Supporting Information

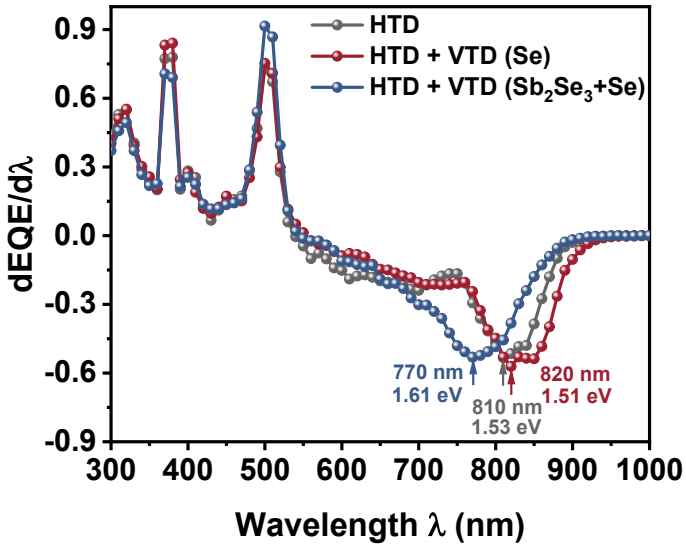

Fig. S1 Bandgaps of $Sb_2(S,Se)_3$ films determined using the peak position of the first-order derivative of the EQE curves.

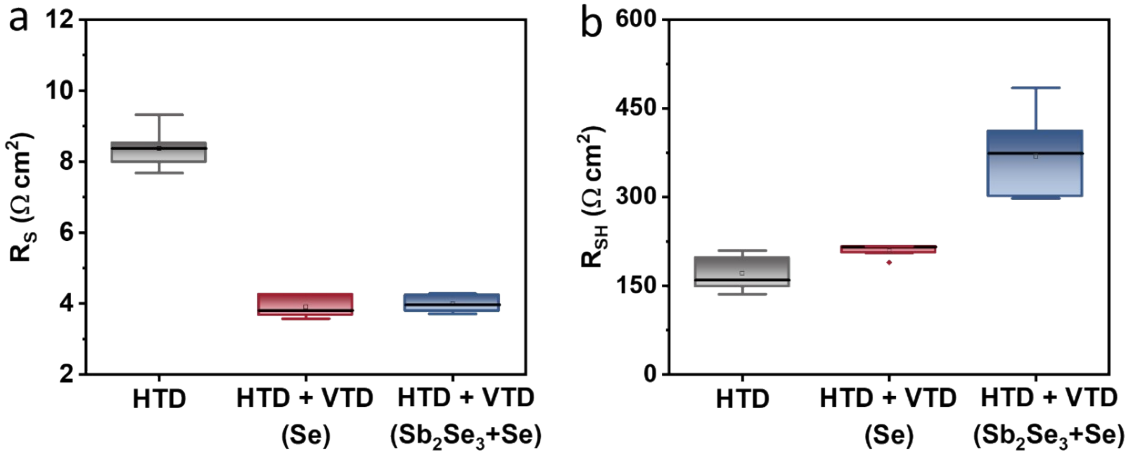

Fig. S2 Statistical box plots of (a) R_S and (b) R_{SH} in HTD, HTD + VTD (Se), and HTD + VTD (Sb_2Se_3+Se) devices.

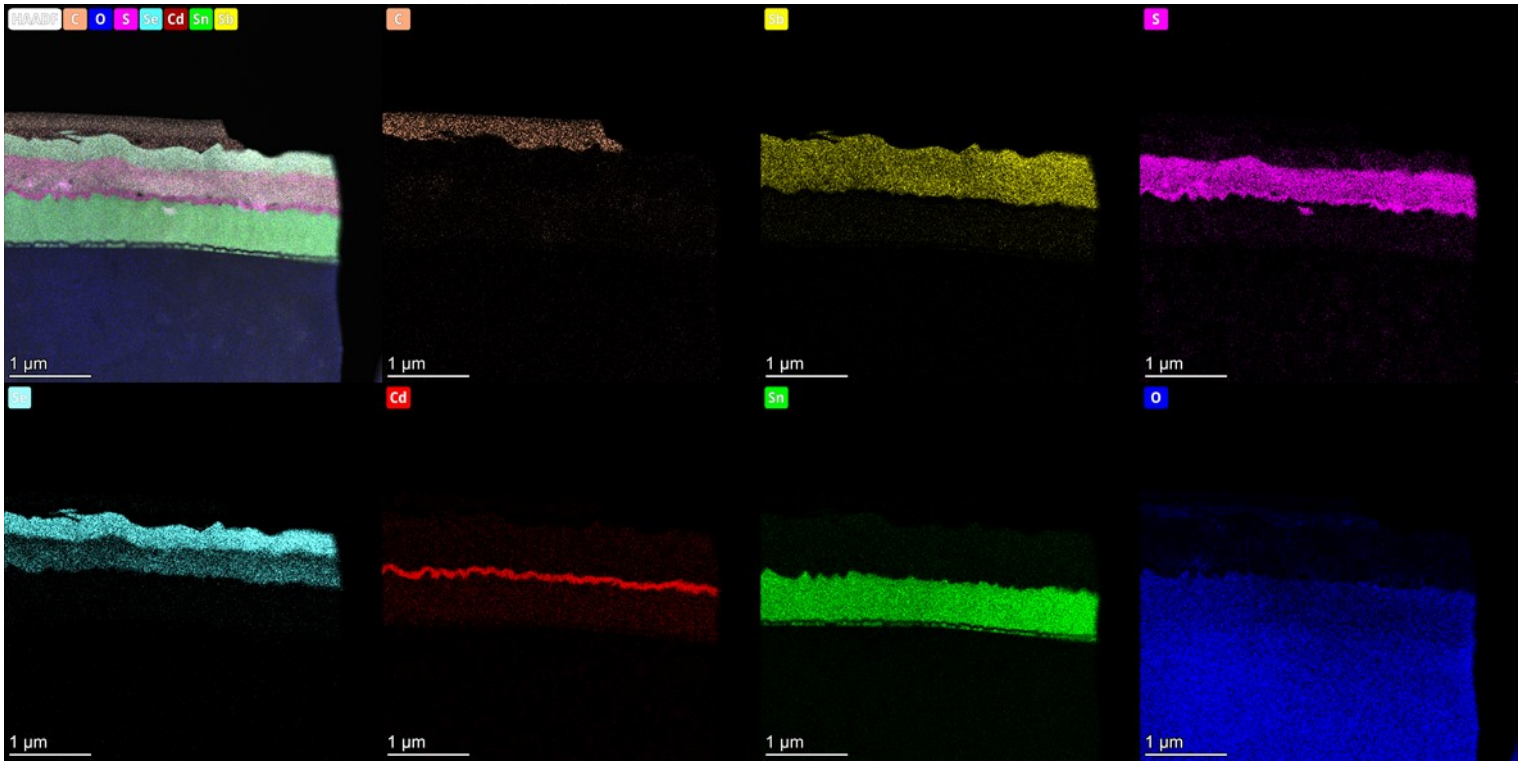

Fig. S3 STEM EDS mapping of HTD + VTD (Sb_2Se_3+Se) thin film.

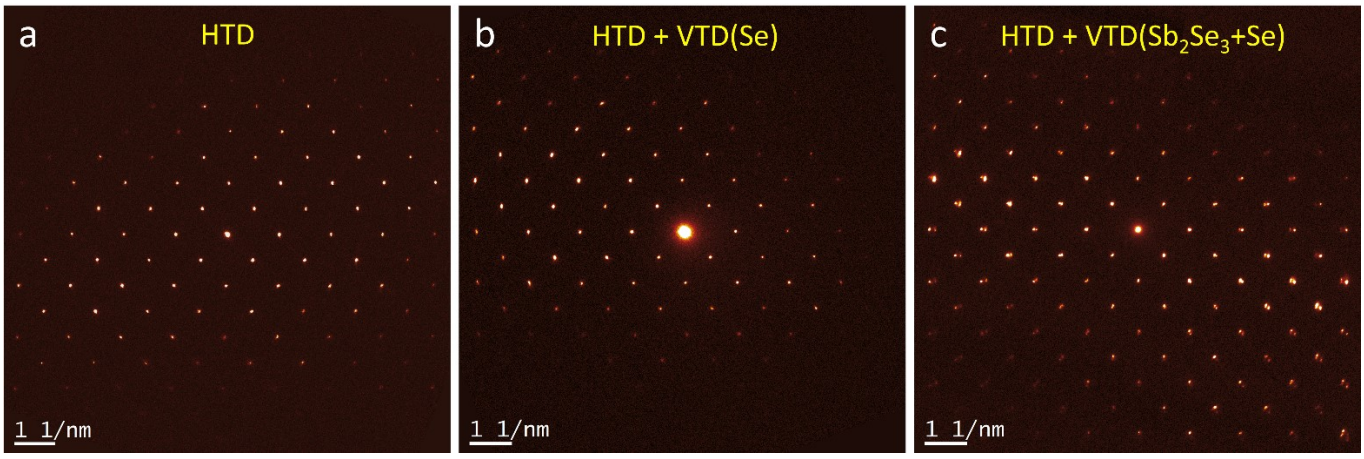

Fig. S4 SAD patterns $Sb_2(S,Se)_3$ films fabricated by (a) HTD only, (b) HTD + VTD (Se), and (c) HTD + VTD (Sb_2Se_3+Se). Please note that HTD only and HTD + VTD (Se) show a single array of diffraction spots with slightly different lattice parameters, while HTD + VTD (Sb_2Se_3+Se) exhibits well distinguished splits of diffraction spots.

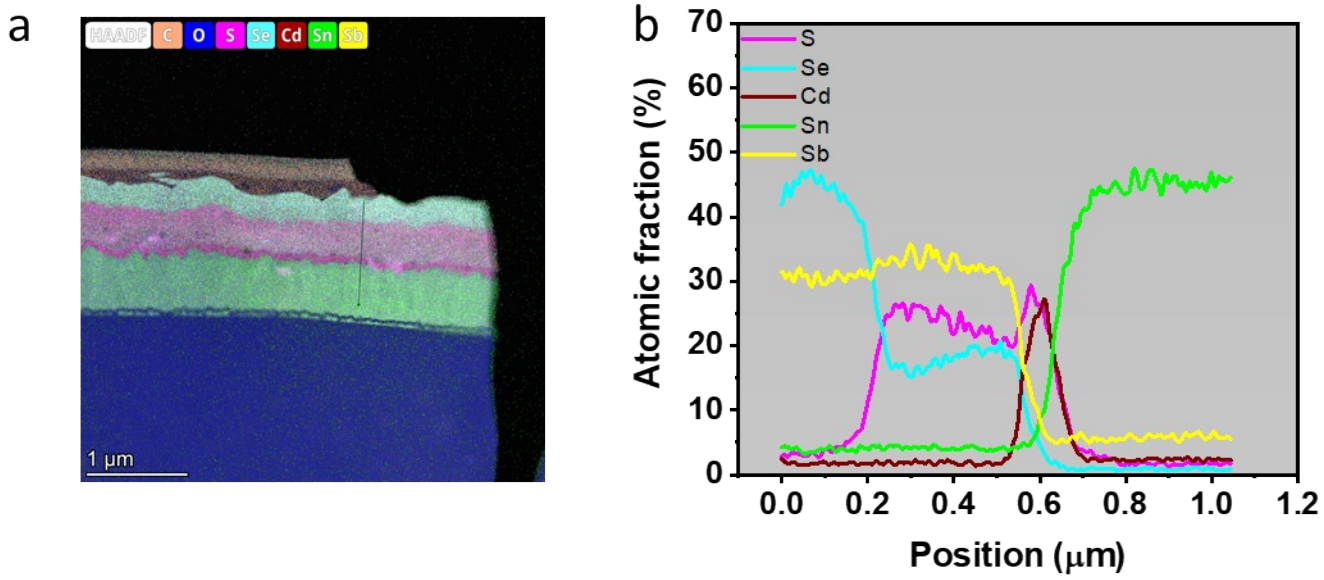

Fig. S5 (a) STEM cross-sectional image with EDS mapping and (b) In-depth atomic fraction of HTD + VTD (Sb_2Se_3+Se) thin film.

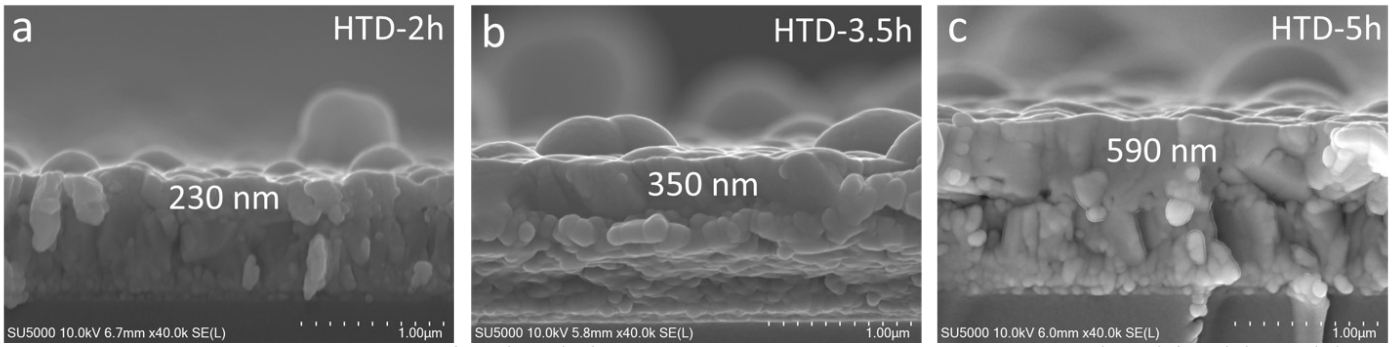

Fig. S6 Cross-sectional SEM images of $Sb_2(S,Se)_3$ films undergoing hydrothermal deposition (HTD) for: (a) 2 h, (b) 3.5 h, and (c) 5 h. 3.5 h is the optimal deposition duration leading to the champion device.

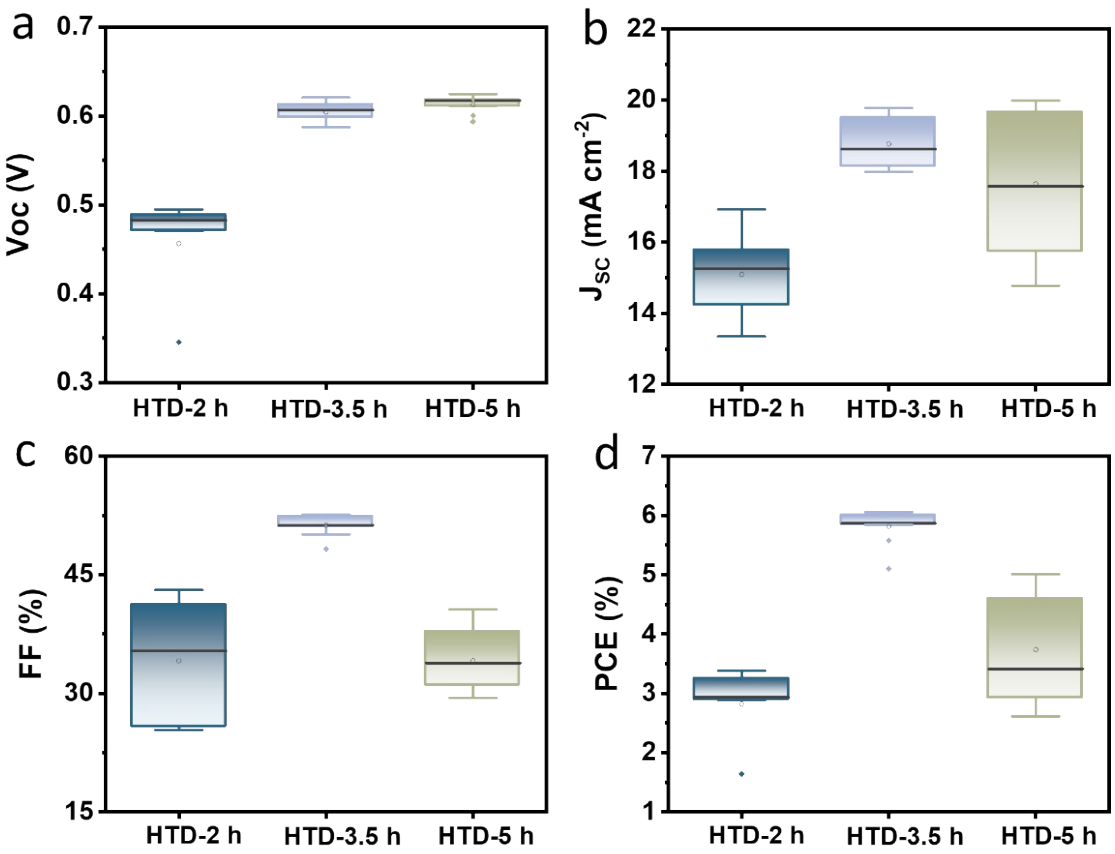

Fig. S7 Photovoltaic performance of $Sb_2(S,Se)_3$ solar cells fabricated by hydrothermal deposition method for 2 h, 3.5 h, and 5 h: Statistical box plots of (a) V_{oc}, (b) FF, (c) J_{sc}, and (d) PCE. 3.5 h is the optimal deposition duration leading to the champion device.

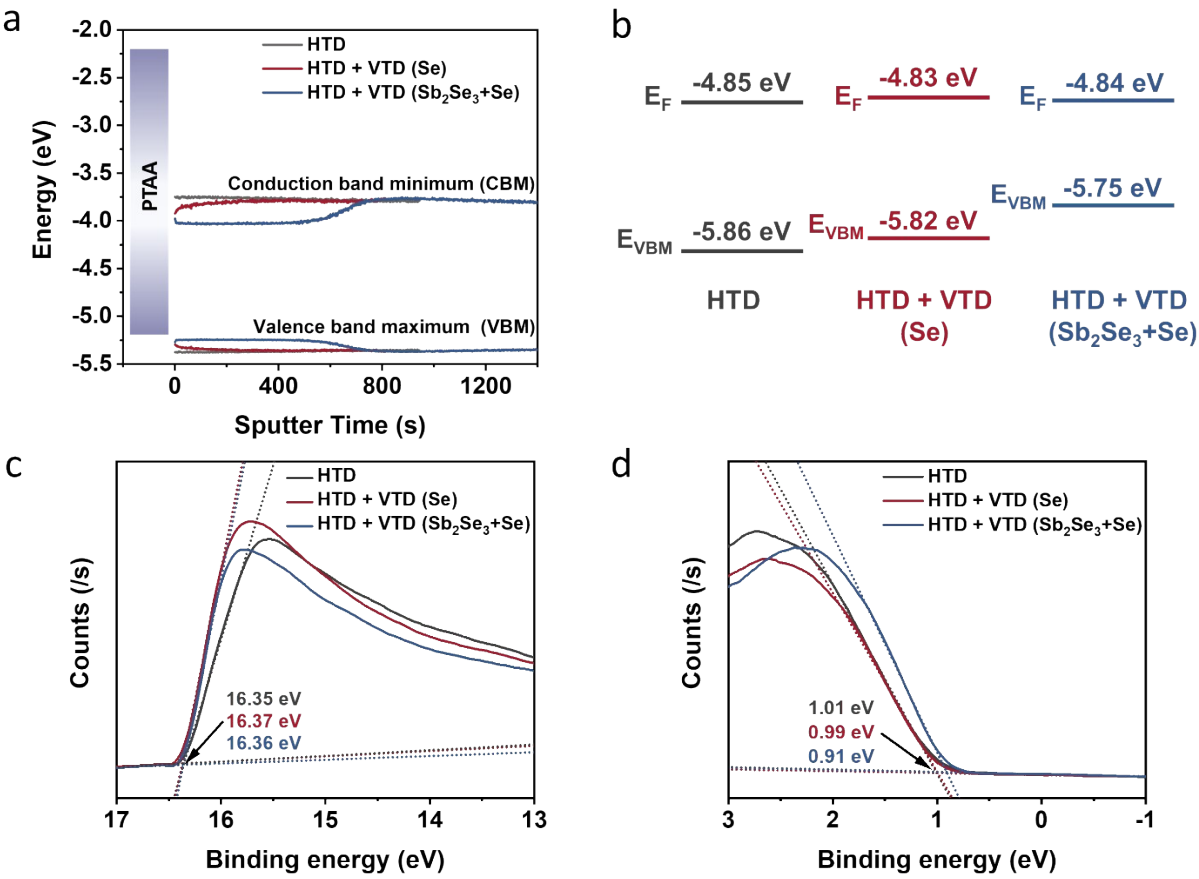

Fig. S8 (a) Energy level positions constructed from literature values,[39] (b) Valence band maximum positions measured from UPS, (c) Secondary cut-off regions, and (d) valence band regions of UPS spectra.