

Supporting Information

ZnS_xSe_{1-x} Alloy Passivation Layer for High Efficiency Quantum Dot Sensitized Solar Cells

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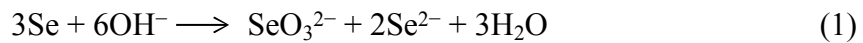
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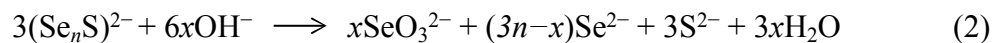
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Formation mechanism of the $\text{ZnS}_x\text{Se}_{1-x}$ alloy passivation layer

The formation method of $\text{ZnS}_x\text{Se}_{1-x}$ alloy passivation layer is similar to the method of constructing $\text{CdS}_x\text{Se}_{1-x}$ in previous report.¹ It has been demonstrated that elemental Se can undergo disproportionation reaction in alkaline media:^{2,3}



Since Se in polyselenosulfide ions has similar properties to elemental selenium, the disproportionation reaction of polyselenosulfide ions will also take place in alkaline media:



The generated Se^{2-} and S^{2-} react with Zn^{2+} to form the alloy passivation layer according to reaction 3, and the consumption of Se^{2-} promoted the reaction 2 to proceed to the right.

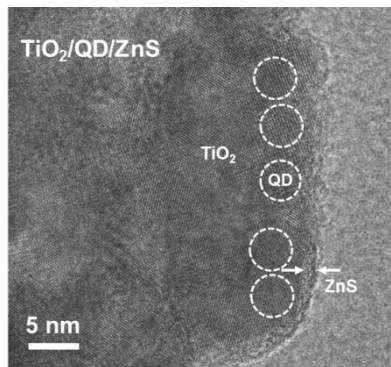


Figure S1. HRTEM image of QD-sensitized TiO_2 film coated with ZnS passivation layer.

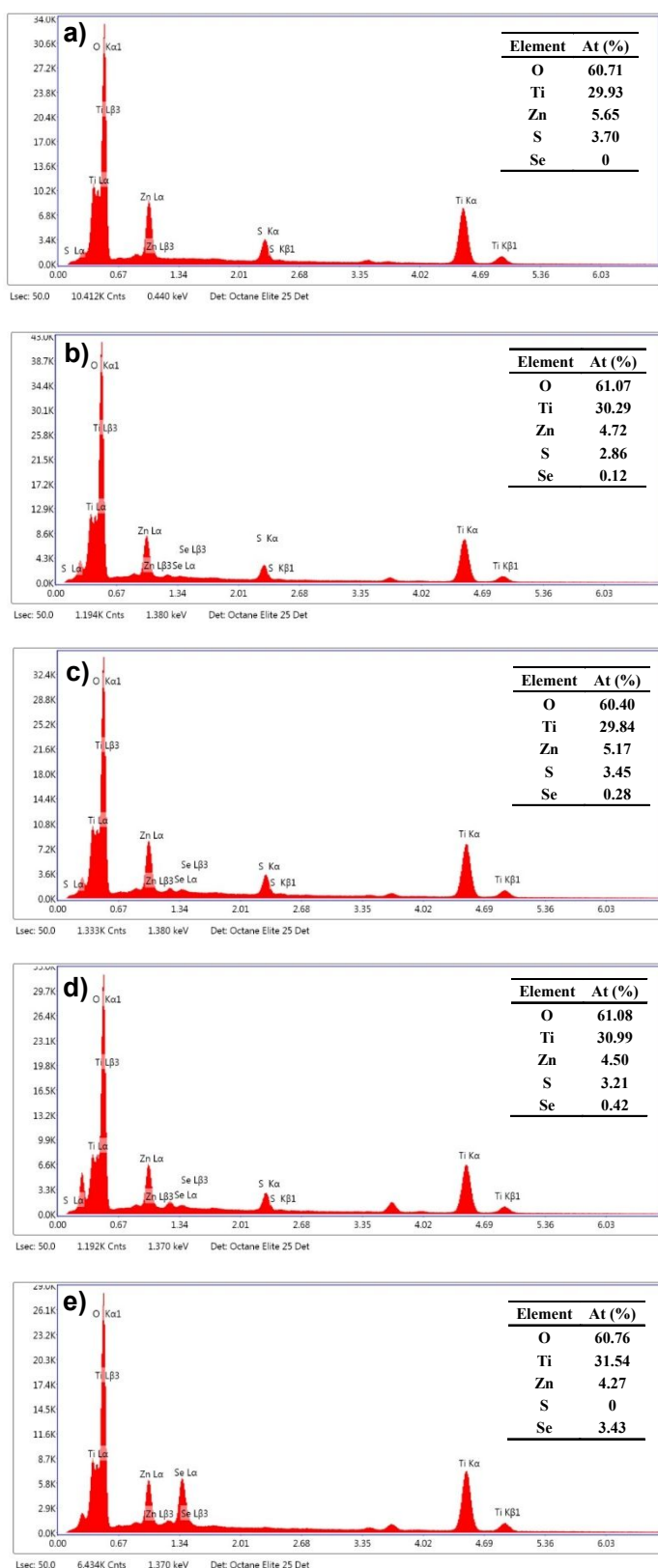


Figure S2. Energy dispersive X-ray spectrum of the (a) ZnS, (b) ZnSSe-5, (c) ZnSSe-10, (d) ZnSSe-15, and (e) ZnSe coated TiO₂ mesoporous films.

Table S1. The calculated Se/S atom ratio according to EDX results.

Passivation layer	ZnS	ZnSSe-5	ZnSSe-10	ZnSSe-15	ZnSe
Se/S ratio	0	0.04	0.08	0.13	

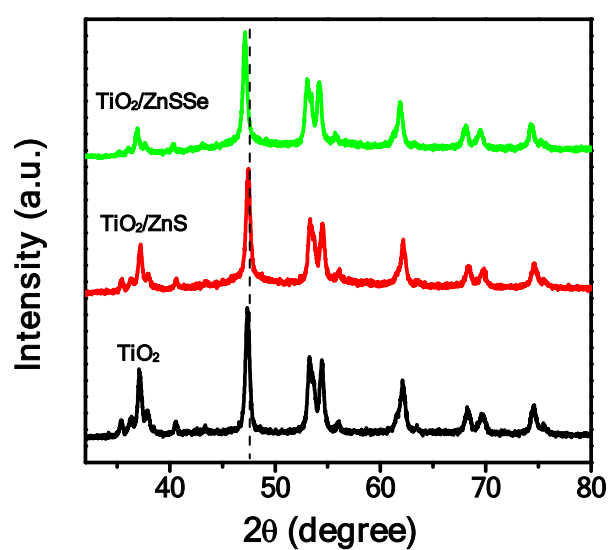


Figure S3. XRD patterns of TiO₂ films coated with ZnS and ZnSSe passivation layers.

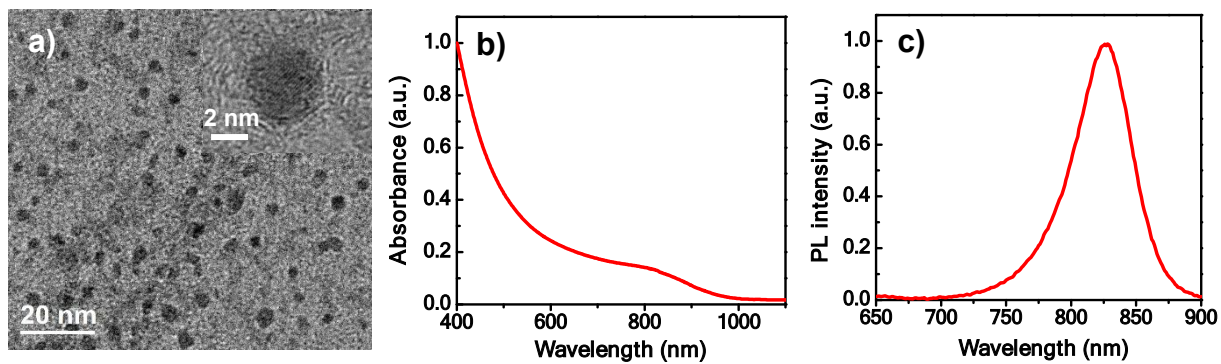


Figure S4. (a) TEM and HRTEM images of ZCISe QDs. (b) UV-vis absorption, and (c) PL emission spectra of ZCISe QD dispersion in hexane.

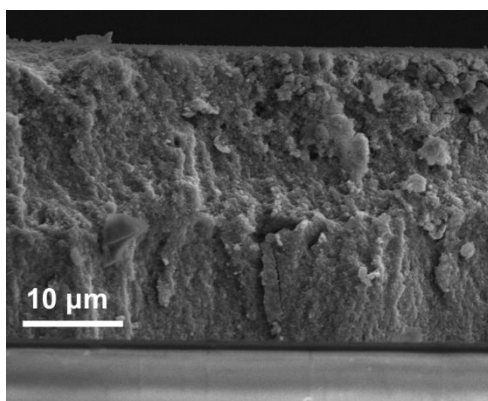


Figure S5. Cross-sectional SEM image of the TiO₂ film electrode.

Table S2. Individual photovoltaic parameters of ZCISe QDSCs with different passivation layers based on Cu₂S/brass counter electrode.

Passivation Layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
ZnS	25.99	0.598	59.70	9.28
	25.66	0.605	59.62	9.25
	25.98	0.603	59.31	9.29
	26.03	0.596	59.47	9.23
	25.80	0.602	60.12	9.34
Average	25.89±0.16	0.601±0.004	59.64±0.30	9.28±0.04
ZnSSe-5	26.83	0.594	60.42	9.63
	26.84	0.597	60.60	9.71
	26.80	0.594	60.75	9.66
	26.91	0.596	60.28	9.67
	26.81	0.594	60.31	9.60
Average	26.84±0.04	0.595±0.001	60.47±0.20	9.65±0.04
ZnSSe-10	27.71	0.590	61.68	10.09
	27.92	0.589	61.58	10.13
	27.95	0.589	61.37	10.11
	27.77	0.592	61.68	10.13
	27.87	0.590	61.50	10.12
Average	27.84±0.10	0.590±0.001	61.56±0.13	10.11±0.02
ZnSSe-15	25.65	0.585	62.83	9.43
	26.12	0.582	62.03	9.43
	25.67	0.585	63.00	9.46
	26.25	0.584	62.44	9.56
	25.56	0.584	62.49	9.32
Average	25.85±0.31	0.584±0.001	62.56±0.38	9.44±0.09
ZnSe	24.04	0.562	65.55	8.85
	23.68	0.564	65.47	8.74
	23.85	0.566	64.98	8.76
	23.45	0.570	64.96	8.68
	23.73	0.563	65.56	8.76
Average	23.75±0.22	0.565±0.003	65.30±0.31	8.76±0.06

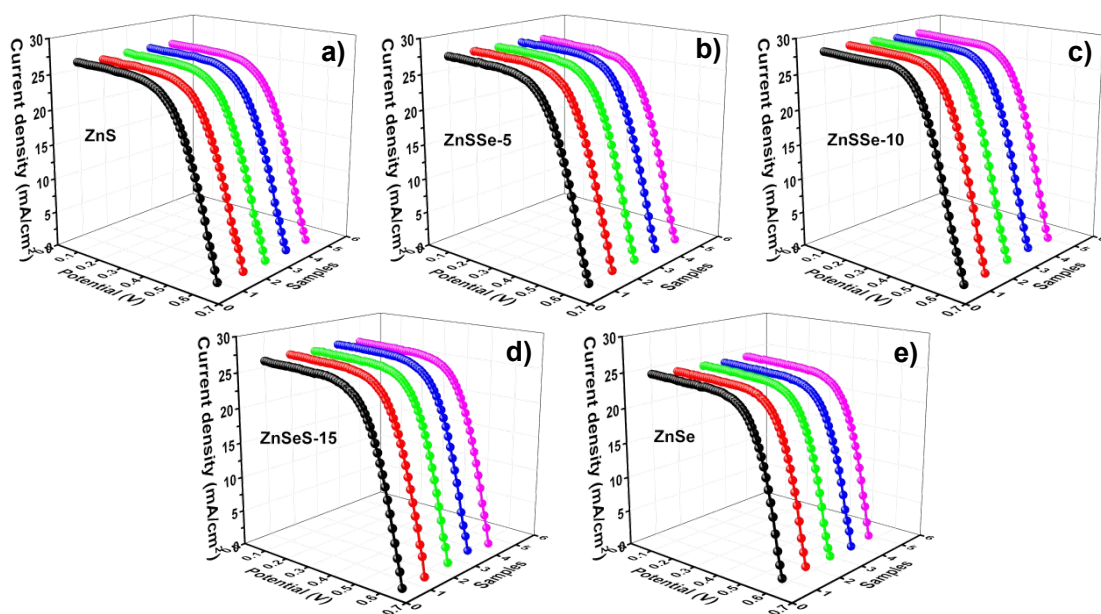


Figure S6. J - V curves of ZCISe QDSCs with different passivation layers based on Cu₂S/brass counter electrode. (a) ZnS, (b) ZnSSe-5, (c) ZnSSe-10, (d) ZnSSe-15, and (e) ZnSe.

Table S3. Average photovoltaic parameters of ZCISe QDSCs without passivation layer and with ZnS and ZnSe passivation layers constructed with different SILAR cycles. The cells were fabricated with Cu₂S/brass counter electrodes.

Passivation Layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
None	20.95	0.504	53.62	5.66
ZnS-2	22.36	0.542	63.17	7.65
ZnS-4	24.17	0.576	61.35	8.54
ZnS-6	25.89	0.601	59.64	9.28
ZnSe-2	21.77	0.527	61.05	7.00
ZnSe-4	22.93	0.547	63.51	7.96
ZnSe-6	23.75	0.565	65.30	8.76

Table S4. Individual photovoltaic parameters of ZnS and ZnSSe-10 coated ZCISe QDSCs based on MC/Ti counter electrode.

Passivation Layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
ZnS	25.18	0.749	64.85	12.23
	25.03	0.745	65.12	12.14
	25.07	0.742	65.68	12.22
	25.28	0.739	64.64	12.08
	25.44	0.735	65.09	12.17
Average	25.20±0.17	0.742±0.006	65.08±0.39	12.17±0.06
ZnSSe-10	26.49	0.733	68.52	13.30
	26.41	0.736	67.08	13.04
	26.22	0.745	66.83	13.05
	26.34	0.732	66.99	12.92
	26.55	0.737	66.77	13.07
Average	26.40±0.13	0.737±0.005	67.24±0.73	13.08±0.14

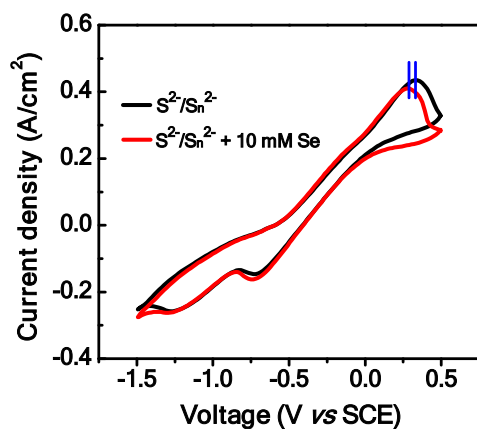


Figure S7. Cyclic voltammetry measurements. Cyclic voltammogram of S^{2-}/Sn^{2-} redox couple (2.0 M Na_2S and 2.0 M S) with and without Se. A mesoporous carbon/Ti mesh electrode, a Pt wire and a saturated calomel electrode were used as working, counter and reference electrode, respectively. The scan rate is 50 mV s^{-1} .

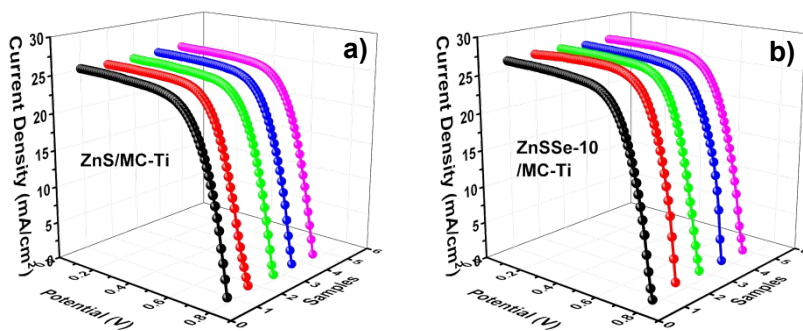


Figure S8. J - V curves of ZnS (a) and ZnSSe-10 (b) passivated ZCISe QDSCs based on MC/Ti counter electrode.

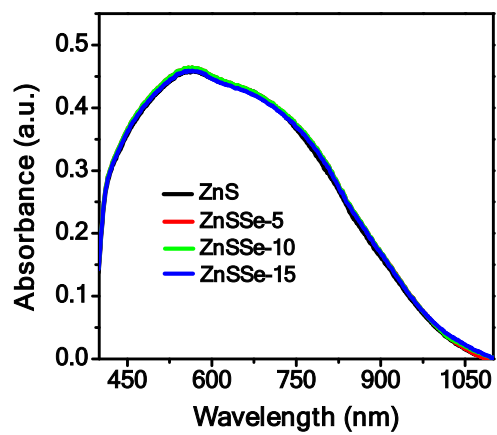


Figure S9. Absorption spectra of the ZCISE QD sensitized TiO_2 films coated with different passivation layers.

Table S5. Impedance parameters under the forward bias of -0.55 V: R_s , the series resistance; R_{ce} , the charge transfer resistance at CE/electrolyte interface; R_{rec} , the recombination resistance at photoanode/electrolyte interface; C_μ , the chemical capacitance at photoanode/electrolyte interface; and electron lifetime τ_n ($\tau_n = R_{rec} \times C_\mu$).

Passivation Layer	R_s $\Omega \cdot \text{cm}^2$	R_{ce} $\Omega \cdot \text{cm}^2$	R_{rec} $\Omega \cdot \text{cm}^2$	C_μ $\text{mF} \cdot \text{cm}^{-2}$	τ_n ms
ZnS	3.94	1.81	190.9	4.51	861
ZnSSe-5	6.17	2.38	259.1	4.52	1171
ZnSSe-10	6.47	3.18	296.3	4.53	1342
ZnSSe-15	8.18	4.14	223.3	4.54	1014
ZnSe	9.98	5.16	98.20	4.50	442

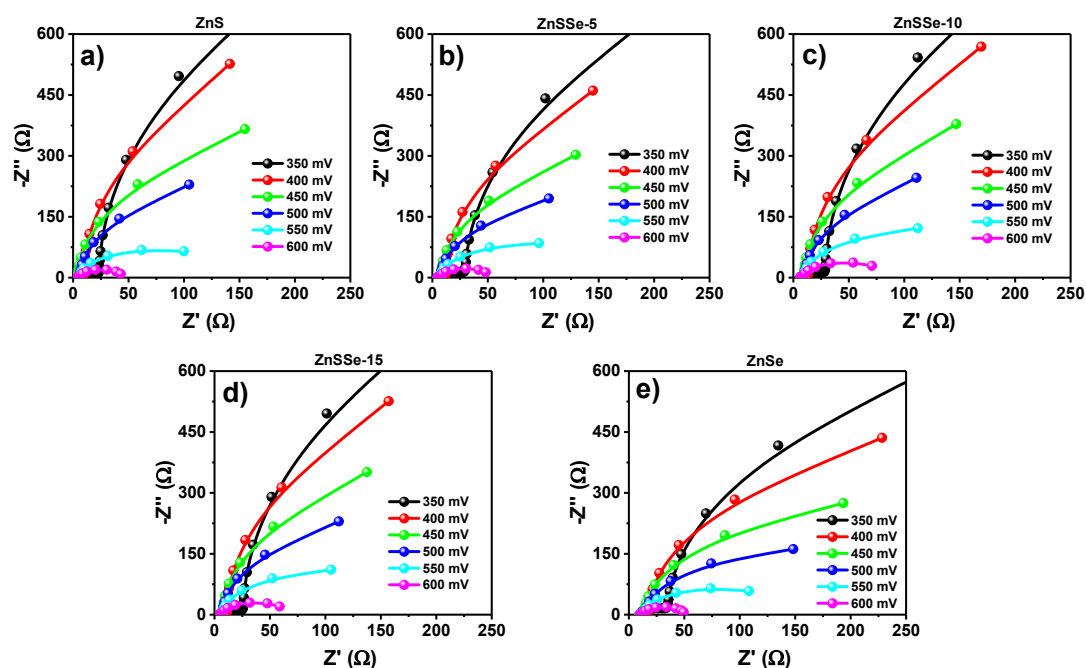


Figure S10. Nyquist curves under different bias voltages for QDSCs with different passivation layers: (a) ZnS, (b) ZnSSe-5, (c) ZnSSe-10, (d) ZnSSe-15, and (e) ZnSe.

References

- (1) Yang, J. W.; Zhong, X. H. CdTe Based Quantum Dot Sensitized Solar Cells with Efficiency Exceeding 7% Fabricated from Quantum Dots Prepared in Aqueous Media. *J. Mater. Chem. A* **2016**, *4*, 16553–16561.
- (2) Yan, S.; Wang, H.; Zhang, Y.; Li, S.; Xiao, Z. Direct Solution-Phase Synthesis of Se Submicrotubes Using Se Powder as Selenium Source. *Mater. Chem. Phys.* **2009**, *114*, 300–303.
- (3) Bo, F.; Zhang, C.; Wang, C.; Xu, S.; Wang, Z.; Cui, Y. From Red Selenium to Cuprous Selenide: A Novel and Facile Route to A High Performance Metal Selenide Cathode for Sensitized Solar Cells. *J. Mater. Chem. A* **2014**, *2*, 14585–14592.