were prepared and constructed according to a literature[1]. A thin ZnS passivation layer (4 cycles) was deposited onto the CdS/CdSe-sensitized electrodes to hinder the backward electron flow from sensitizers to the oxidized species in electrolyte[1]. A full description of the solar cell assembly and material characterization is presented in the Supporting Information.

Before studying the CdS cycles effect on the performance of $TiO_2/CdS/CdSe$, the thickness of CdSe and TiO_2 film was firstly optimized using the chemical bath deposition (CBD) method. For the thickness of CdSe, the absolute adsorption of $TiO_2/CdS/CdSe$ samples increases with the thickness of CdSe, which is controlled by the deposition time. Fig. S1 shows a broaden adsorption range under larger thickness tuned by the deposition time. The current-potential (*J-V*) curves (see Fig. S2, Table S2) and incident photon-to-current efficiency (IPCE) (Fig. S3) both suggested that the more thickness of CdSe produces better performance. It is important to mind that the increase of IPCE is significantly reduced after 2 days. Therefore, the CdSe thickness with 4 days was adopted in the following. For the thickness of TiO_2 film, the *J-V* and IPCE curves were shown in Fig. S4 and S5 and Table S3, and we found the cell performance changes slight as the increase of TiO_2 film thickness. Thus, 6 μm thick TiO_2 film was adopted in the following.

Material characterization

The UV-vis absorbance data were obtained using HITACHI U-3010 ultraviolet-visible spectrophotometer. The *J-V* curves of the solar cells were obtained using Keithley 2611 source meter under one sun condition using a solar light simulator. The power of the simulated light was calibrated to 100 mW/cm^2. Electrochemical impedance spectroscopy (EIS) experiments were measured in the light by using Solartron workstation with 1255B frequency response and SI 1287 potentiostat. The frequency range of EIS experiments was from 0.1 Hz to 100 kHz with a bias voltage of 0 V. Transmission electron microscopy (TEM) was carried out on a JEM 2011 TEM.

Theoretical Section.

All DFT calculations were performed using VASP[2] with the projector augmented waves method[3] and the generalized gradient approximation exchange-correlation function[4]. A plane wave cutoff of 500 eV and a 2 × 3 × 1 k-point mesh of the Monkhorst-Pack sampling scheme are used. The structural relaxation is performed using the conjugated gradient minimization method with the maximum force on each atom less than 0.02 eV/Å. DFT + U was applied to evaluate the interaction between electrons of 4d orbitals. The U-J value of Ti and Cd is 5.5 and 7.0 eV, respectively. The calculated band gap of TiO_2 and CdS is about 2.70 eV and 1.89 eV, which are smaller than experimental values of those (TiO_2, 3.2 eV;[5] CdS, 2.4 eV[6]), respectively. Given DFT method always underestimating the band gap of transitional metal oxide or sulfide, the calculated band gap errors were acceptable. Both TiO_2(101) and TiO_2/CdS was modeled having four O-Ti-O layers, and the bottom two O-Ti-O layers were fixed to the bulk parameters, while the surface is relaxed. The slabs were separated by a vacuum space of 20 Å to prevent interaction between periodic slabs. A 2 × 3 × 1 k-grids were used for all surface calculations. The optimized configurations of TiO_2/CdS and TiO_2/CdS/CdSe were shown in Fig. S7.

The CBM energy of bulk phase can be given by

$$\varepsilon_{\text{CBM, bulk}} = E_{\text{CBM, bulk}} - E_{\text{M, bulk}} \quad (1)$$

where the $E_{\text{CBM, bulk}}$ is the band energy and the $E_{\text{M, bulk}}$ is the M ion core potential energy (M = Ti, Cd). And the CBM energy of slab are recpect to their bulk phase, that is,

$$\varepsilon_{\text{CBM, slab}} = E_{\text{CBM, slab}} - E_{\text{M, slab}} - \varepsilon_{\text{CBM, bulk}} \quad (2)$$

where $E_{\text{CBM, slab}}$ and $E_{\text{M, slab}}$ are the band energies and core potential energies of M in the slab system, respectively.

Table S1. J-V characteristics of $TiO_2/(CdS)n/CdSe$ quantum-dot solar cells fabricated with different number of CdS SILAR cycles (equal to n in (CdS)n) for optimization incorporating platinized FTO cathode under simulated illumination.

SILAR cycles	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
1	7.77	465	0.72	2.60
2	11.30	485	0.68	3.74
3	12.99	495	0.68	4.37
4	15.35	495	0.66	4.98
5	16.16	495	0.64	5.13
6	18.47	505	0.64	5.94

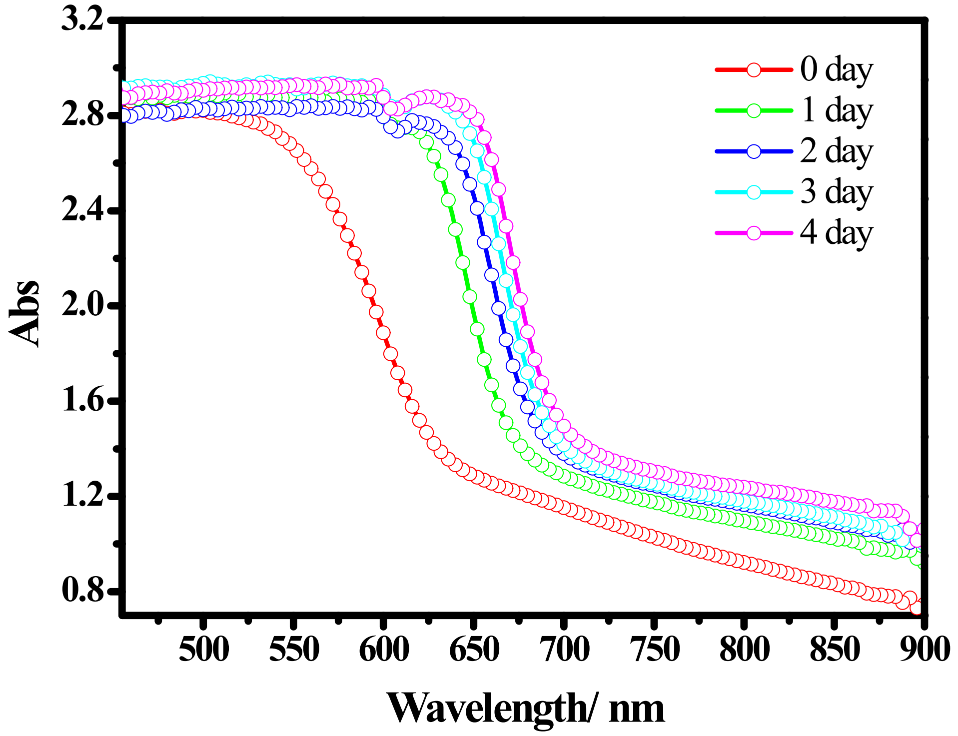

Fig. S1. UV-vis absorption spectra of TiO_2/CdS/CdSe QDSSSs using the CBD method at different deposition days.

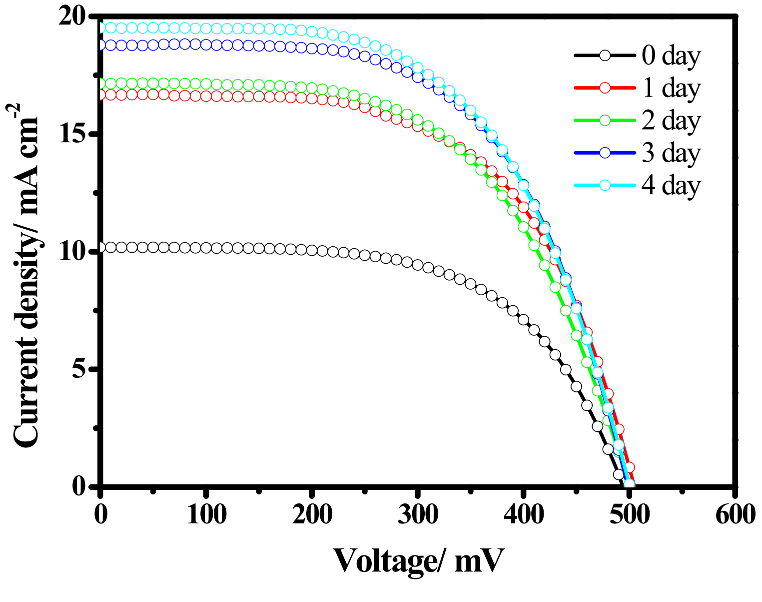

Fig. S2. *J-V* characteristics of TiO_2/CdS/CdSe QDSSSs prepared by the CBD method at different deposition days measured under the illumination of one sun (AM1.5, 100 mWcm^2).

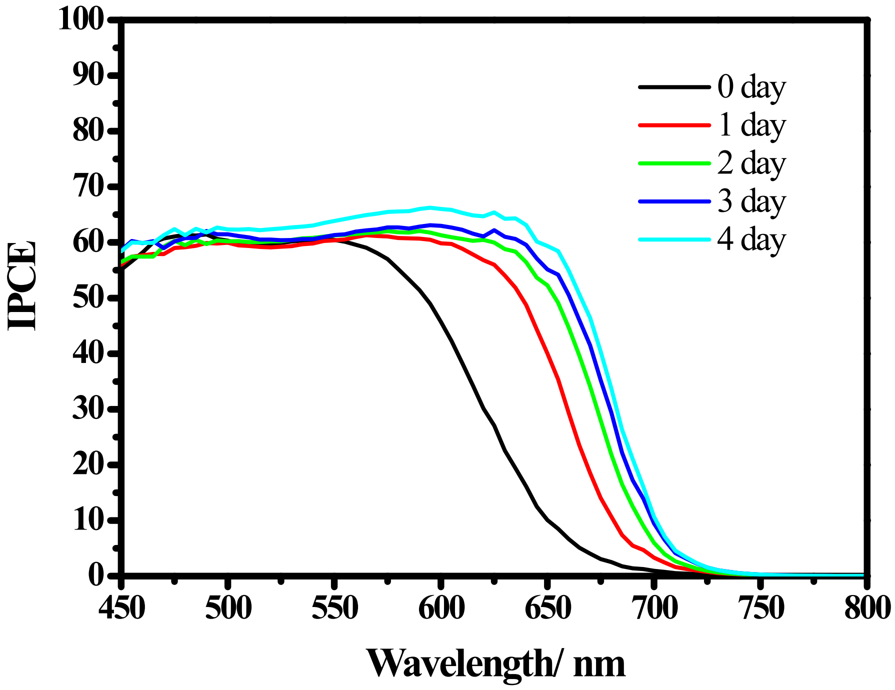

Fig. S3. Incident photon to current conversion efficiencies (IPCEs) measured as a function of wavelength for $TiO_2/CdS/CdSe$ QDSSSs prepared by the CBD method.

Table S2. Detailed photovoltaic parameters of $TiO_2/CdS/CdSe$ QDSSSs.

	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
0 day	10.20	492	0.6028	3.02
1 day	16.68	504	0.5913	4.97
2 day	18.05	504	0.5724	5.21
3 day	18.79	496	0.5946	5.54
4 day	19.51	500	0.5740	5.60

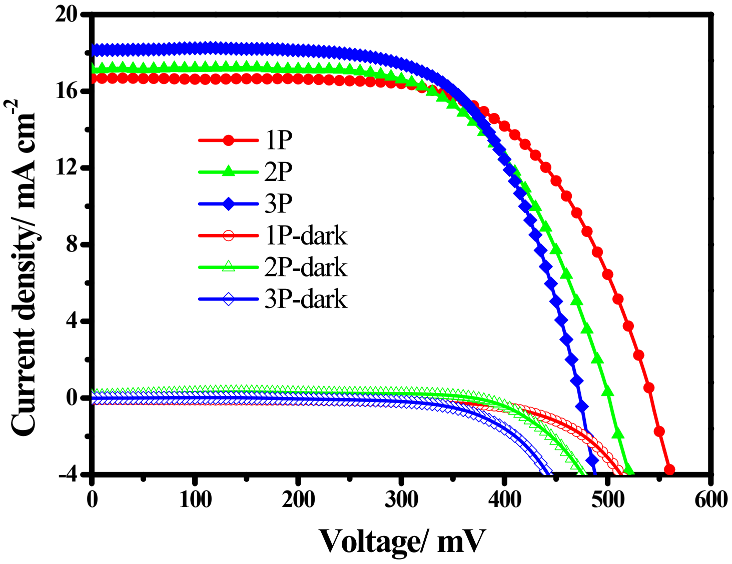

Fig. S4. *J-V* characteristics of TiO_2/CdS/CdSe QDSSSs prepared by the CBD method for different thickness measured under the illumination of one sun (AM1.5, 100 mWcm^2) under different TiO_2 film thickness.

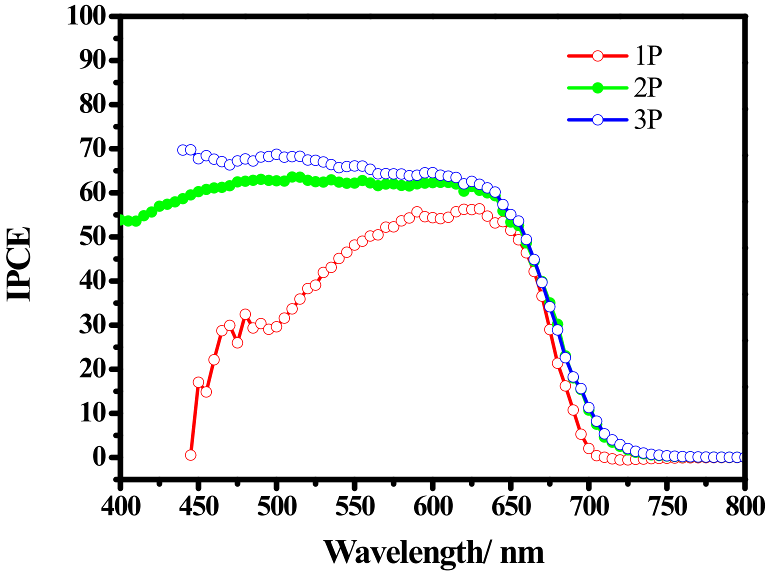

Fig. S5. Incident photon to current conversion efficiencies (IPCEs) measured as a function of wavelength for TiO_2/CdS/CdSe QDSSSs prepared by the CBD method under different TiO_2 film thickness.

Table S3. Detailed photovoltaic parameters of TiO_2/CdS/CdSe with different TiO_2 film thickness QDSSSs.

	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
1P-48h	16.68	535	0.6372	5.68
2P-48h	17.12	495	0.6322	5.36
3P-48h	18.14	465	0.6657	5.61

Table S4. Detailed photovoltaic parameters of TiO_2/(CdS)n/CdSe with different SILAR cycles of QDSSSs

SILAR cycles	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
3	15.17	495	0.63	4.74
5	19.04	485	0.59	5.49
6	19.72	507	0.60	6.01
7	20.64	501	0.57	5.95
8	19.84	525	0.60	6.31
9	20.69	527	0.56	6.16
10	20.63	522	0.54	5.84
11	20.69	532	0.53	5.94

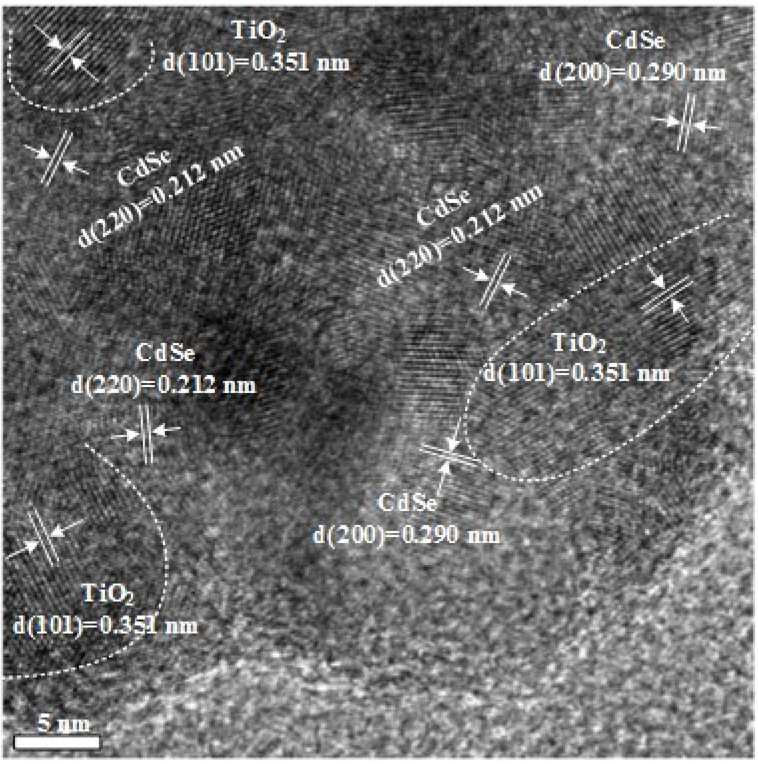

Fig. S6. High-resolution TEM image showing the arrangement of TiO_2/CdS/CdSe samples.

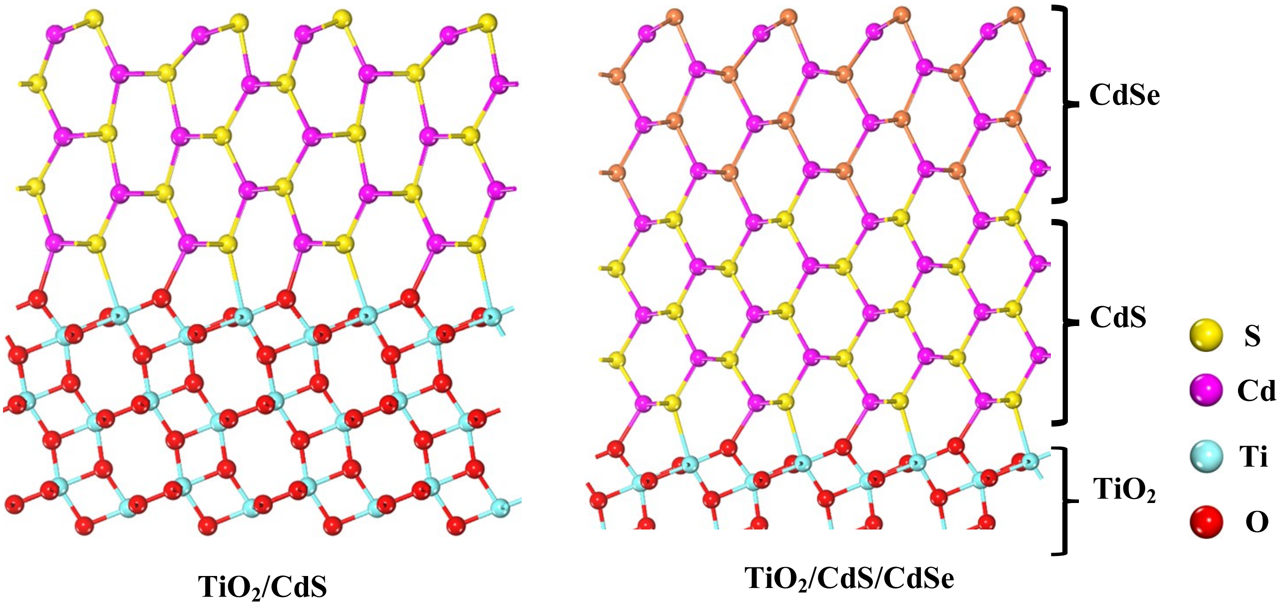

Fig. S7. The optimized configurations of TiO_2/CdS and TiO_2/CdS/CdSe, respectively.

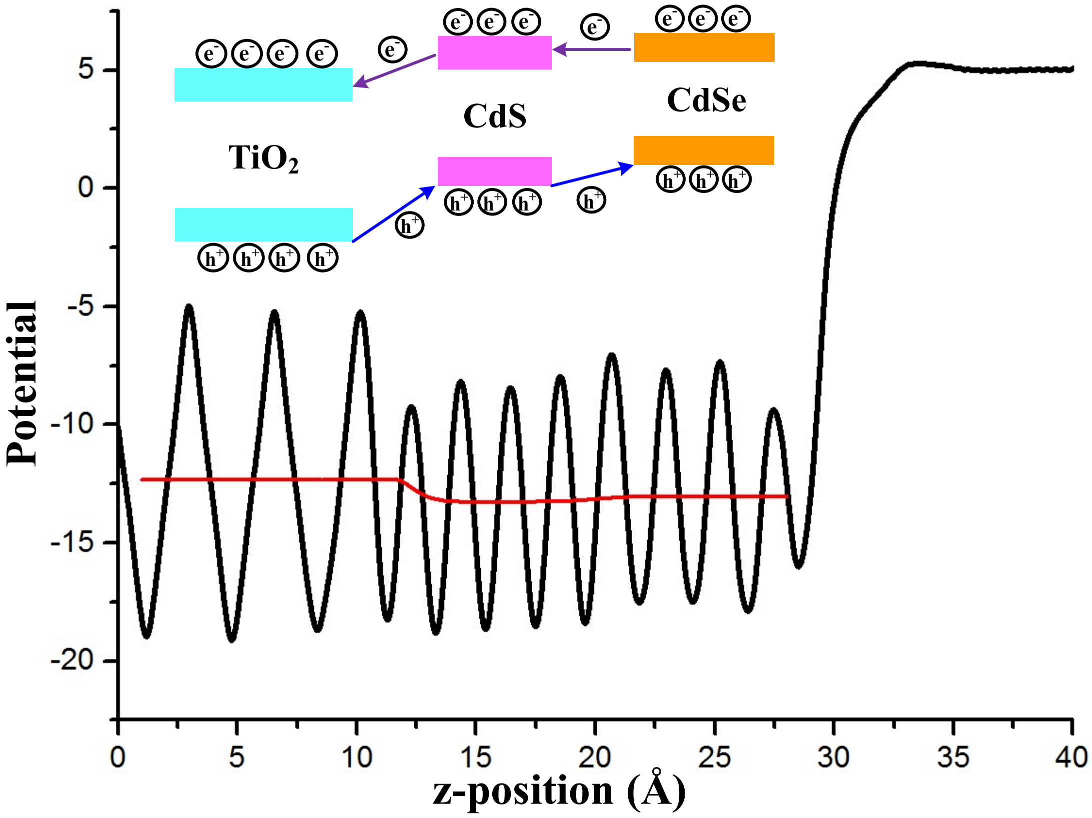

Fig. S8. Schematic diagram of electronic potential profile and the band offsets for TiO_2/CdS/CdSe.

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