electronic supplementary information (ESI)

9.6%-Efficient All-Inorganic $Sb_2(S,Se)_3$ Solar Cell with MnS Hole-Transporting Layer

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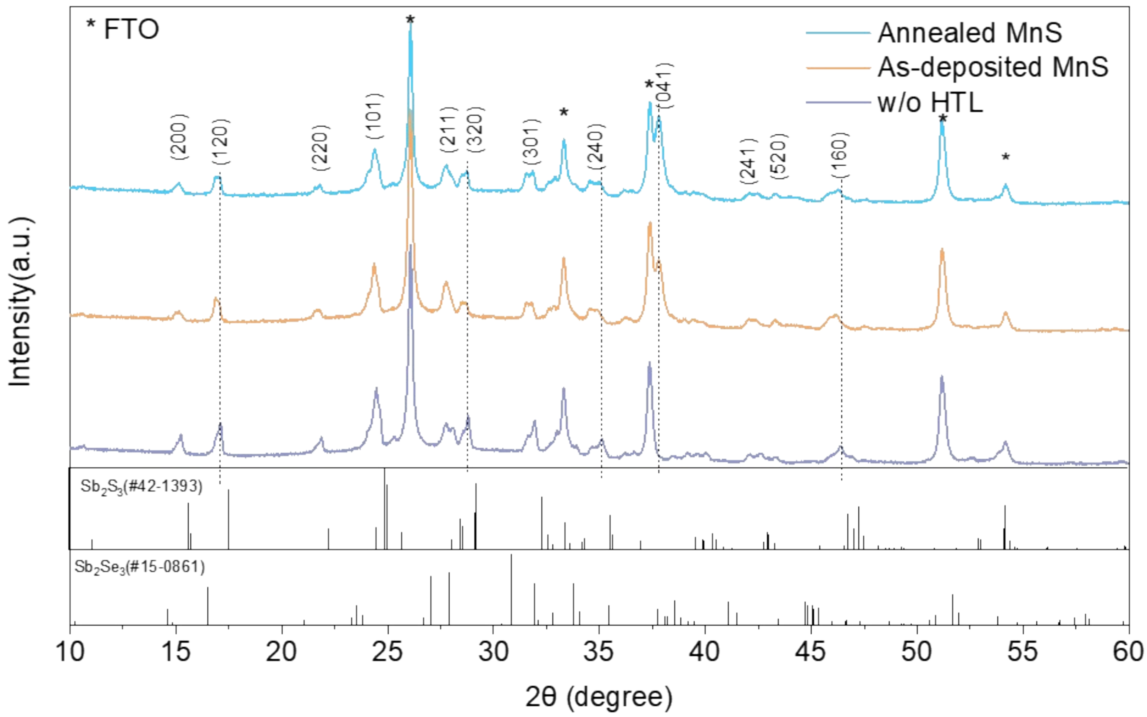

Figure S1. XRD of Sb2(S,Se)3 specimens without HTL, with as-deposited MnS HTL and with post-annealed MnS HTL.

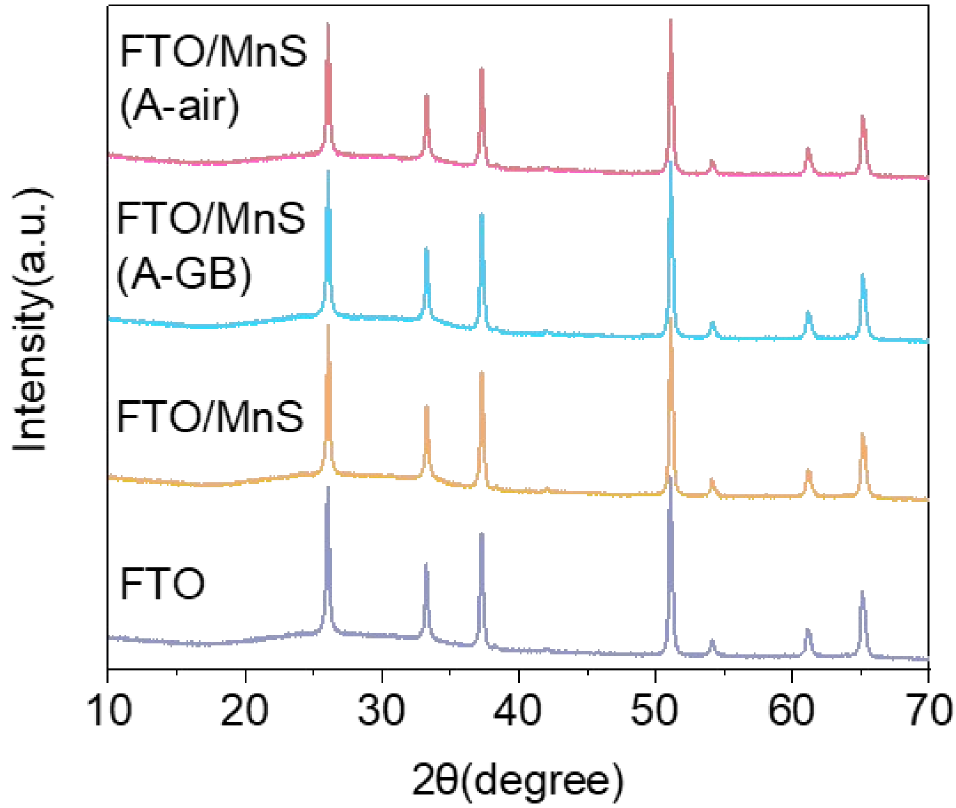

Figure S2. XRD of FTO, as-deposited MnS on a FTO glass substrate, annealed MnS (in a nitrogen-filled glove box) and annealed MnS (in ambient air) on a FTO glass substrate.

Table S1. *J-V* data of FTO/CdS/$Sb_2(S,Se)_3$/MnS/Au with an annealing after the deposition of

Serial NO.	Voc/V	Jsc/mA.cm-2	FF/%	η/%
5 minutes	0.655	20.472	54.017	7.249
10 mimutes	0.638	21.216	59.985	8.124
15 mimutes	0.655	20.277	60.811	8.082
30 mimutes	0.638	20.104	60.176	7.723
45 mimutes	0.630	20.611	59.572	7.732
60 mimutes	0.647	19.220	59.493	7.397

MnS at 175 ℃ in a glove box for various times.

Serial NO.	Voc/V	Jsc/mA.cm-2	FF/%	η/%
150 ℃	0.638	20.602	60.542	7.962
175 ℃	0.638	21.216	59.985	8.124
200 ℃	0.638	19.099	59.122	7.208

Table S2. *J-V* data of FTO/CdS/$Sb_2(S,Se)_3$/MnS/Au with an annealing after the deposition of MnS in a glove box for 10 minutes at various temperatures.

Serial NO.	Voc/V	Jsc/mA.cm-2	FF/%	η/%
Glove Box	0.638	21.216	59.985	8.124
Air	0.621	17.904	31.952	3.554

Table S3. *J-V* data of FTO/CdS/$Sb_2(S,Se)_3$/MnS/Au with an annealing after the deposition of MnS at 175 ℃ for 10 minutes in various atmospheres.

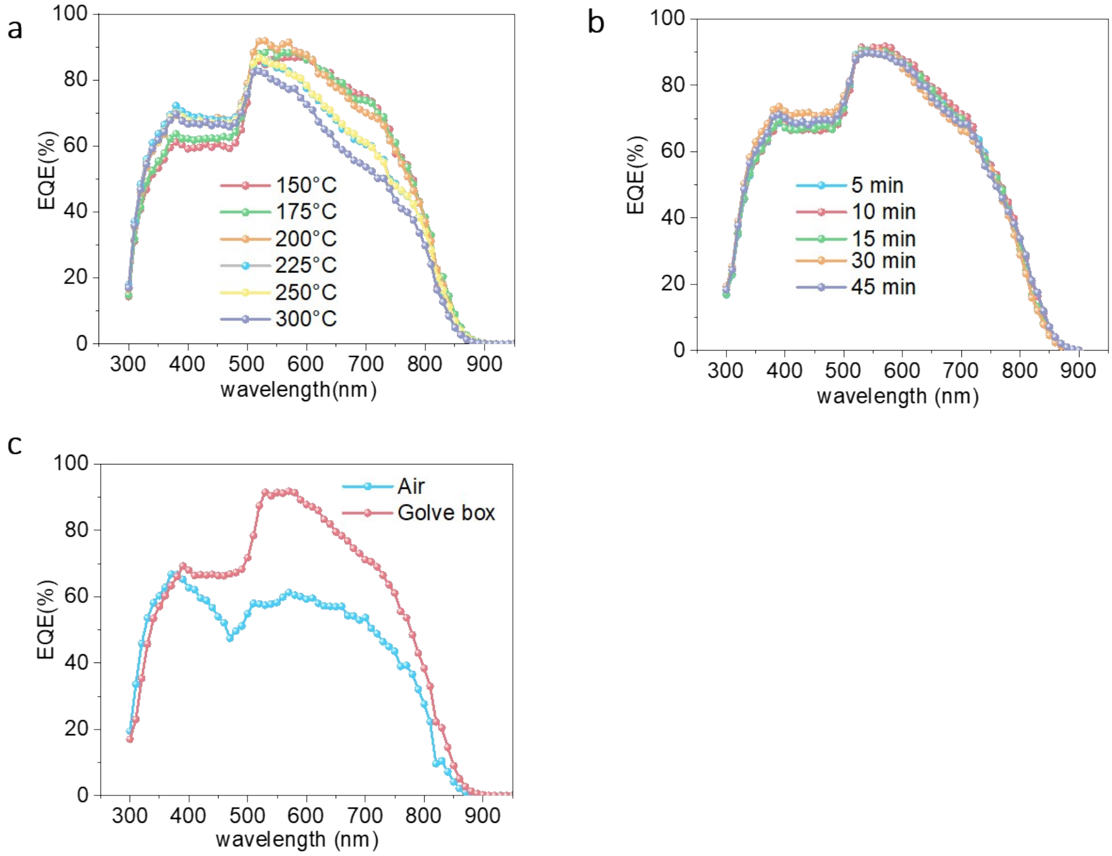

Figure S3. EQE curves of devices with MnS HTL subjected to various post-deposition treatment conditions, including different a) annealing temperature, b) annealing time, and c) annealing atmosphere.

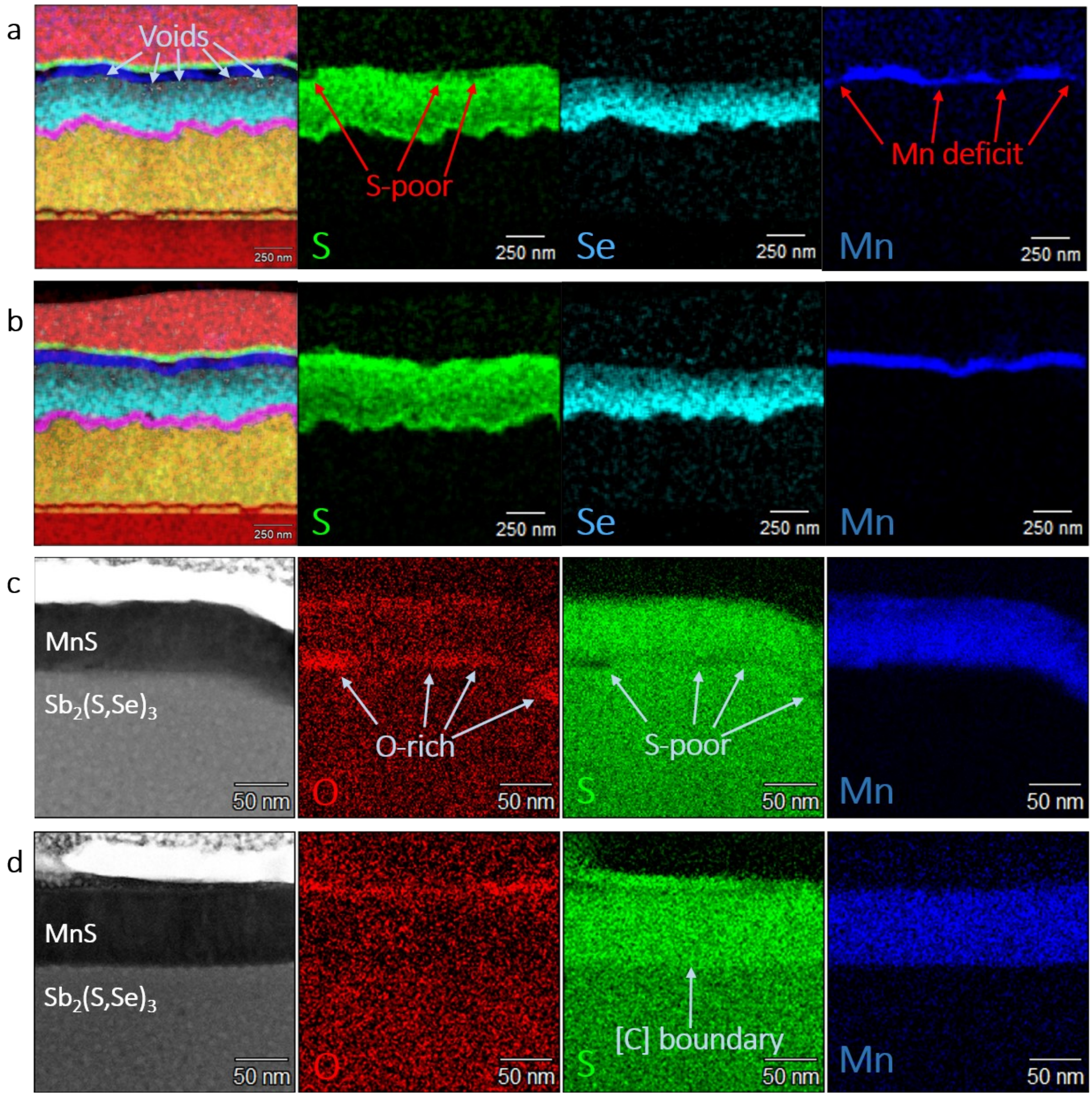

Figure S4. EDS mapping of $Sb_2(S,Se)_3$ solar cells with a) as-deposited MnS HTL and b) post-annealed MnS HTL. EDS elemental mapping of $Sb_2(S,Se)_3$/MnS interface with c) as-deposited MnS HTL and d) post-annealed MnS HTL.

The post-annealing modifies the composition and microstructure of MnS. As shown in the EDS mapping in **Figure S4**, the S intensity obviously increases in MnS (a brighter S signal in **Figure S4 b,d**) whilst decreases in $Sb_2(S,Se)_3$. The difference in S content in MnS and $Sb_2(S,Se)_3$ layers is evidenced in the line scan profile in **Figure S5** as well. In addition, as shown in **Figure S4c,** some oxygen-rich and sulfur-poor regions were observed at the interface of MnS/$Sb_2(S,Se)_3$ in the sample with as-deposited MnS HTL, which may be caused by exposure to air when we transfer specimens. The antimony oxide formed at the interface due to the oxidation may act as a charge trap, resulting in high back contact resistance and thereby low *FF* and J_{sc}.[1] Interestingly, these detrimental areas were not detected after post-deposition annealing treatment as illustrated in **Figure S4d**. The oxygen initially aggregated at the interface might diffuse and uniformly distribute in the $Sb_2(S,Se)_3$ layer after annealing. It has been reported that the unintentionally introduced oxygen in $Sb_2(S,Se)_3$ layer could help passivate defects in the bulk, which benefits device performance.[2, 3] Moreover, the post-deposition annealing treatment facilitates a more uniform MnS layer. The element re-distribution caused by post-deposition annealing treatment can improve the quality of both MnS layer and $Sb_2(S,Se)_3$/MnS interface, likely accounting for the improvement of the device performance.

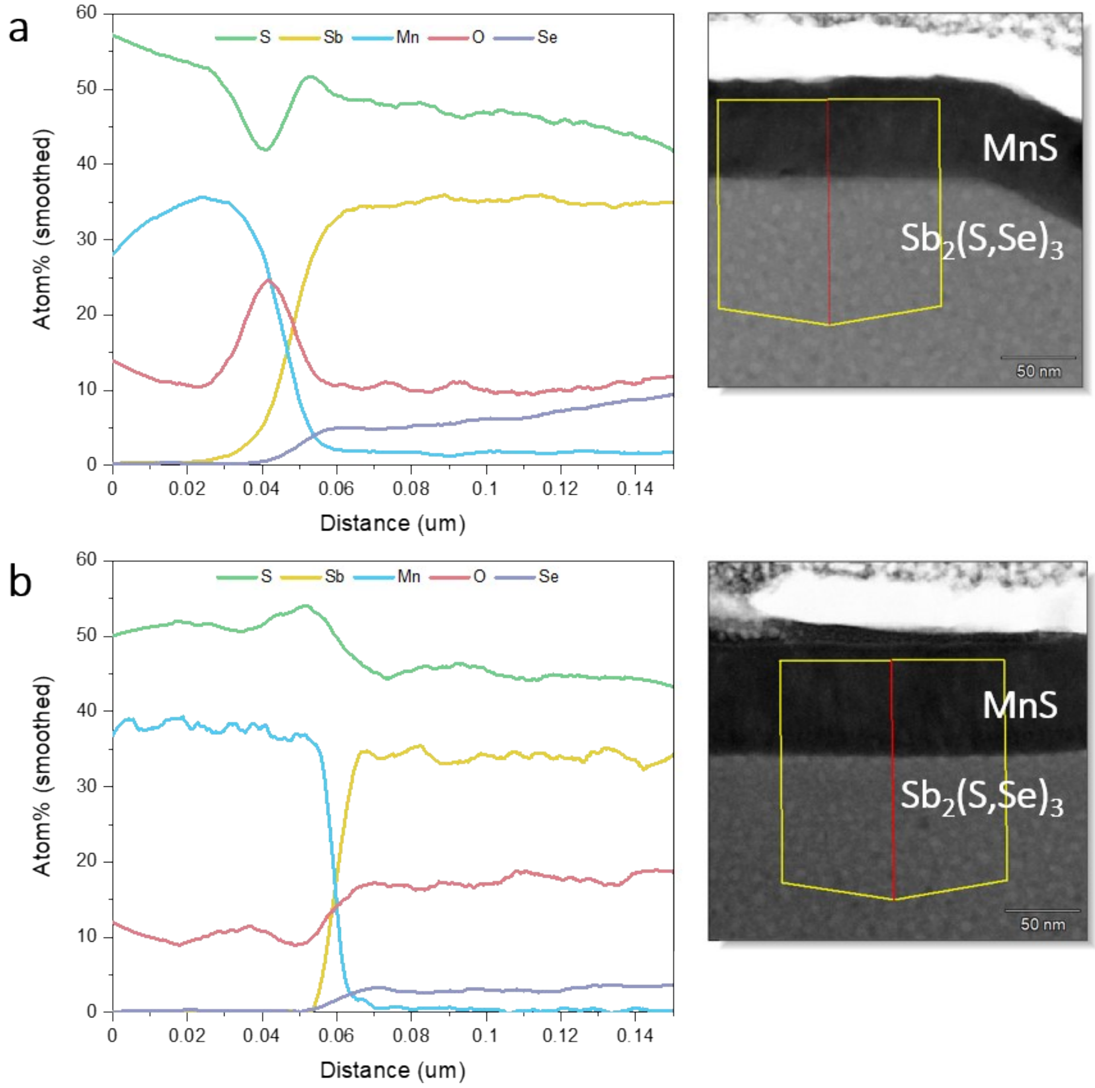

Figure S5. Line scan profiles of the atomic conentration at the $Sb_2(S,Se)_3$/MnS interface and MnS layer. $Sb_2(S,Se)_3$ solar cell with a) as-deposited MnS HTL and b) post-annealed MnS HTL.

Table S4. Hall test of as-deposited and post-annealed MnS layers

Sample	As-deposited MnS	Post-annealed MnS
Thickness/ um	0.08	0.08
Sheet rho/ ohm/square	2.61×10^{7}	1.90×10^{6}
Resistivity/ ohm.cm	208.4	15.21
C.C/ cm^{-3}	$(0.52\text{-}1.07)\times10^{17}$	$(1.86\text{-}2.69)\times10^{18}$

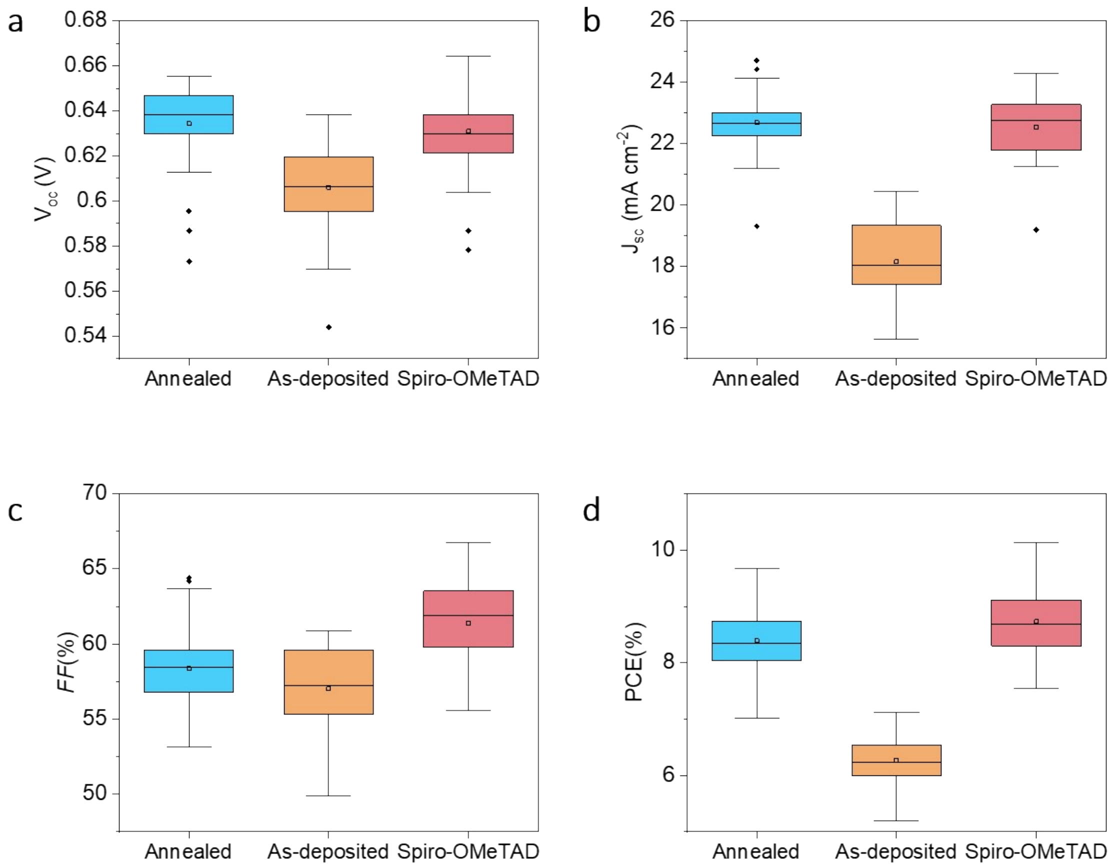

Figure S6. Statistic results of **a**) Voc, **b**)Jsc, **c**)FF and **d**)PCE for Sb2(S,Se)3 solar cells with as-deposited MnS HTL (28 cells), post-annealed MnS HTL (66 cells) and Spiro-OMeTAD HTL (43 cells) respectively (the same devices in Figure 2a).

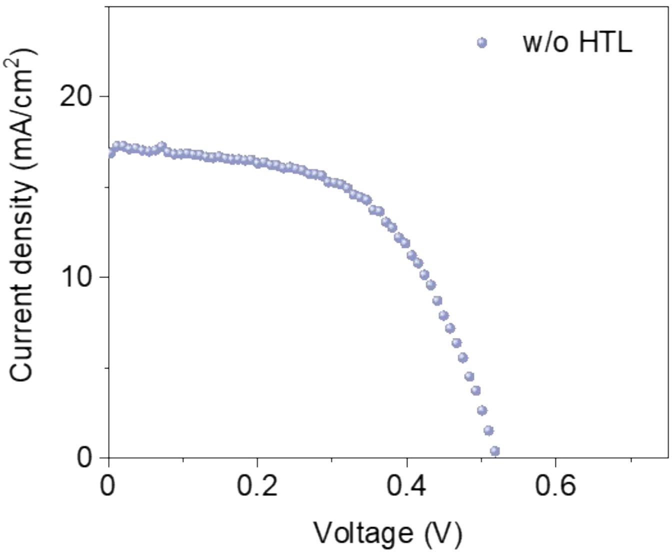

Figure S7. J-V curve of the Sb2(S,Se)3 solar cell without HTL. i.e. Glass/FTO/CdS/ Sb2(S,Se)3/Au.

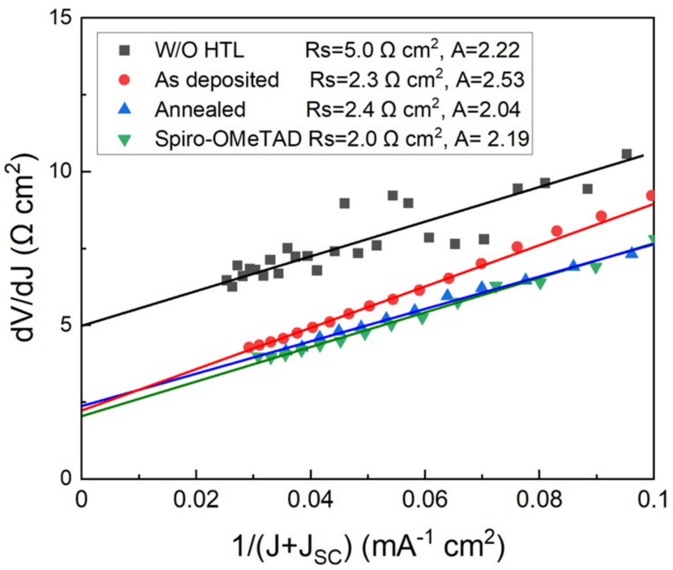

Figure S8. Dark/light J-V cross-over curve of $Sb_2(S,Se)_3$ devices without an HTL, with an as-deposited MnS HTL, with an annealed MnS HTL and with a Spiro-OMeTAD HTL.

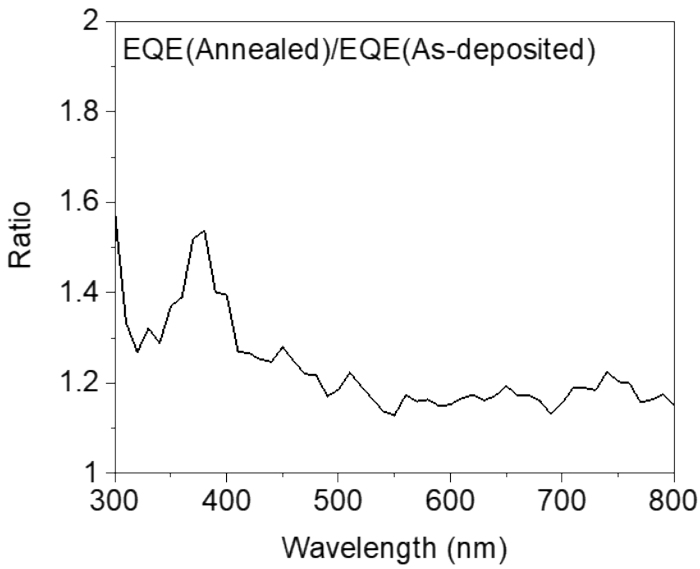

Figure S9. The ratio between external quantaum efficiency (EQE) of the Sb2(S,Se)3 solar cell with post-annelaed and as-deposited MnS HTL.

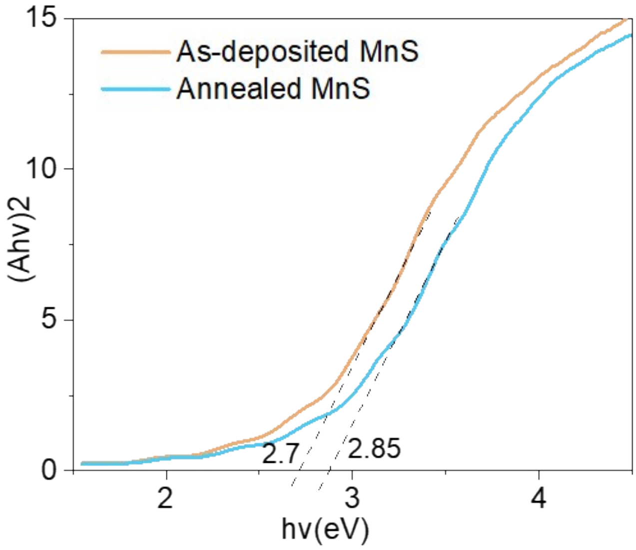

Figure S10. UV-vis characterization of as-deposited and post-annealed MnS respectively.

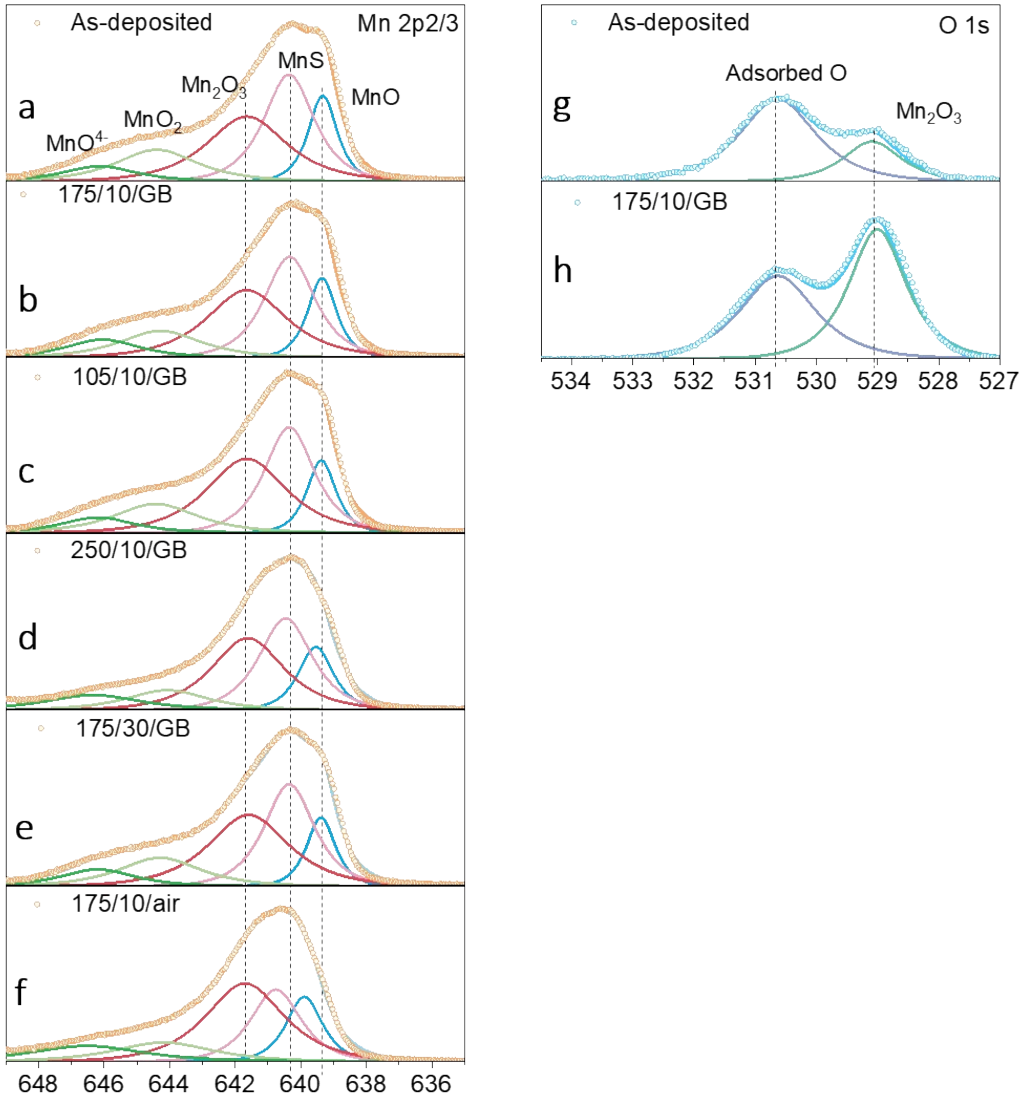

Figure S11. Component analysis of MnS after post-annealed under various conditions. XPS characterizations of Mn 2p in **a)** as-deposited MnS, **b-f)** MnS post-annealed under 175/10/GB (i.e. at 175 ℃ for 10 minutes in a glove box), 105/10/GB, 250/10/GB, 175/30/GB, 175/10/air, O 1s in **g)** as-deposited MnS, **h)** MnS post-annealed under 175/10/GB (10nm etched for all specimens).

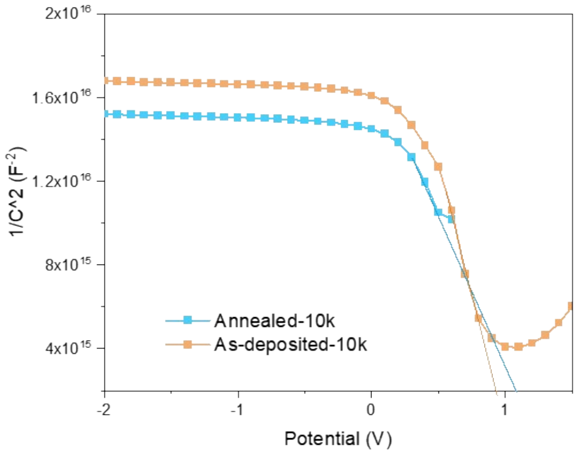

Figure S12. Mott-Schottky curves of Sb2(S,Se)3 solar cells with as-deposited and annealed MnS HTL respectively.

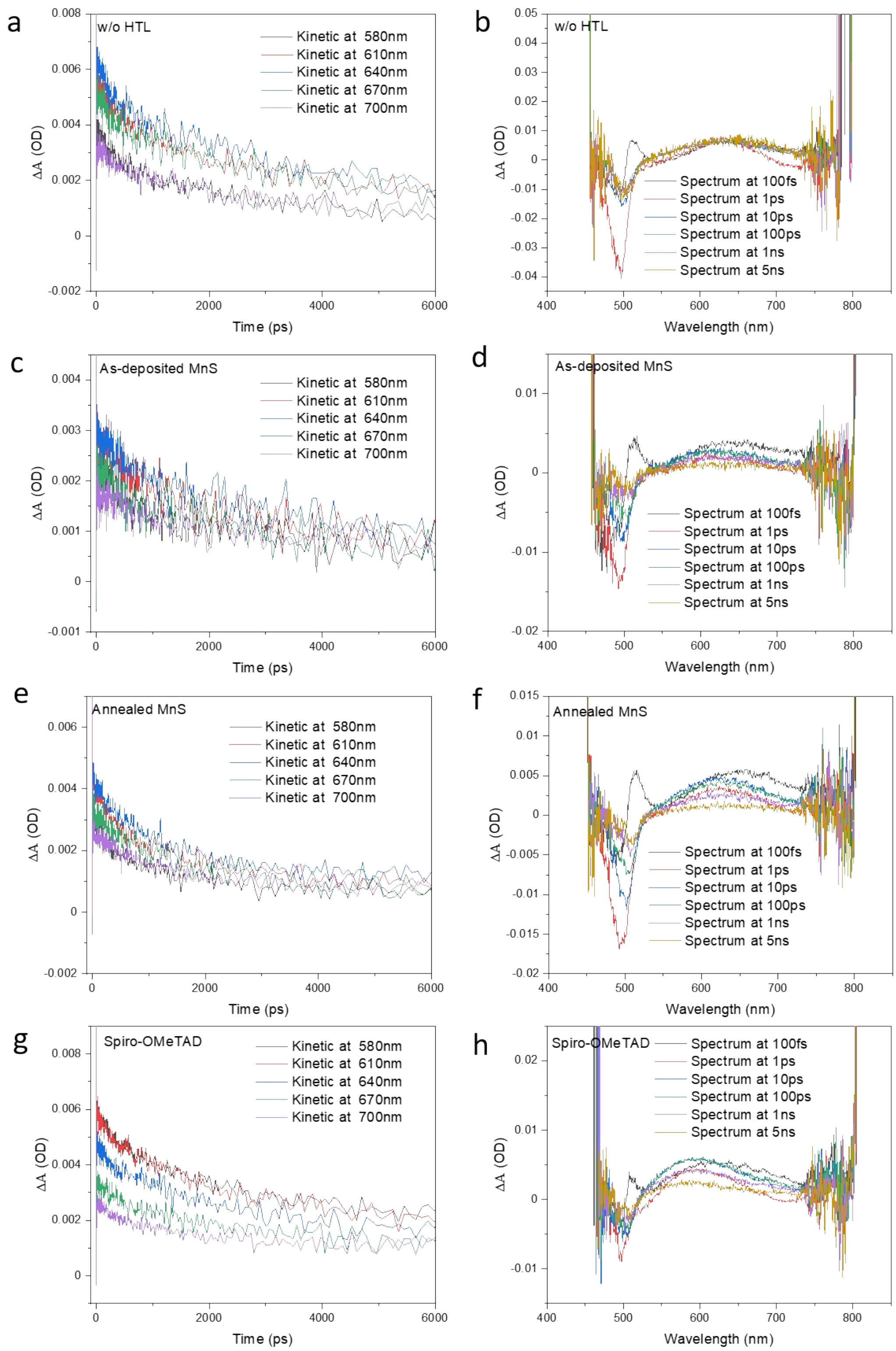

Figure S13. TAS spectrums of specimens a) without HTL, c) with as-deposited MnS HTL, e) with post-annealed MnS HTL and g) with spiro-OMeTAD HTL respectively. Kinetic of specimens b) without a HTL, d) with as-deposited MnS HTL, f) with post-annealed MnS HTL and h) with spiro-OMeTAD HTL respectively.

Reference

1. J. Dong, Y. Liu, Z. Wang and Y. Zhang, *Nano Select*, 2021, 1-31.
2. W. Lian, C. Jiang, Y. Yin, R. Tang, G. Li, L. Zhang, B. Che and T. Chen, *Nat. Commun.*, 2021, **12**.
3. C. Wang, S. Lu, S. Li, S. Wang, X. Lin, J. Zhang, R. Kondrotas, K. Li, C. Chen and J. Tang, *Nano Energy*, 2020, **71**.