Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

High performance photoelectrochemical hydrogen generation and solar cells with a double type II heterojunction

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This supplementary information includes:

1. Electrochemical reaction at the photoanode and cathode.
2. The effects of MPA ligand exchange for QDSSCs.
3. Absorbance, transmittance and reflectance spectra.
4. Photoluminescence of samples with different deposition sequence of CdSe and ZnS on TiO_2.
5. TRPL fitting results.
6. Electrochemical impedance spectroscopy (EIS) measurements.
7. Equivalent circuit fitting results of EIS and other parameters of cells.

1. Electrochemical reactions

Photoelectrochemical H_2 generation

- Reaction at the photoanode

$2S^{2-}+2h_{vb}^{+}\rightarrow S_2^{2-}$

$S_2^{2-}+SO_3^{2-}\rightarrow S_2O_3^{2-}+S^{2-}$

$S^{2-}+SO_3^{2-}+2h_{vb}^{+}\rightarrow S_2O_3^{2-}$

$SO_3^{2-}+2OH^{-}+2h_{vb}+\rightarrow SO_4^{2-}+H_2O$

$2SO_3^{2-}+2h_{vb}^{+}\rightarrow S_2O_6^{2-}$

- Reaction at the cathode

$2H^{+}+2e^{-}\rightarrow H_2$

QDSSC:

- Reaction at the photoanode

$TiO_2+CdSe+h\nu \rightarrow TiO_2+CdSe(e^{-}+h^{+})\rightarrow TiO_2(e-)+CdSe(h^{+})$

$TiO_2(e-)+CdSe(h^{+})\rightarrow TiO_2+CdSe$

$CdSe(h^{+})+ S^{2-}\rightarrow CdSe+S^{-\cdot}$

$S^{-\cdot}+S_n^{2-}\rightarrow(S_{n+1})^{-\cdot}$

$S_n+S^{2-}\rightarrow(S_{n+1})^{2-}$

$TiO_2(e^{-}) + (S_{n+1})^{-\cdot}\rightarrow TiO_2 +(S_{n+1})^{2-}$

$TiO_2(e^{-}) + S_n^{2-}\rightarrow(S_{n-1})^{2-}+ S^{-}$

- Reaction at the cathode

$e^{-} + (S_{n+1})^{-\cdot}\rightarrow(S_{n+1})^{2-}$

$e^{-} + S_n^{2-}\rightarrow(S_{n-1})^{2-}+ S^{-\cdot}$

2. The effects of MPA ligand exchange for QDSSC

The MPA ligand is used to replace the pristine ligand (oleic-acid) on the CdSe nanocrystals. The J-V curves of the QDSSC before and after MPA ligand exchange are shown in Figure S1, where the enhancement of both photocurrent and photovoltage is observed. The TRPL measurements (not shown here) show shorter PL lifetime after MPA ligand exchange.

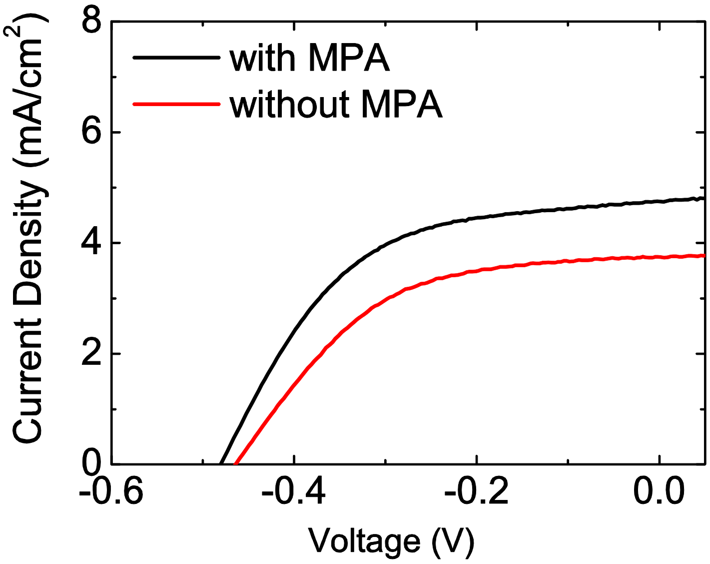

Figure S1. J-V curves of CdSe QD sensitized solar cell with and without MPA ligand exchange. The samples are not coated with ZnS.

3. Absorbance, transmittance and reflectance spectra

The absorption and photoluminesce spectra of the CdSe colloidal solution used for device fabrication are shown in Figure S2.

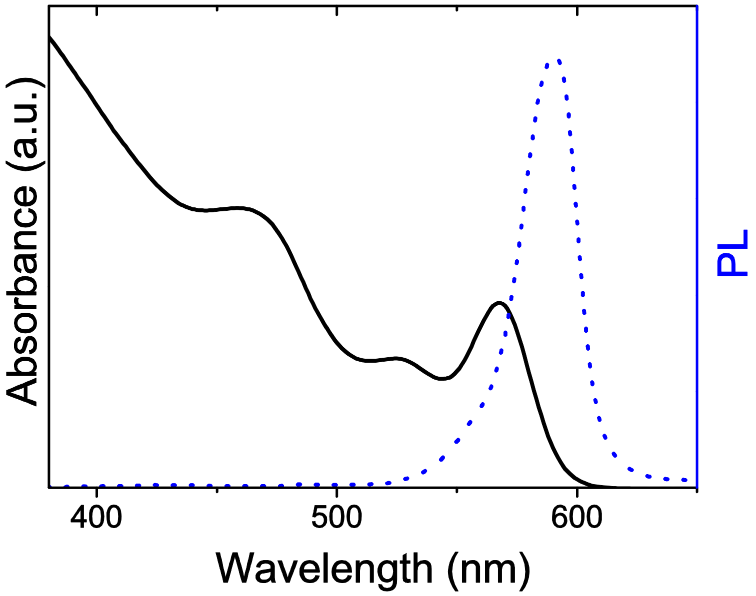

Figure S2. Absorption spectra and emission spectra of the CdSe colloidal solution of 4.2 nm diameter.

Absorbance, transmittance and reflectance spectra of QD-sensitized electrodes are measured by an UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu Scientific Instruments) equipped with 3 detectors (PMT, InGaAs and PbS) and an integrating sphere.

To calculate the IQE, the real absorption of the active layer (TiO_2/CdSe/ZnS) need to be calculated. The absorption spectra of the active layer can be calculated according to Figure S3, where $A_1\%=100-R_1\%-T_1\%$ and $A_2\%=T_1\%\times(R_2\%-2A_e\%)\times(100-R_1\%-T_1\%)$, where R% and T% are noted as the reflectance and transmittance, respectively. The absorption of the photons in the active layer driving from the reflection of the brass ($A_2\%$) is less than 3% (Figure S3).

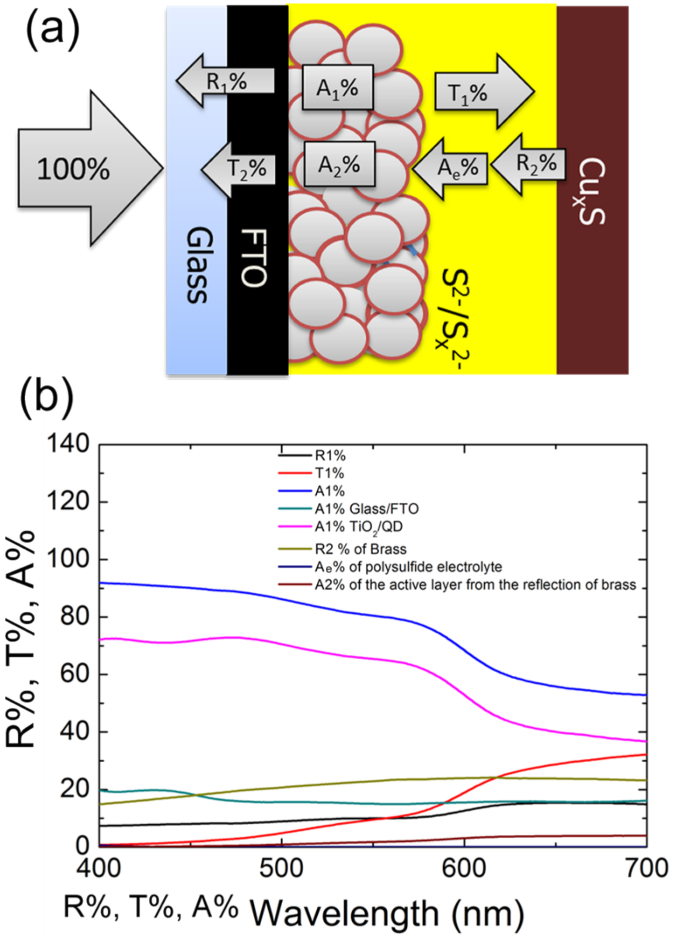

Figure S3. (a) Scheme of the transmission, reflection and absorption of the cells, (b) absorbance, transmittance, and reflectance spectra of the QD sensitized electrodes with 5L ZnS coating.

The absorption spectra of the active layer (TiO_2/CdSe/ZnS) with different number of layers of ZnS are shown in Figure S4. The absorbance above 600 nm is due to scattering from TiO_2 particles.

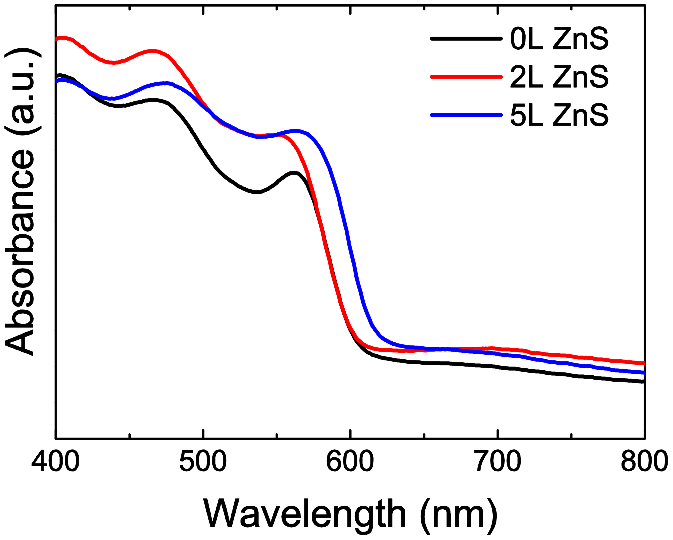

Figure S4. Absorption spectra of QD-sensitized electrodes (TiO_2/QDs) with different number of layers of ZnS.

4. Photoluminescence spectra of samples with different deposition sequence of CdSe and ZnS (2L) on TiO_2

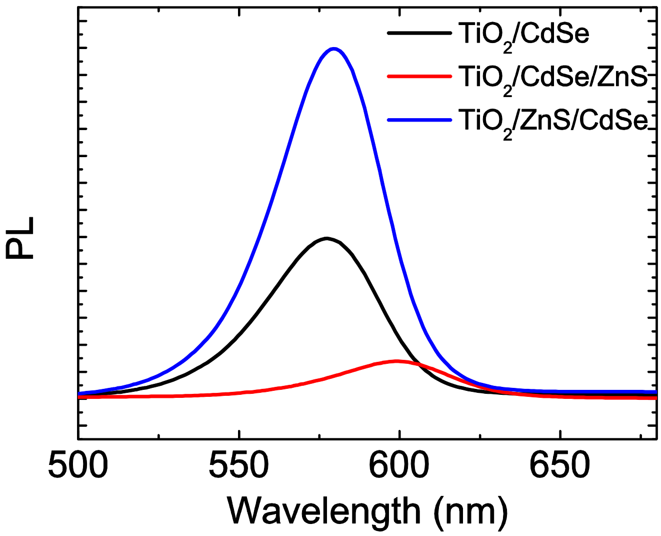

Figure S5. Photoluminescence spectra of samples with different deposition sequence of CdSe and ZnS on TiO_2.

5. TRPL fitting results

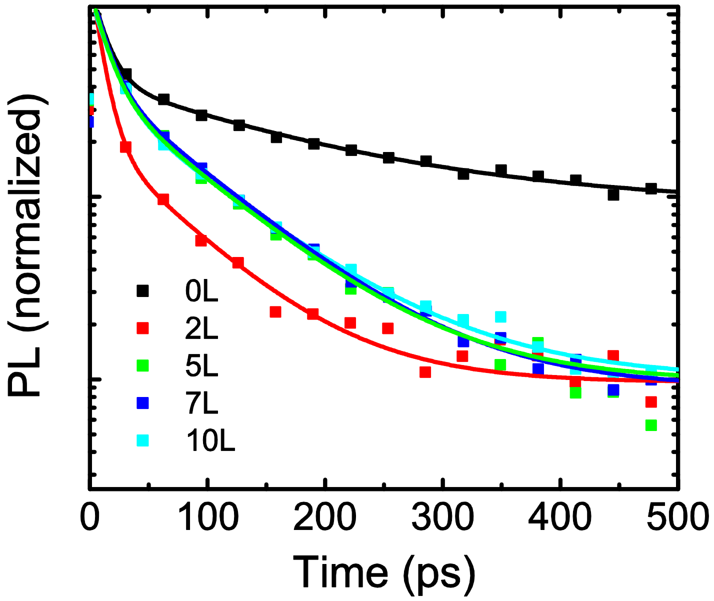

Figure S6. TRPL of QD-sensitized electrodes (TiO_2/QDs) with different number of layers of ZnS (symbols) and fitting curves (line).

Table S2. Summary of TRPL fitting results

$$PL = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

# of ZnS layer	A1	τ_1 (ps)	A2	τ_2 (ps)
0	1.16	11	0.31	150
2	1.38	8	0.31	41
5	0.92	12	0.46	67
7	0.99	10	0.53	61
10	0.88	16	0.40	80

6. Electrochemical impedance spectroscopy (EIS)

The impact of ZnS coating is also investigated by impedance spectroscopy. Impedance spectroscopy was performed by applying a 15 mV ac signal over the frequency range 1 MHz-50 mHz at open circuit voltage under different light intensity (from AM 1.5, 1 sun to 0.1 sun). The measurements and the equivalent circuit of transmission line model[S1-S4] for the impedance spectroscopy fitting is shown in Figure S7.

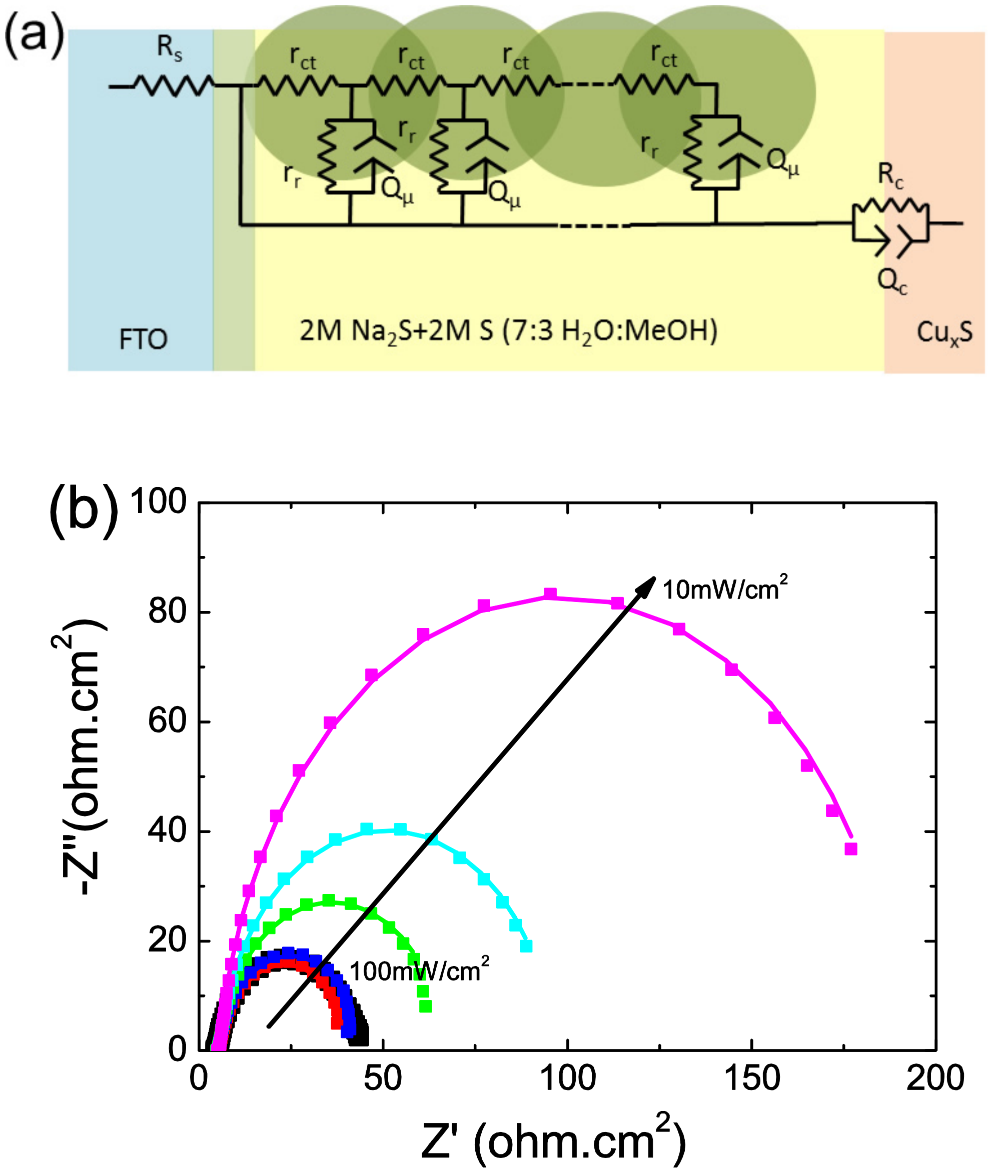

Figure S7. (a) Equivalent circuit for the transmission line model, where R_s is the series resistance, r_{ct} is the electron transport resistance, r_r is the interfacial charge recombination resistance, Q_μ is the chemical capacitance between photoanode and electrolyte, R_c is the charge transfer resistance between Cu_xS counter electrodes and electrolyte, Q_c is the chemical capacitance between Cu_xS counter electrodes and electrolyte. (b) Electrochemical impedance spectra of TiO_2/CdSe/ZnS(5L) photoelectrodes under different light intensity at open-circuit condition (symbols) and fitting curves (line).

The electron mobility, electron lifetime, electron transit time and electron diffusion length are the most direct evidence of the carrier transport dynamics in QDSSC. The transmission line model shown in Figure S7a is employed to extrapolate the electron transport resistance (r_{ct}) and the interfacial charge recombination (transfer) resistance (r_r) by fitting the electrochemical impedance spectra (Figure S7b). The charge transfer resistance (r_{ct}) and interfacial charge recombination resistance (r_r), as shown in Figure S8a, shows light intensity dependent characteristics; namely, both resistances decrease with increasing light intensity. The decreasing of r_r under strong light intensity conditions results from the higher carriers density, which leads to increasing possibility of carrier recombination with the electrolyte. While the decreasing of r_{ct} in strong light results from both the enhanced carrier concentration and the filling of trapping states which increase the electron mobility in TiO_2.

The electron lifetime (τ_n) is measured by electrochemical impedance spectroscopy (EIS) with a small ac signal perturbation under variable light intensity. The electron lifetime measured by EIS is reported in Figure S8b. Figure S8b shows that the electron lifetime increases from 60 ms to 174 ms after 5 layers ZnS coating under AM 1.5 at 1sun light intensity. The enhanced electron lifetime is believed by most of the authors resulting from either the blocking of electrons, which could otherwise recombine with electrolyte, or the passivation of defect states of electrodes which trap carriers.[S5]

The electron transit time (τ_d) is the average diffusion time of the electrons from the QDs to the electrode, which can be defined as: $\tau_d = L^2/D_e$, where L is the TiO_2 thickness and

D_e is the electron diffusion coefficient, which can be derived from $D_e=(r_r/r_{ct})L^2f_p$, where f_p is the peak frequency of the low frequency arc in the Nyquist impedance plot. Figure S8b shows that the electron transit time is not affected by the ZnS coating. In both devices (0L and 5L ZnS), electron lifetime is more than 2.5 times higher than the electron transit time under different light intensity.

Figure S8c shows that the charge collection efficiencies of both devices are over 90% under variable light intensity. The charge collection efficiency increases under weak light intensity. After the charge collection efficiency is obtained, the charge injection efficiency can be calculated.

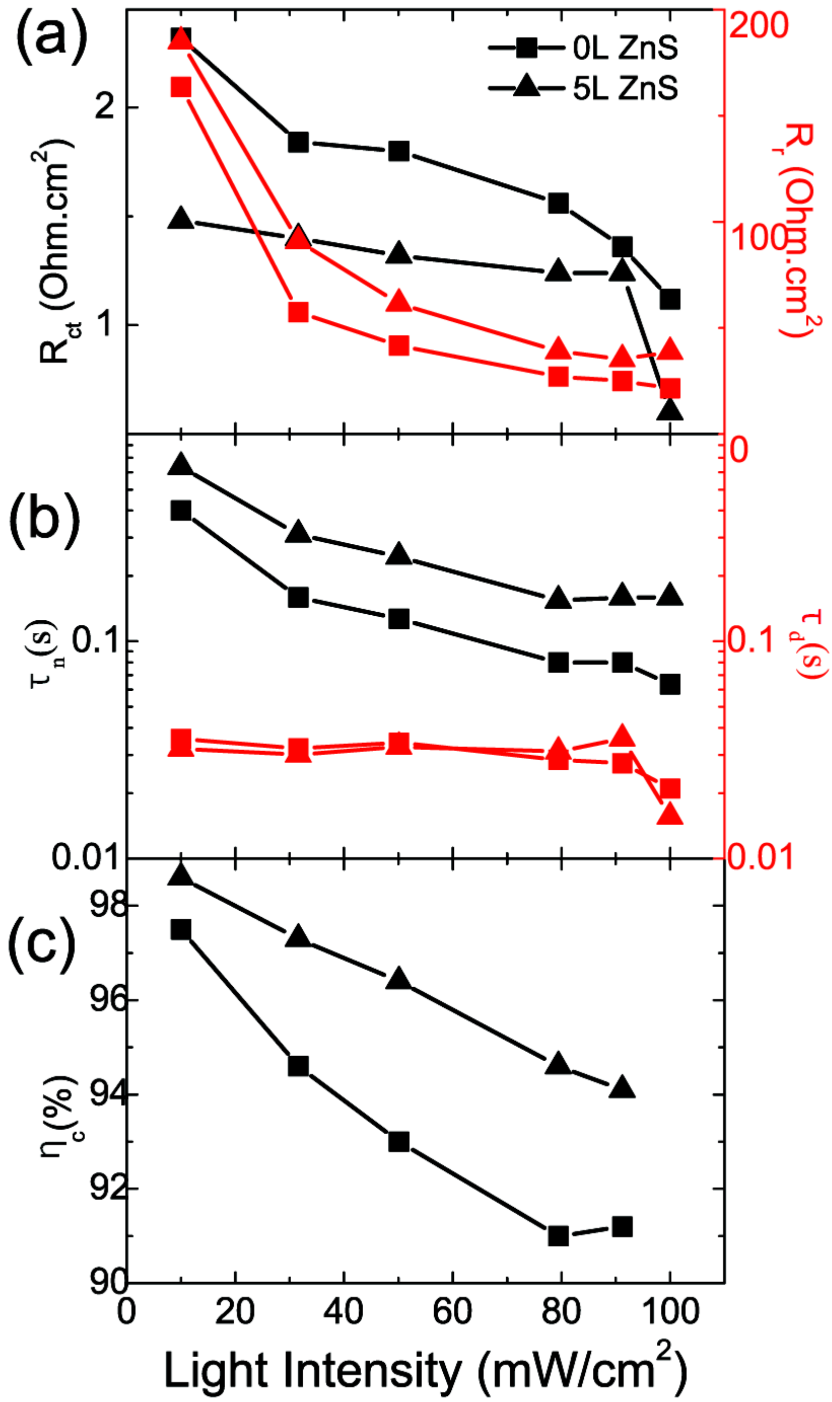

Figure S8. Light intensity dependent (a) charge transfer resistance (R_{ct}) and charge recombination resistance (R_r), (b) electron lifetime (τ_n) and transit time (τ_d), (c) electron diffusion length (L_d) and charge collection efficiency (η_c).

7. Equivalent circuit fitting results and other parameters of cells

Table S1. Equivalent circuit fitting results and other parameters of cells [a]

Light Intensity	c_μ' a)	r_{ct}' b)	r_r' c)	σ d)	τ_n e)	D_e f)	μ_e g)	n h)	L_d i)	η_c j)
$mWcm^{-2}$	$\mu Fcm^{-2}\mu m^{-1}$	$\Omega\ cm^2\mu m^{-1}$	$\Omega\ cm^2\mu m$	Sm^{-1}	ms	m^2s^{-1}	$cm^2V^{-1}s^{-1}$	$\#cm^{-3}$	μm	%
Without ZnS										
100.0	686.92	0.28	86.32	3.52E-02	59.3	8.2E-10	3.1E-04	6.98E+18	7.0	91.7
91.2	744.03	0.34	100.24	2.92E-02	74.6	6.3E-10	2.4E-04	7.56E+18	6.8	91.2
79.4	747.89	0.39	108.56	2.60E-02	81.2	5.5E-10	2.1E-04	7.60E+18	6.7	91.0
50.1	729.09	0.45	166.40	2.24E-02	121.3	4.9E-10	1.9E-04	7.41E+18	7.7	93.0
31.6	709.66	0.46	229.60	2.17E-02	162.9	4.9E-10	1.9E-04	7.21E+18	8.9	94.6
10.0	598.47	0.58	654.00	1.73E-02	391.4	4.6E-10	1.8E-04	6.08E+18	13.4	97.5
5L ZnS										
100.0	1125.25	0.15	154.56	6.65E-02	173.9	9.4E-10	3.6E-04	1.14E+19	12.8	97.3
91.2	1046.29	0.31	141.28	3.18E-02	147.8	4.8E-10	1.9E-04	1.06E+19	8.5	94.1
79.4	1030.43	0.31	155.92	3.19E-02	160.7	4.9E-10	1.9E-04	1.05E+19	8.9	94.6
50.1	1048.90	0.33	246.00	3.07E-02	258.0	4.7E-10	1.8E-04	1.07E+19	11.0	96.4
31.6	987.02	0.35	363.68	2.85E-02	359.0	4.6E-10	1.8E-04	1.00E+19	12.9	97.3
10.0	904.05	0.37	740.08	2.69E-02	669.1	4.7E-10	1.8E-04	9.19E+18	17.8	98.6

a) chemical capacitance; b) charge transfer resistance ; c) interfacial charge recombination resistance; d) electrical conductivity; e) electron lifetime; f) electron diffusion coefficient; g) electron mobility; h) free electron concentration; i) electron diffusion length; j) the charge collection efficiency is calculated based on:[S6-S8] $\eta_c = \frac{\left(-L_d\alpha\cosh\left(\frac{L}{L_d}\right)+\sinh\left(\frac{L}{L_d}\right)+L_d\alpha e^{-\alpha L}\right)L_d\alpha}{(1-e^{-\alpha L})(1-{L_d}^2\alpha^2)\cosh\left(\frac{L}{L_d}\right)}$, where α is the extinction coefficient of quantum dot-sensitized TiO_2 film. Here we assume the αL equals to 1 for the calculation. Another well-adopted formula for the charge collection efficiency is $\eta_c=1-(L/L_d)^2$. However, it is only valid when the cell active layer is thin enough so that the photo-generated electrons either immediately are transported to the electrodes or recombine. In the case $L=L_d$ results in $\eta_c=0$, indicating that this formula obviously deviates from the real physical situation of the quantum dot-sensitized solar cells.

Supplementary References

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