

Supplementary Material (ESI) for Physical Chemistry Chemical Physics
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Supporting Information

High-efficiency cascade CdS/CdSe quantum dot-sensitized solar cells based on hierarchical tetrapod-like ZnO nanoparticles

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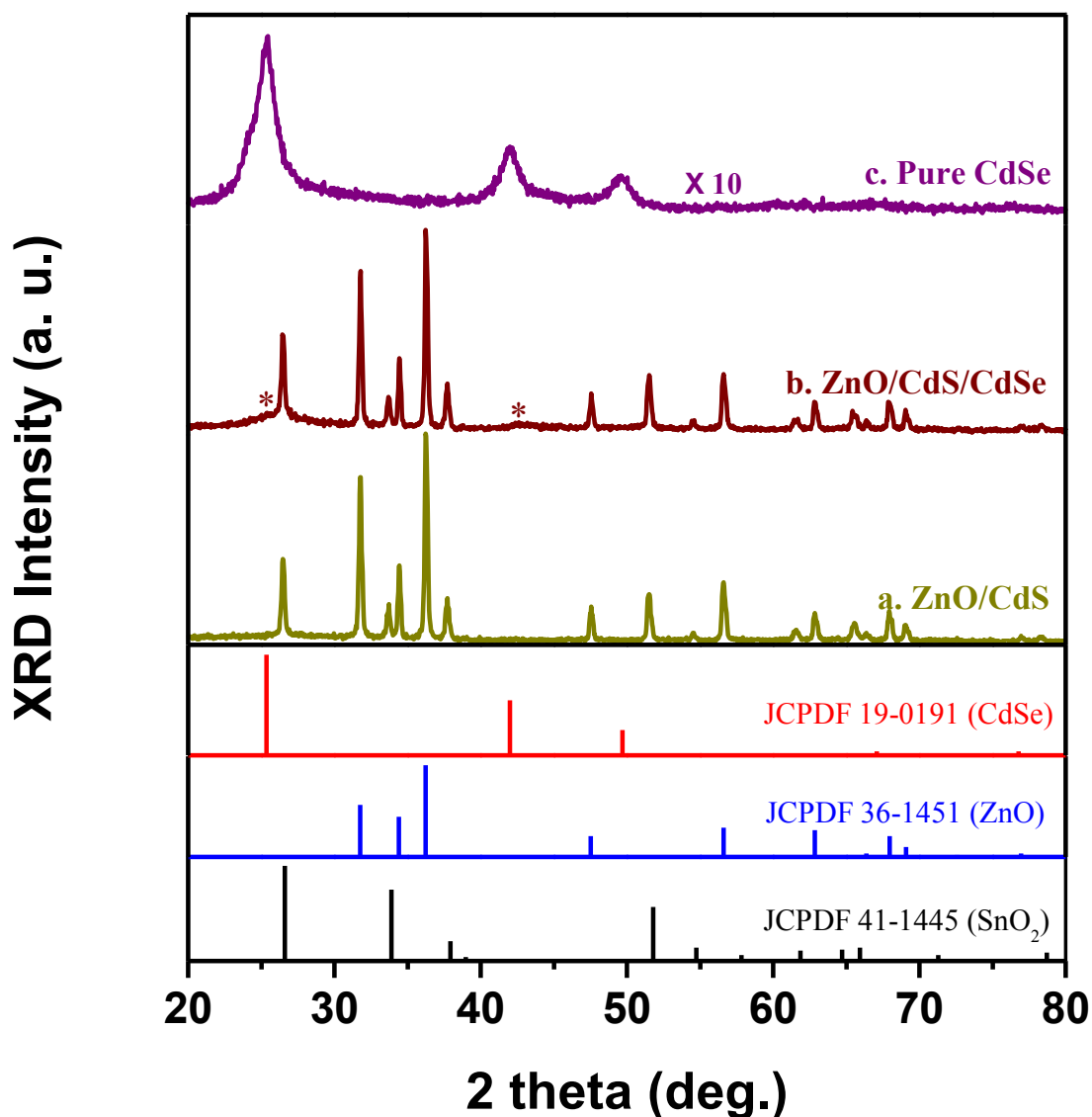


Figure S1. X-ray diffraction patterns of CdS-sensitized ZnO photoelectrode (curve a), CdS/CdSe sensitized ZnO photoelectrode (curve b) and pure CdSe QDs on glass (curve c). SnO₂ signal comes from the fluorine doped tin oxide (FTO) substrate. The CdS layer doesn't contribute any diffraction peak because of the nanocrystalline or amorphous nature as the SILAR method. After CdSe synthesis, additional broad weak peaks (denoted as asterisk) appear which may be attributed to the formation of CdSe QDs with zinc blende (cubic) phase (JCPDS file No. 19-0191). The pure CdSe QDs obtained from the residual CBD solutions revealed zinc blende reflection that confirms the aforementioned assumption.

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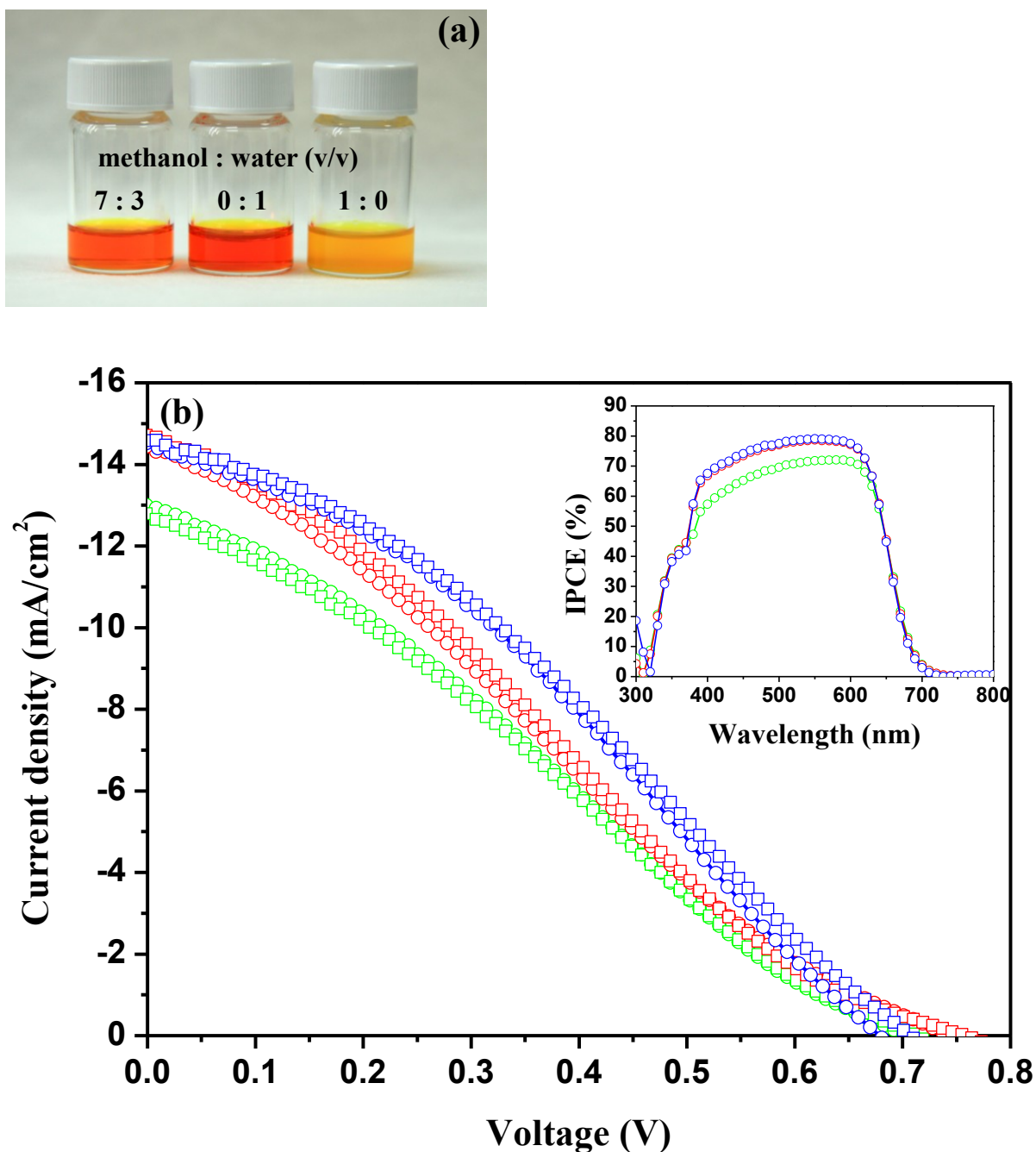


Figure S2. (a) Digital pictures of polysulfide electrolytes composed of 2 M Na₂S, 2 M S, and 0.2 M KCl in a mixture of methanol/water co-solvents with various volume ratios (left: 7: 3 v/v; middle: 0: 1 v/v ; right: 1: 0 v/v). (b) The photocurrent–voltage (J–V) curves of CdS/CdSe-sensitized QDSCs with different methanol/water co-solvent electrolytes. The open circles and open squares represent the measurements through first and secondary cycles of exchange of electrolytes, respectively. Blue curves: 7: 3 v/v, red curves: 0: 1 v/v, and green curves: 1: 0 v/v. The inset shows the corresponding IPCE spectra of QDSCs with various electrolytes while first cycle.

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Experimental procedure of solvent exchange: The typical CdS/CdSe-Sensitized ZnO photoelectrode were prepared through the sequence of the experiments section in the manuscript. One device was fabricated with polysulfide electrolytes consist of 2 M Na₂S, 2 M S, 0.2 M KCl in a mixture of methanol and deionized water (7:3, v/v). The photocurrent–voltage (J-V) curve was measured while the device was stable (usually few hours after filling of the electrolytes to make sure that well penetration of the electrolyte in the mesoporous ZnO matrix). The device was then decomposed. The photoelectrode was washed by pure deionized water and then dried in a gentle stream of N₂ gas. The same photoelectrode was used to construct a new device but with polysulfide electrolytes consist of 2 M Na₂S, 2 M S, 0.2 M KCl in purely deionized water. Similarly, the J-V curve was measured while the device was stable. After that, the device was decomposed again. The same photoelectrode was washed by pure methanol and used to construct a new device but with polysulfide electrolytes consist of 2 M Na₂S, 2 M S, 0.2 M KCl in pure methanol. The first cycle of solvent exchange was finished after the J-V curve was completed. The secondary cycle was processed step by step as the aforementioned procedure after the photoelectrode was washed with a mixture of methanol and deionized water (7:3, v/v). We carefully deal with this experiment to make sure the selected photoelectrode undamaged. The J-V curve changed immediately also reflects the successful solvent exchange which also can be reproduced as well.

TABLE S1. A summarized data set of short-circuit current density (J_{sc}), opencircuit voltage (V_{oc}), fill factor (FF), and overall conversion efficiencies from the J–V curves in Figure S2. Measurements were performed under illumination of one Sun condition (AM 1.5, 100 mW cm⁻²).

Solvent of electrolyte (methanol/ water, v/v)		J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
7:3	cycle 1	14.4	0.678	33.2	3.26
0:1	cycle 1	14.4	0.743	25.5	2.73
1:0	cycle 1	13.0	0.702	27.7	2.52
7:3	cycle 2	14.6	0.707	32.2	3.32
0:1	cycle 2	14.7	0.758	25.6	2.86
1:0	cycle 2	12.8	0.712	27.2	2.48

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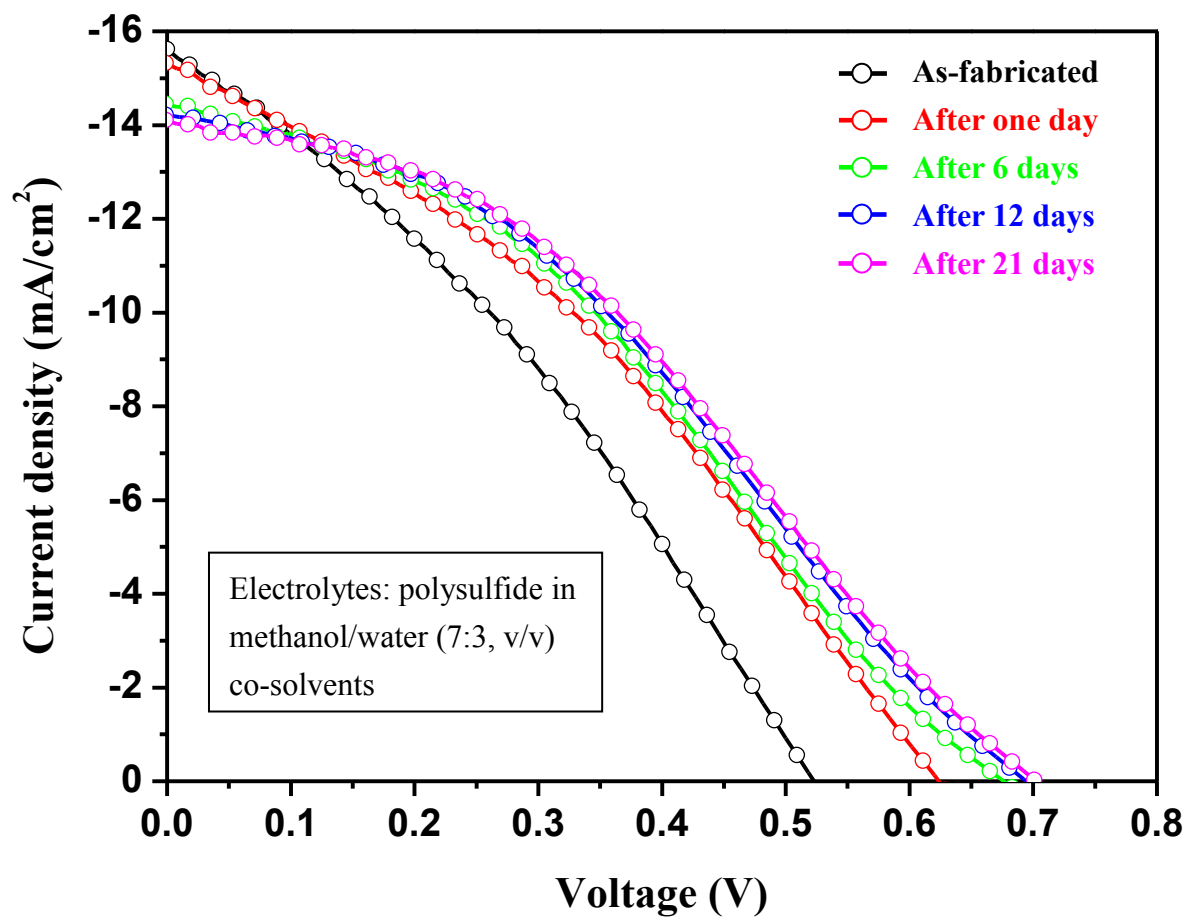


Figure S3. The comparative J-V curves of a QDSC with different aging times. The device was stored in the dark at room temperature beyond measurements.

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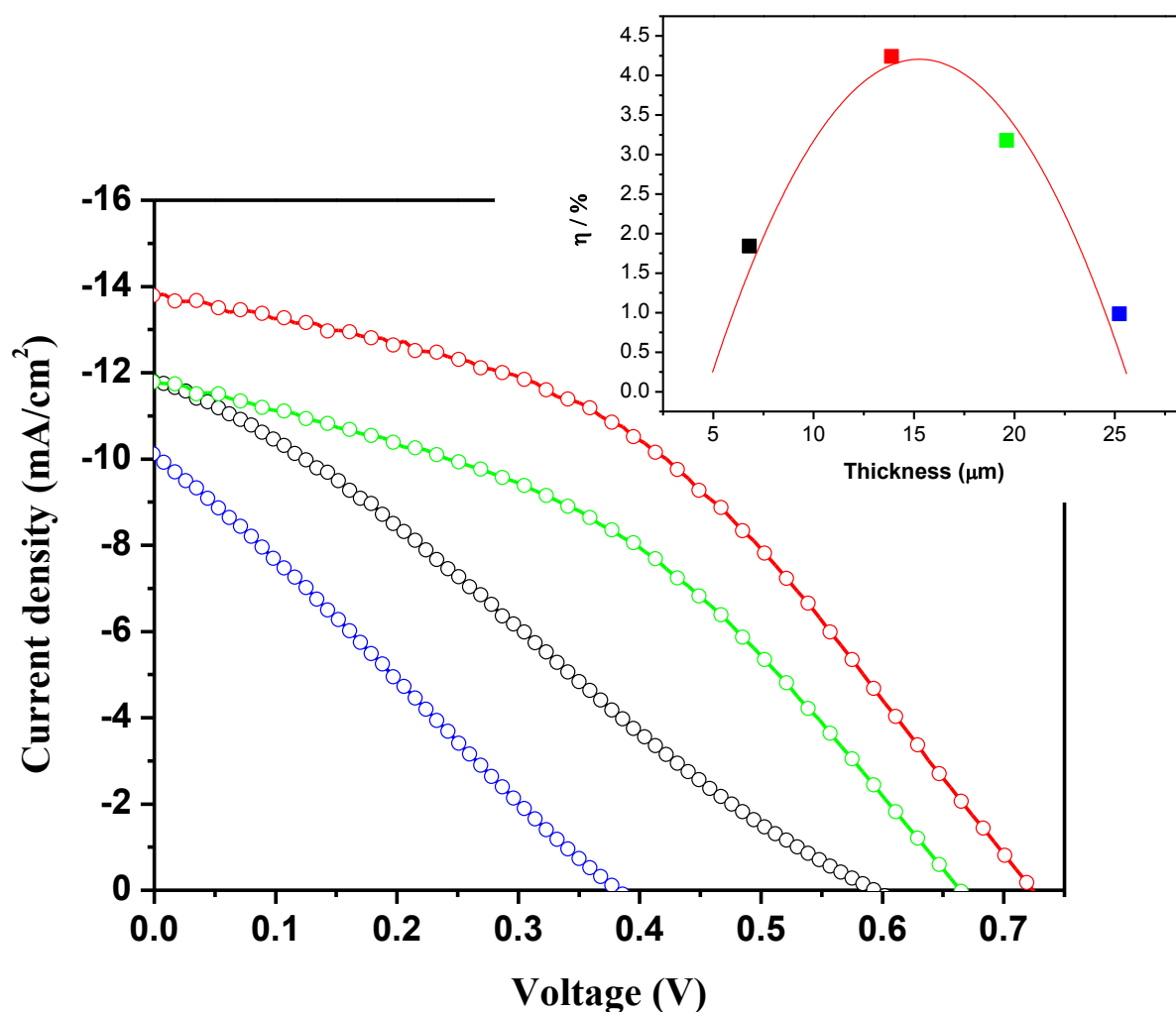


Figure S4. The photocurrent–voltage (J–V) curves of CdS/CdSe-sensitized QDSCs with various thicknesses of ZnO photoelectrode. Black open circles: ~7 μm, red open circles: ~14 μm, green open circles: ~20 μm, and blue open circles: ~25 μm. The relationship between power conversion efficiency and photoelectrode thickness is compared as shown in the upper right inset that reveals the optimum thickness would be located at about 15 μm.

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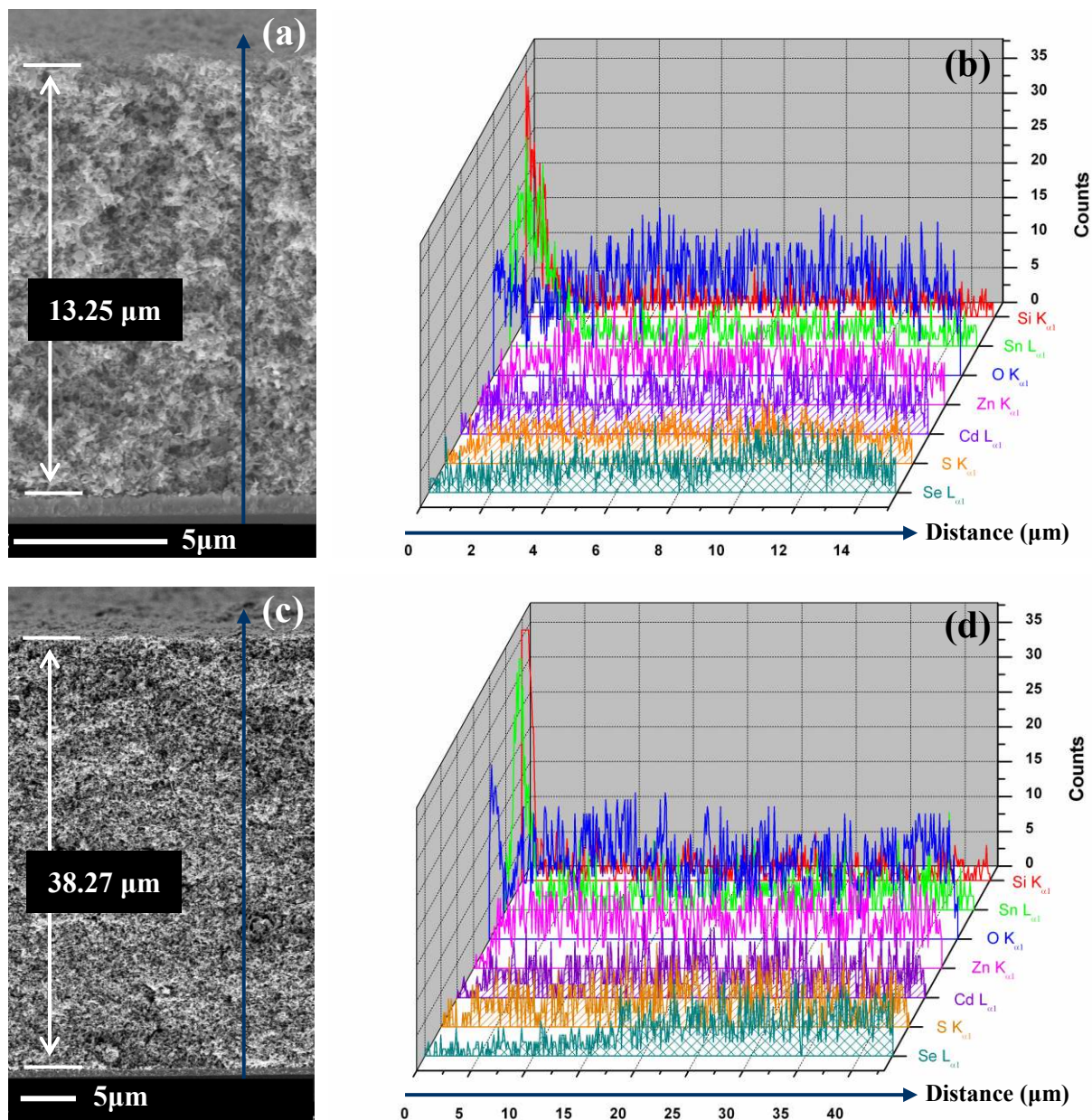


Figure S5. (a) and (b) FESEM cross-section image and corresponding elemental linescan mapping of 13.25 μm CdS/CdSe-sensitized ZnO photoelectrode. (c) and (d) FESEM cross-section image and corresponding elemental linescan mapping of 38.27 μm CdS/CdSe-sensitized ZnO photoelectrode. It can be noted that the uniformity of Se element is poor at the bottom of photoelectrode indicates the bad infiltration of CdSe during CBD process for thick ZnO photoelectrode.

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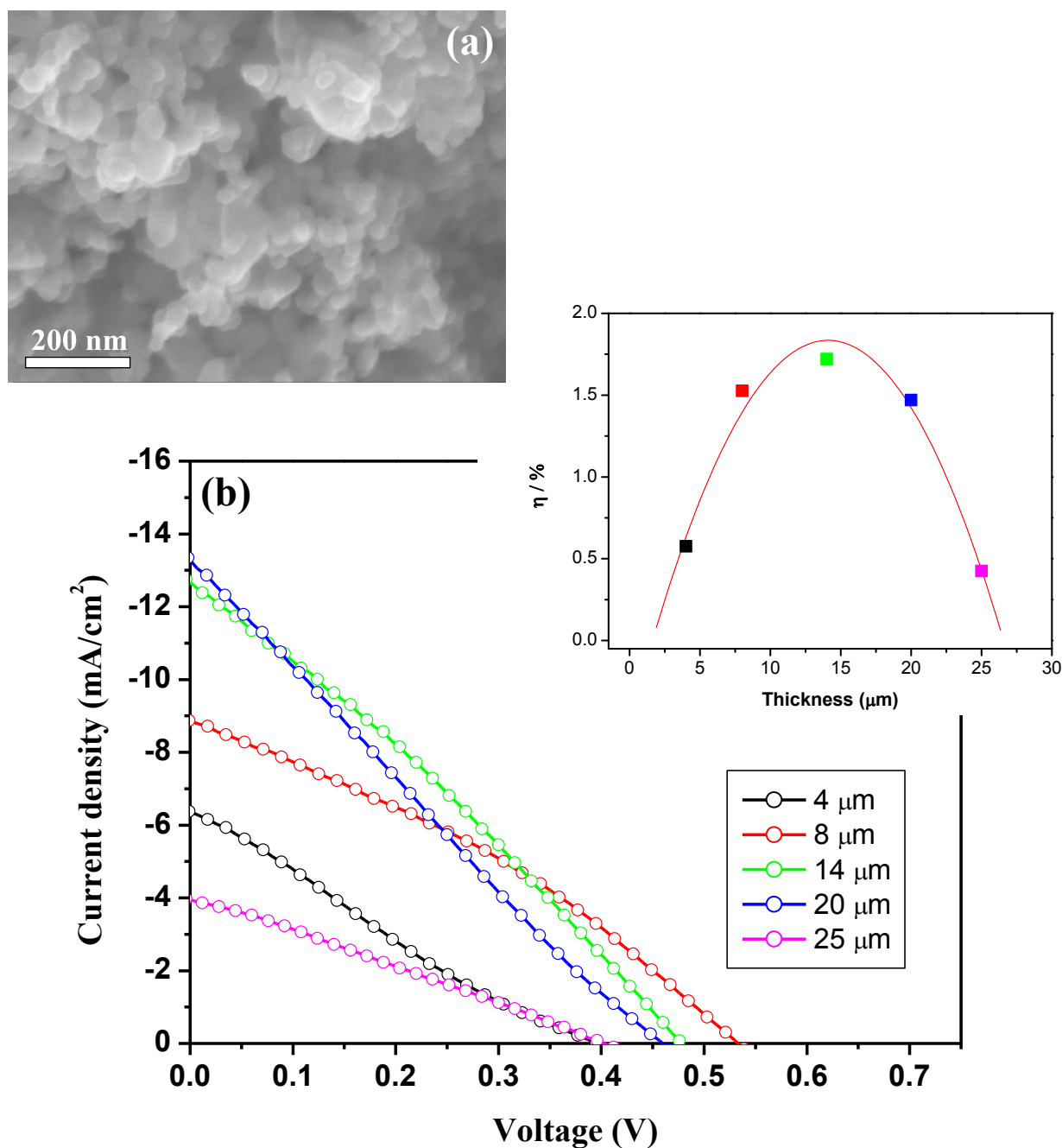


Figure S6. (a) FESEM image of commercial ZnO nanoparticles (Aldrich Ltd; spherical shape, average size ~30 nm). (b) J-V curve of QDSCs composed with commercial ZnO nanoparticles with various thicknesses of photoelectrode. The Brunauer-Emmett-Teller (BET) surface areas are 18.03 and 10.9 m²/g for commercial and tetrapod-like ZnO nanoparticles, respectively. The more loading of sensitizers for commercial ZnO photoelectrodes can be observed from the darker color after QDs decoration. However, the lower performance could be attributed to the unfavorable carrier transport as a result of additional interparticle hops while using commercial ZnO nanoparticles.

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TABLE S2. Kinetic parameters of the transient absorption of various photoelectrodes. The 2 μm -thick ZnO films are particularly performed to avoid the unnecessary light scattering. (Note: time coefficients, including lifetime and corresponding intensity, can be obtained from fitting the biphasic decay function as $a_1e^{-t/\tau_1} + a_2e^{-t/\tau_2}$. The intensity weighted average lifetimes $\langle\tau\rangle = \sum_i a_i\tau_i^2/a_i\tau_i$.)

Photoelectrode	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\langle\tau\rangle$ (ps)
SiO ₂ /CdSe	0.31	12.9	0.69	126	121
ZnO/CdSe	0.43	1.01	0.57	42	41.3
ZnO/CdS/CdSe	0.23	6.3	0.77	134	132

TABLE S3. Performances and electron transport properties of CdS/CdSe-sensitized QDSCs composed of 14 μm -thick photoelectrodes with commercial ZnO nanoparticles (denoted as n-ZnO) and tetrapod-like ZnO nanoparticles (denoted as T-ZnO), respectively.

QDSCs with	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)	k_{eff} (s ⁻¹)	τ_{eff} (ms)	R_k (Ω)	R_w (Ω)	D_{eff} (cm ² /s)	L_n (μm)
n-ZnO photoelectrode	12.62	0.478	28.5	1.72	91	11	108	445	4.3×10^{-5}	6.9
T-ZnO photoelectrode	13.85	0.722	42.4	4.24	137	7.3	159	46	9.2×10^{-4}	25.9