Supporting Information

Zinc-based Electron Transport Materials for Over 9.6 %-Efficient S-rich $Sb_2(S,Se)_3$ Solar Cells

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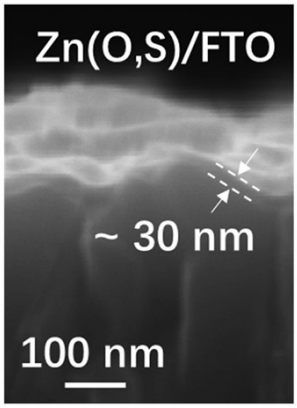


Figure S1 SEM image of Zn(O,S) layer deposited onto FTO substrate. The thickness of Zn(O,S) is about 30 nm.

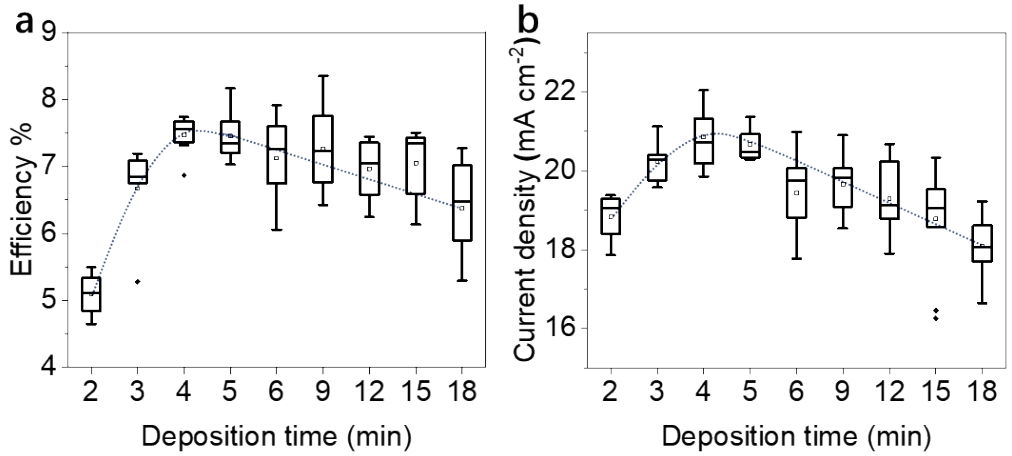


Figure S2 Statistical boxplot of conversion efficiency (%) and current density (mA cm^{-2}) for Zn(O,S)/CdS-based $Sb_2(S,Se)_3$ solar cells as a function of CdS deposition time (2 min - 18 min).

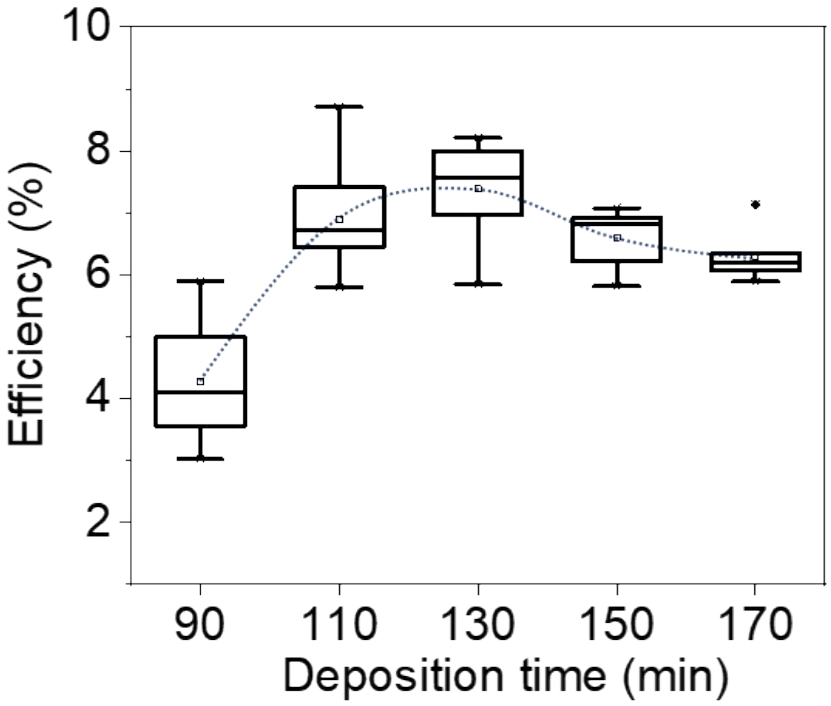


Figure S3 Statistical boxplot of conversion efficiency for Zn(O,S)/CdS ETL -based $Sb_2(S,Se)_3$ solar cells as a function of $Sb_2(S,Se)_3$ deposition time (90 min - 170 min), for which CdS deposition time is fixed at 4 min.

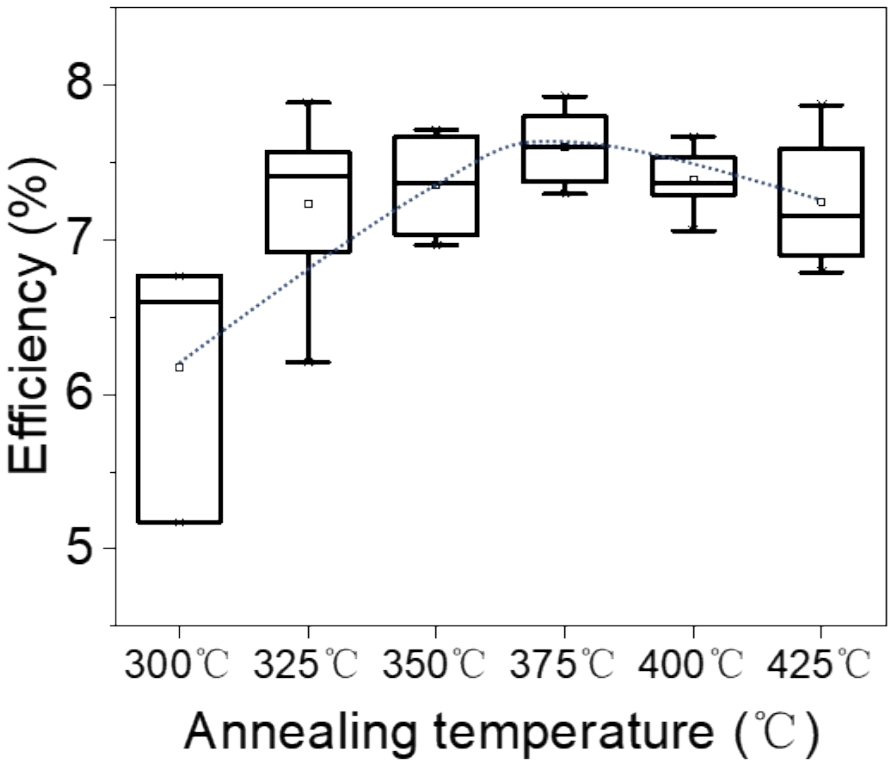


Figure S4 Statistical boxplot of conversion efficiency for Zn(O,S)/CdS ETL-based $Sb_2(S,Se)_3$ solar cells as a function of annealing temperature of $CdCl_2$ treatment (300℃ - 425℃). The CdS deposition time is fixed at 4 min and the $Sb_2(S,Se)_3$ deposition time at 130 min.

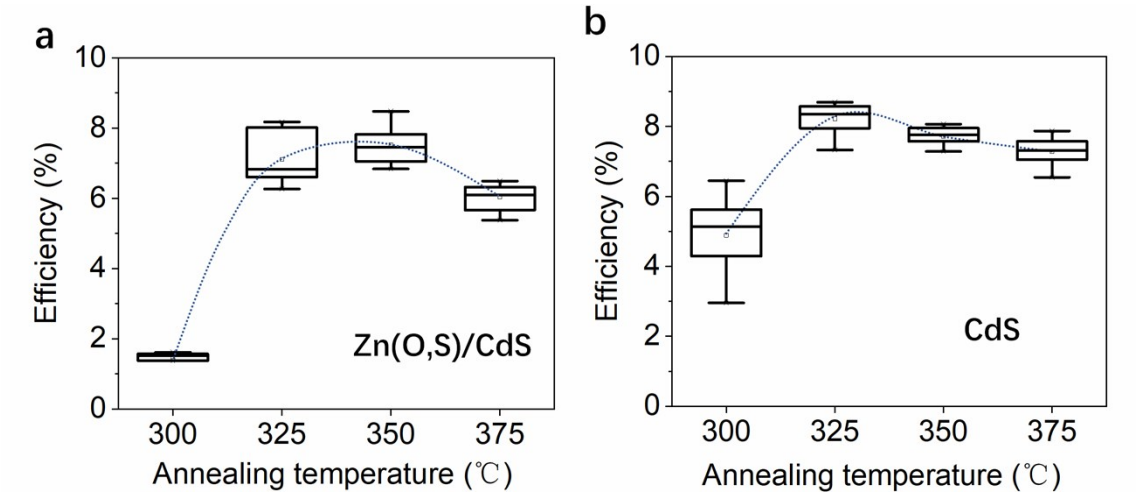


Figure S5 Statistical boxplot of conversion efficiency (%) for Zn(O,S)/CdS ETL-based and CdS ETL-based $Sb_2(S,Se)_3$ solar cells as a function of annealing temperature of $Sb_2(S,Se)_3$ layer.

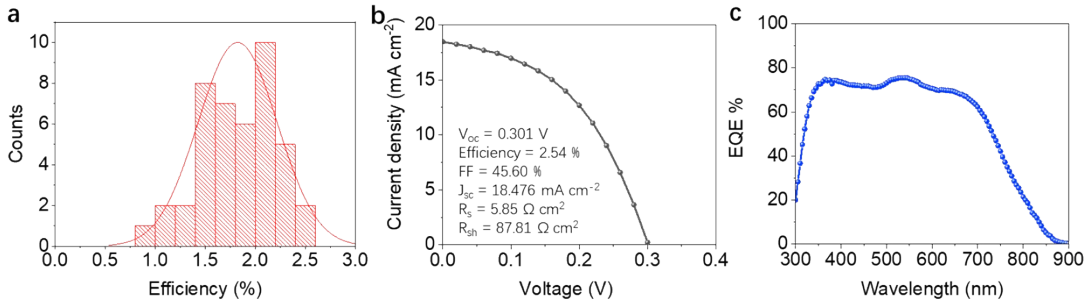
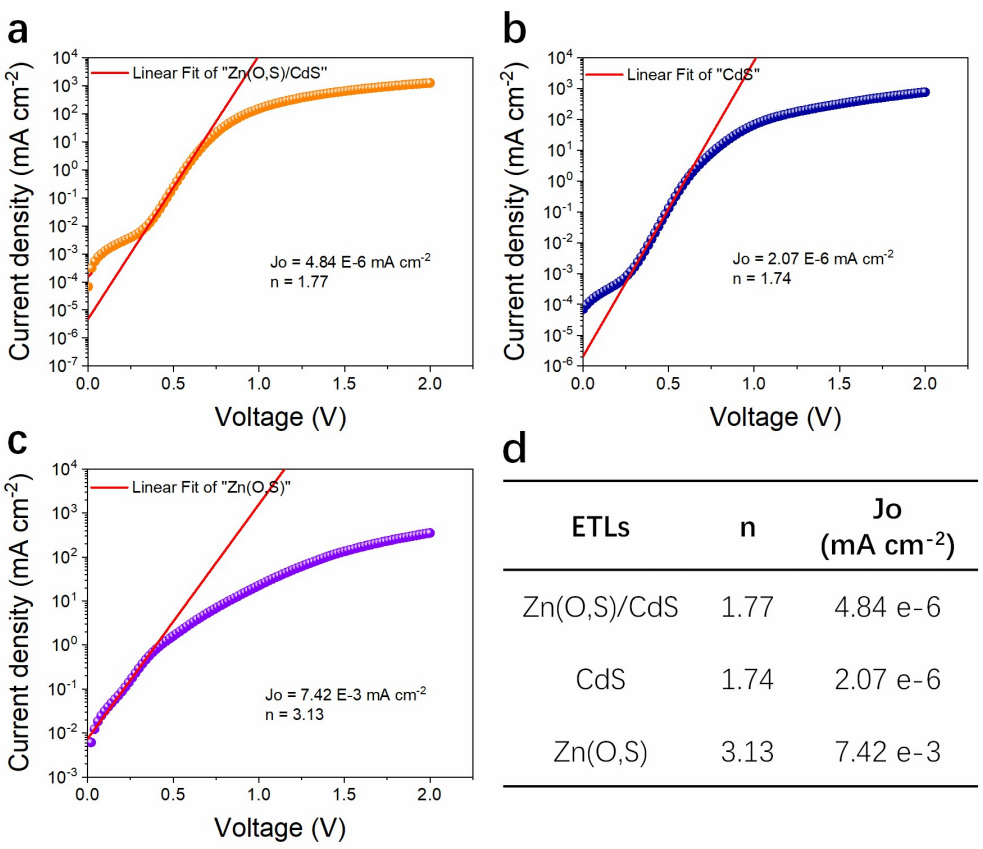


Figure S6 (a) Histogram of device conversion efficiencies obtained from over 40 individual solar cells fabricated with a thin CdS ETL that only uses 4 min deposition time. (b) *J-V* curve and (c) EQE spectrum of a representative solar cell with only 4 min CdS deposition.



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ETLs	n	Jo (mA cm^{-2})
Zn(O,S)/CdS	1.77	4.84 e-6
CdS	1.74	2.07 e-6
Zn(O,S)	3.13	7.42 e-3

Figure S7 Semi-logarithmic *J-V* plots for diode ideality factor (n) and saturation current density (J_0) calculations.

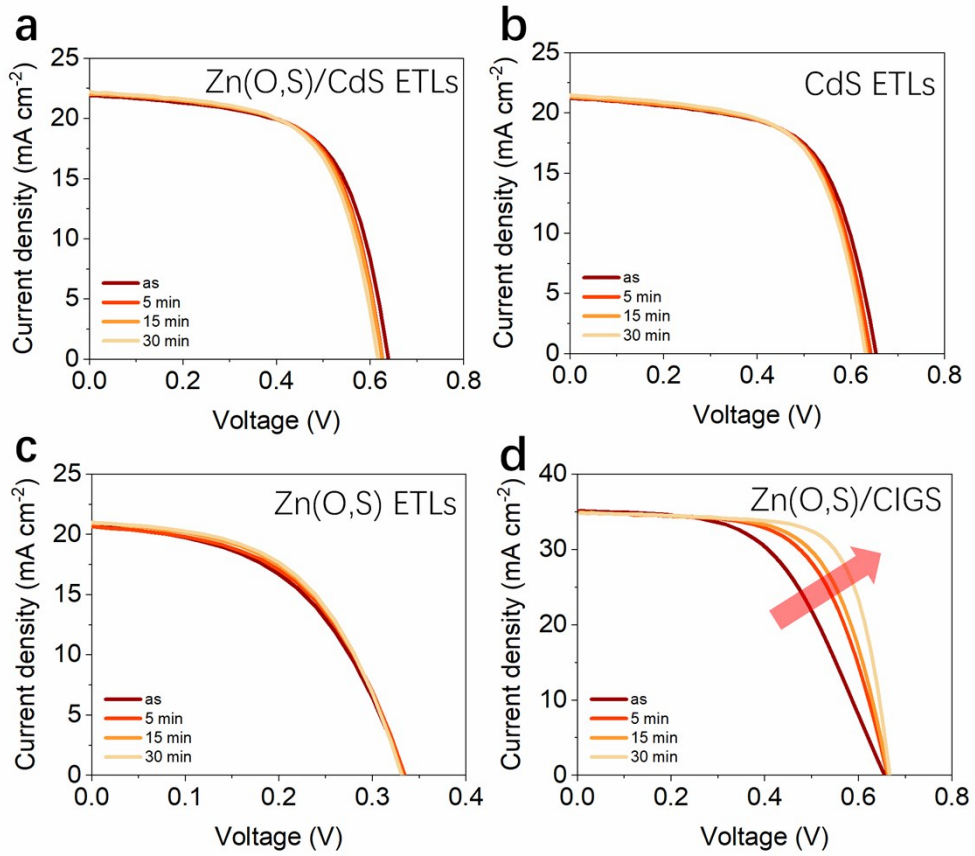

Figure S8 Illumination time dependence of *J-V* curves for $Sb_2(S,Se)_3$ solar cells: (a) with Zn(O,S)/CdS ETL, (b) with CdS ETL, and (c) with Zn(O,S) ETL. (d) Illumination time dependence of *J-V* curves for a Zn(O,S)-based CIGS thin-film solar cell.

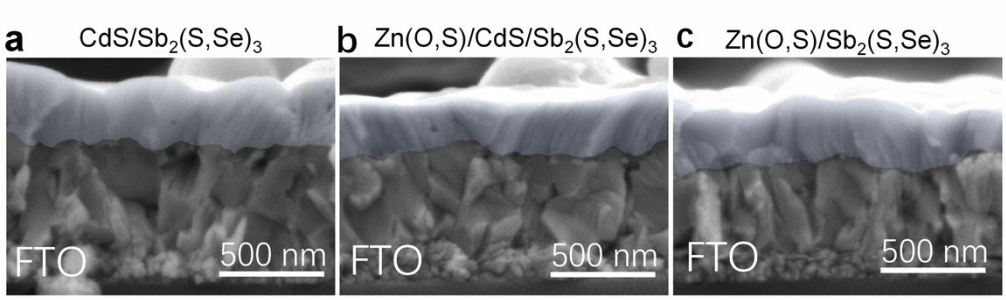

Figure S9 Cross-sectional SEM images of annealed $Sb_2(S,Se)_3$ layer deposited on CdS, Zn(O,S)/CdS, and Zn(O,S) ETLs, respectively.

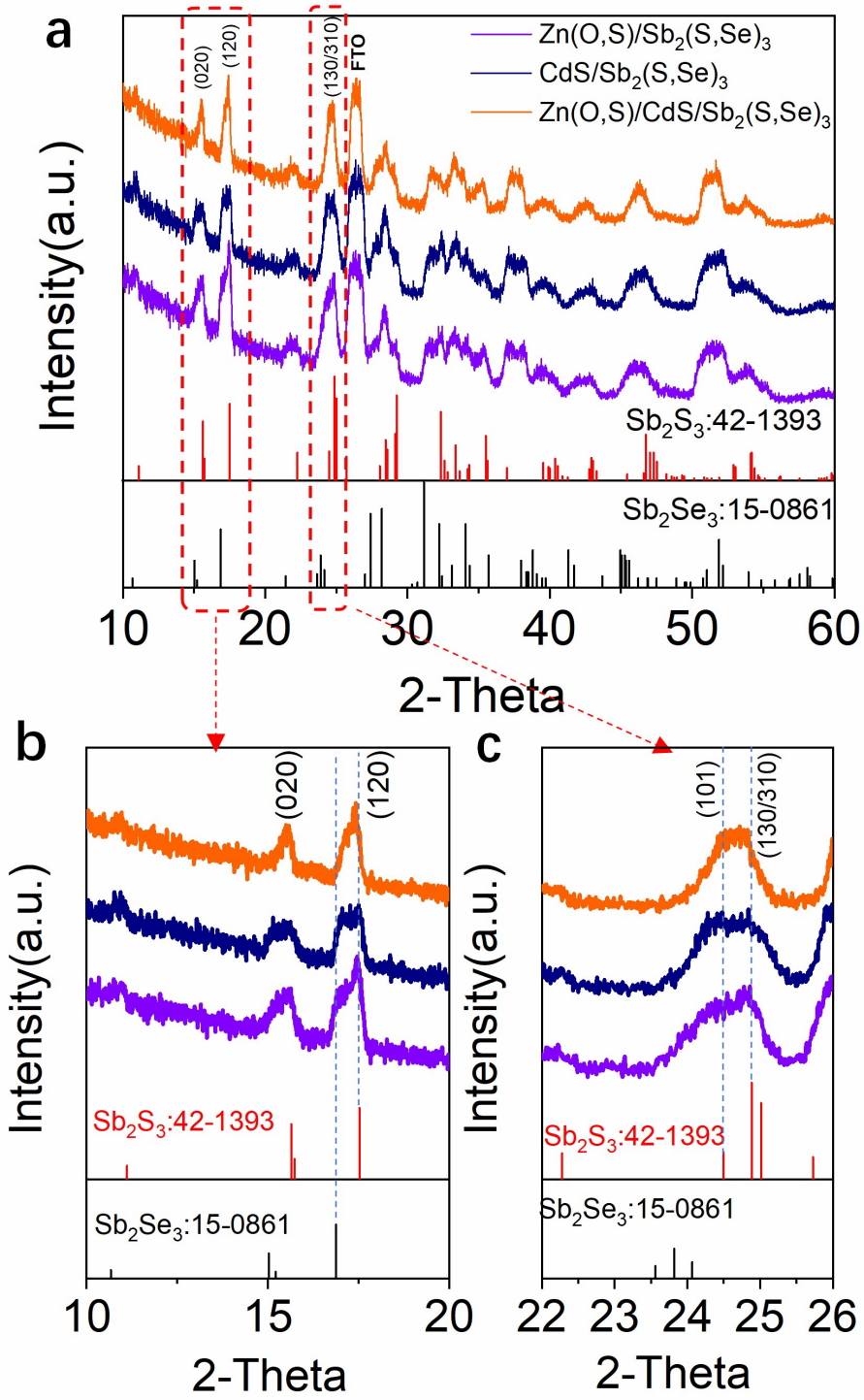

Figure S10 GIXRD spectra of $Sb_2(S,Se)_3$ layer deposited on different ETLs: Zn(O,S)/CdS, CdS, and Zn(O,S).

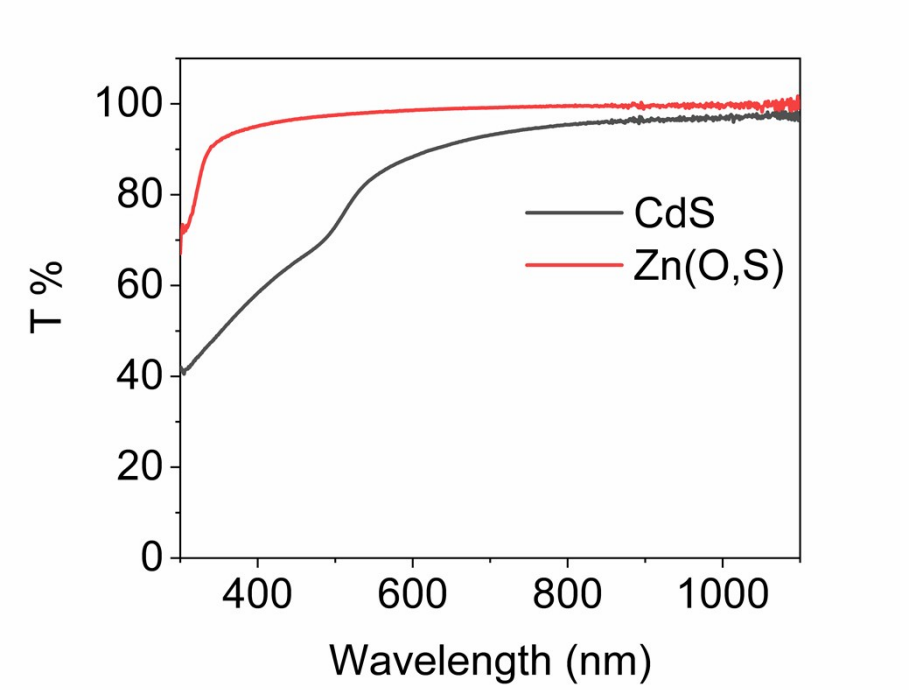

Figure S11 Transmittance spectra of pure Zn(O,S) and CdS layers without $CdCl_2$-PDT.

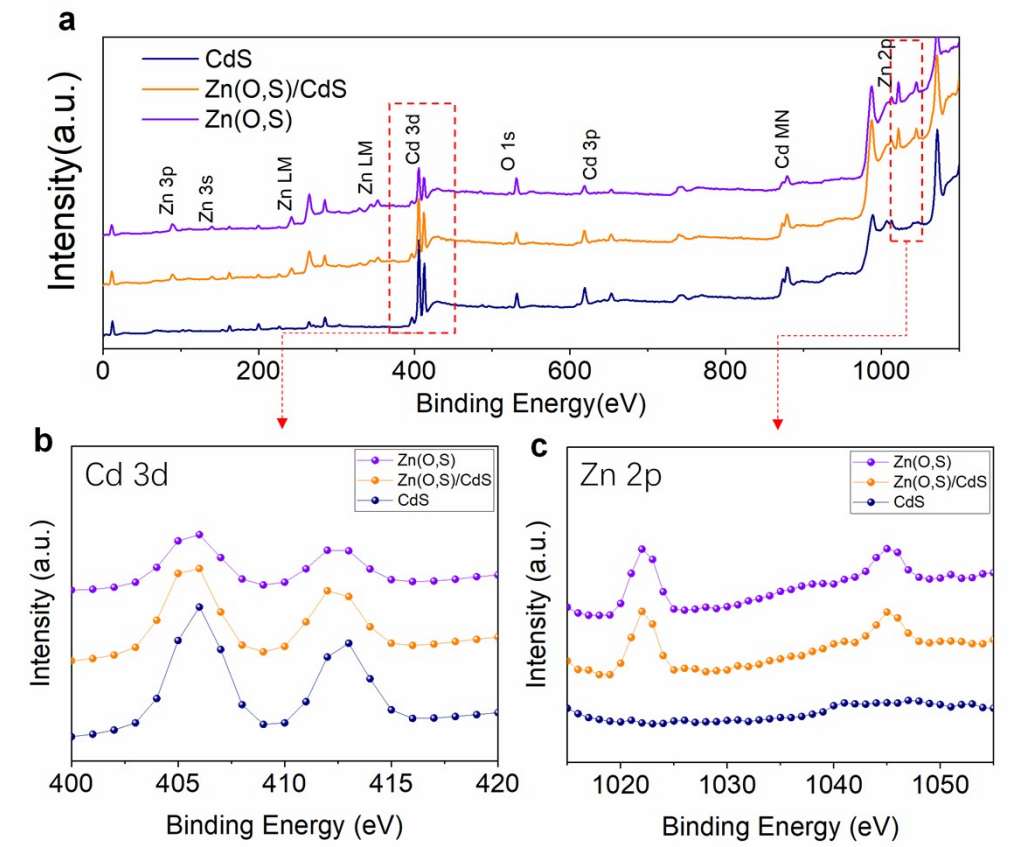

Figure S12 (a) XPS full spectra of different ETLs: Zn(O,S), Zn(O,S)/CdS, CdS. (b) Cd 3d and (c) Zn 2p XPS signals of various ETLs' surfaces.

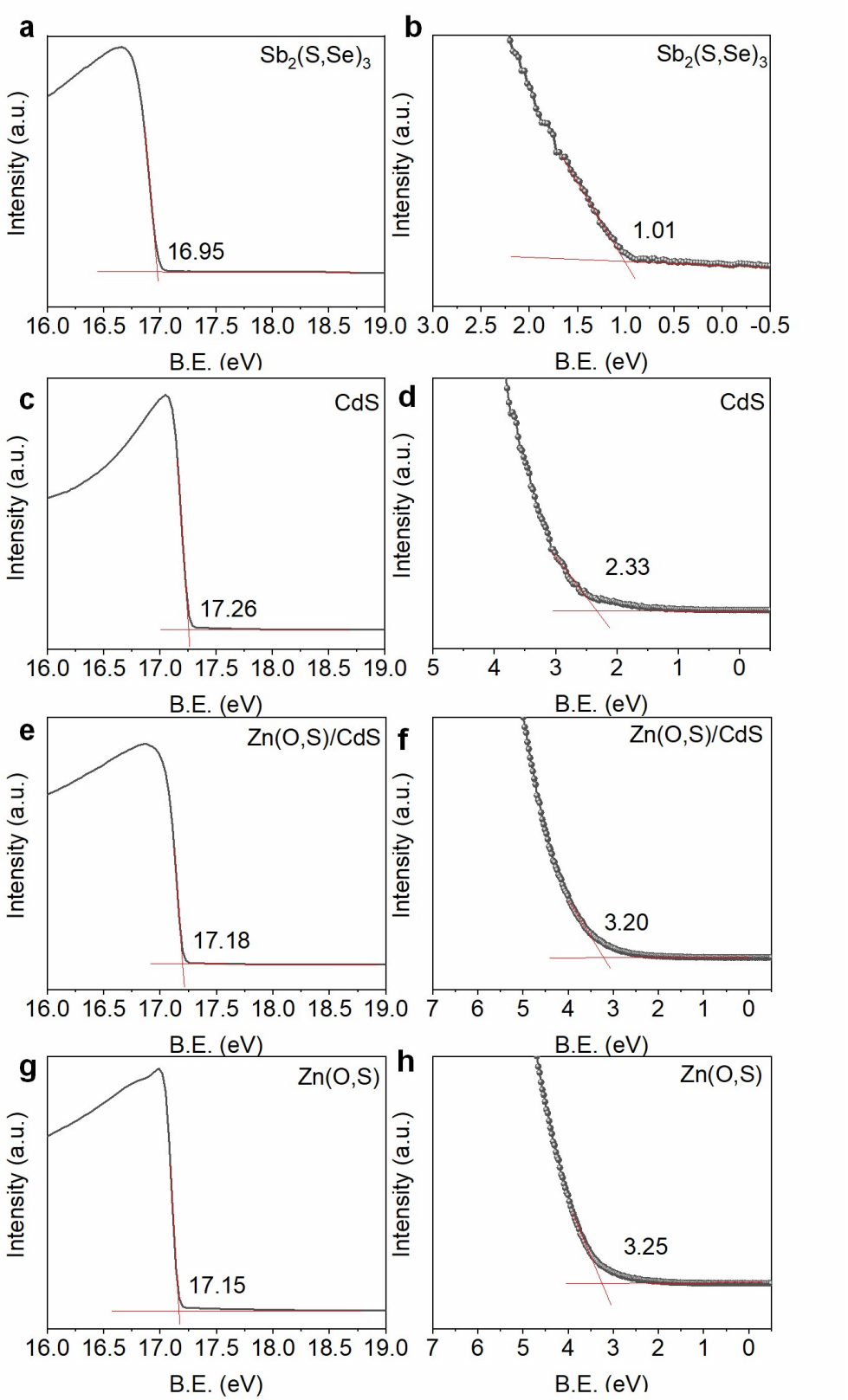

Figure S13 Secondary electron cut-offs and valence band edge estimated from the UPS spectrum of (a-b) $Sb_2(S,Se)_3$, (c-d) CdS ETL, (e-f) Zn(O,S)/CdS ETL, and (g-h) Zn(O,S) ETL.

Table S1 Parameters of Sb-based solar cells with Cd-free or Cd-reduced ETLs.

ETLs	Structure	V_{OC} (V)	PCE (%)	FF (%)	J_{SC} (mA cm^{-2})	ref
TiO_2	FTO/bl-TiO_2/mp-TiO_2/Sb_2S_3/PCPDTBT/PEDOT:PSS/Au	0.711	7.5	65	16.1	[1]
	FTO/c-TiO_2/Sb_2S_3/Spiro-OMeTAD/Au	0.69	6.56	55.18	17.3	[2]
	FTO/TiO_2/Sb_2S_3/spiro-OMeTAD/Au	0.599	4.93	47.62	15.39	[3]
	FTO/mp-TiO_2/Sb_2S_3/PCPDTBT-PCBM/Au	0.595	6.3	65.5	16	[4]
	FTO/c-TiO_2/Sb_2S_3/Spiro-OMeTAD/Au	0.671	6.78	54.8	18.43	[5]
	FTO/TiO_2/Sb_2S_3/P3HT/Au	0.5	1.9	42	8.94	[6]
	FTO/bl-TiO_2/TiO_2 array/Sb_2S_3/Spiro-OMeTAD/Au	0.71	5.8	50.72	16.11	[7]
	FTO/TiO_2/Sb_2S_3/spiro-OMeTAD/Au	0.65	7.08	61.61	17.69	[8]
	FTO/c-TiO_2/Sb_2S_3/Spiro-OMeTAD/Au	0.647	6.35	57.1	17.19	[9]
	FTO/TiO_2/Sb_2S_3/Au	0.69	5.4	51.2	14.3	[10]
	FTO/TiO_2/Sb_2S_3/spiro-OMeTAD/$SbCl_3$/Au	0.72	7.1	57.18	17.24	[11]
	FTO/c-TiO_2/Cs_2CO_3/Sb_2S_3/P3HT/Au	0.596	3.97	56.89	11.71	[12]
	FTO/TiO_2/Sb_2Se_3/SpiroOMeTAD/Au	0.275	2.0	37.7	19.7	[13]
	FTO/TiO_2/Sb_2Se_3/PCDTBT/Au	0.419	6.56	48.5	32.3	[14]
	FTO/TiO_2/Sb_2Se_3/PbS CQD/Au	0.386	7.62	60.6	32.6	[15]
	FTO/c-TiO_2/$Sb_2(S_{1-x}Se_x)_3$/spiro-OMeTAD/Au	0.491	7.42	59.5	25.4	[16]
	FTO/TiO_2/$Sb_2(S_{1-x}Se_x)_3$/spiro-OMeTAD/Au	0.56	5.71	52.34	19.48	[17]
	FTO/mp-TiO_2/Sb_2Se_3/Sb_2S_3/P3HT/Au	0.478	6.6	55.6	24.9	[18]
Al_2O_3	FTO/Al_2O_3/Sb_2S_3/P3HT/PEDOT:PSS/Ag	0.674	2.48	43.7	7.8	[19]
ZrO	FTO/ZrO_2/Sb_2S_3/P3HT/PEDOT:PSS/Ag	0.712	2.64	53.5	6.8	[19]
SnO_2	FTO/SnO_2/Sb_2S_3/P3HT/Au	0.56	1.32	45.4	5.2	[20]
	FTO/SnO_2/Sb_2S_3/P3HT/Au	0.585	2.8	45.24	10.57	[6]
	FTO/SnO_2/Sb_2Se_3/Au	0.32	3.05	38.64	25.26	[21]
	FTO/SnO_2/Sb_2Se_3/Au	0.312	2.33	39.35	18.47	[22]
ZnO	FTO/ZnO/Sb_2Se_3/Au	0.366	3.22	40.5	23.6	[23]
	FTO/r-ZnO/Sb_2Se_3/Au	0.391	5.93	57.8	26.2	[24]
In_2S_3	Mo-foil/$MoSe_2$/Sb_2Se_3/In_2S_3/IZO/ITO/Au	0.37	5.35	51.9	28.22	[25]
ZnO/ZnMgO	FTO/ZnO/ZnMgO/Sb_2Se_3/Au	0.360	4.45	48	26.2	[23]
TiO_2/CdS	FTO/TiO_2/CdS/Sb_2Se_3/SpiroOMeTAD/Au	0.340	3.9	41.9	27.2	[13]
	FTO/ TiO_2/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD / Au	0.792	5.73	60.9	12.03	[26]
	FTO/TiO_2/CdS/$Sb_2(S,Se)_3$/C/Ag	0.51	5.47	48.98	22.03	[27]
	FTO / TiO_2 /In: CdS / $Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	0.59	6.63	62.39	18.14	[28]
CdS/SnO_2	FTO/CdS/SnO_2/Sb_2Se_3/Au	0.360	5.27	52.96	27.8	[22]
	FTO/CdS/SnO_2/Sb_2Se_3/Au	0.432	7.5	63.2	27.6	[29]

SnO_2/CdS	FTO/SnO_2/CdS/Sb_2Se_3/Au	0.385	5.18	55	24.5	[30]
	FTO/SnO_2/CdS/$Sb_2(S,Se)_3$/C/Ag	0.74	5.2	55.8	12.5	[31]
ZnO/CdS	FTO/ZnO/CdS/ $Sb_2(S,Se)_3$/Au	0.48	5.73	54.5	21.89	[32]
$Cd_xZn_{1-x}S$	Mo/Sb_2Se_3/$Cd_xZn_{1-x}S$/IZO/AZO	0.403	6.71	64.78	25.69	[33]

Table S2 Recipes of CdS deposited by CBD method.

$[Cd^{2+}]^a$	$[S^{2-}]^b$	NH_4OH	Deposition time	Deposition Temp.
0.3 mmol	16 mmol	0.38 mol	0-18 min	65℃

a: Cd^{2+}, $CdSO_4$;

b: S^{2-}, CH_4N_2S, thiourea.

Details for CdS layer deposition. First, 140 ml deionized water, 20 ml (0.3 mmol) $CdSO_4$ solution, and 26 ml (0.38 mol) $NH_3 \cdot H_2O$ solution were mixed and stirred for two minutes. Then, 13 ml (16 mmol) CH_4N_2S solution was added into the above solution and stirred for another 30 seconds. After that, the chemically cleaned FTO substrates were immersed into the precursor solution within the glass beaker, which was subsequently transferred to a hot water bath deposition system where the temperature was set at 65℃. After deposition, the coated samples were rinsed thoroughly with deionized water and then blow-dried with N_2.

Table S3 Recipes of Zn(O,S) deposited by CBD method.

$[Zn^{2+}]^a$	$[S^{2-}]^b$	[Complex agent]^c	NH_4OH	Deposition time	Deposition Temp.
2.5 mmol	1.5 mmol	1.3 mmol	0.27 mol	15 min	85℃

a: Zn^{2+}, $ZnSO_4$;

b: S^{2-}, C_2H_5NS, thioacetamide;

c: $C_6H_5Na_3O_7.2H_2O$, trisodium citrate.

Details for Zn(O,S) layer deposition. First, 166 ml deionized water, 7.5 ml (2.5 mmol) $ZnSO_4$ solution, and 2.5 ml (1.3 mmol) $C_6H_5Na_3O_7.2H_2O$ solution were mixed and stirred for five minutes. Then, 6.25 ml (1.5 mmol) C_2H_5NS solution and 18 ml (0.27 mol) $NH_3 \cdot H_2O$ solution were added into the above solution and stirred for another 30 seconds. After that, the chemically cleaned FTO substrates were put into the precursor solution within the glass beaker, which was subsequently transferred to a hot water bath deposition system where the temperature was set at 85℃. After deposition, the coated samples were rinsed thoroughly with deionized water and then blow-dried with N_2.

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