

Supporting Information

Efficient $\text{Sb}_2(\text{S,Se})_3$ Solar Cells *via* Monitorable Chemical Bath

Deposition

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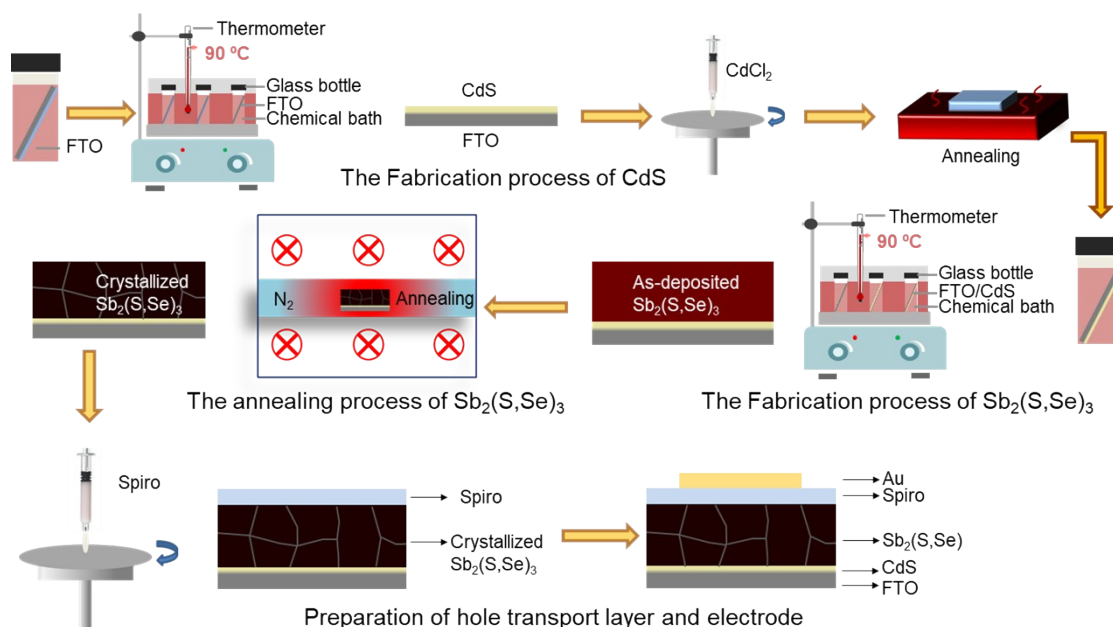


Figure S1. A schematic of the whole process of device preparation. The preparation process of $\text{Sb}_2(\text{S,Se})_3$ solar cells can be divided into four main procedure. First, CdS layers were grown by the CBD method, followed by post-annealing treatment. Then, amorphous $\text{Sb}_2(\text{S,Se})_3$ films were grown on the surface of CdS layers by CBD method. After this, post-annealing treatment was used to crystallize the amorphous $\text{Sb}_2(\text{S,Se})_3$ films. Finally, the HTL was spin-coated and the electrodes were vapor-deposited to obtain a complete device.

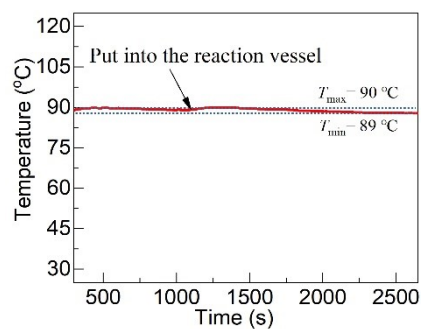


Figure S2. The bath temperature fluctuation of the CBD process. The bath temperature was nearly constant (average fluctuation 1 °C) during the whole deposition process except the slight disturbance when putting in the reaction vessel. $T_{\max}$ and $T_{\min}$ denote the maximum and minimum temperature during the reaction, respectively.

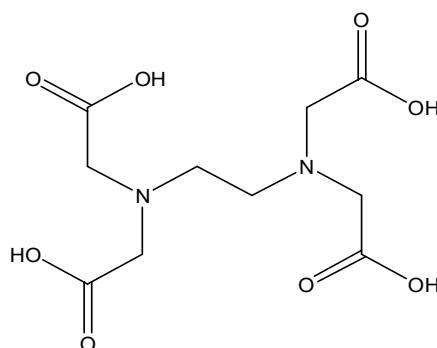


Figure S3. The molecule of EDTA. An EDTA molecule contains four -COOH groups, so adding EDTA to the solution will quickly degrade the pH.

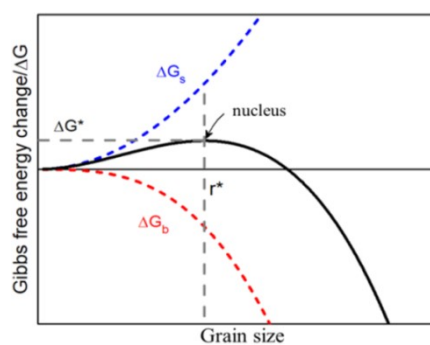


Figure S4. The relationship between grain growth energy and grain size. The energy of crystal growth has a huge relationship with the grain size. Crystal nucleus below the critical size will degenerate, and nucleus larger than the critical size will grow rapidly. ΔG^* = Critical Gibbs free energy, ΔG_s = Surface Gibbs free energy, ΔG_b = Bulk Gibbs free energy, r^* =critical radius.

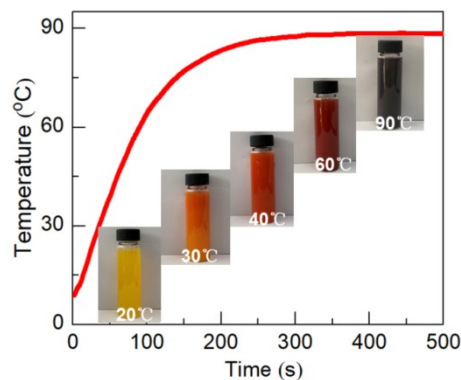


Figure S5. The pictures of the CBD reaction as the temperature rises. With the increase of the reaction temperature, the color of the reaction solution turned from yellow to black.

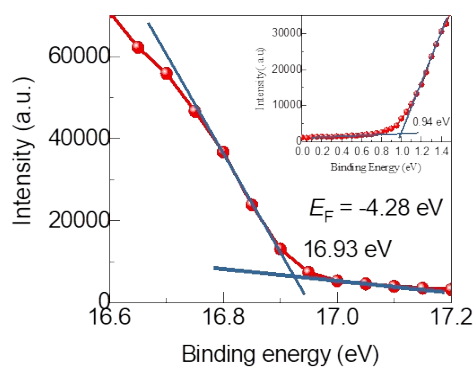


Figure S6. Ultraviolet photoelectron spectroscopy of annealed CBD-Sb₂(S,Se)₃ film. According to our UPS results, the Fermi level (E_f) of the Sb₂(S,Se)₃ film is -4.28 eV, and the distance between valence band (E_v) and E_f is 0.94 eV. Therefore, the E_v of the film should be -5.22 eV. Since the bandgap of Sb₂(S,Se)₃ is 1.48 eV, the recalculated conduction band (E_c) position should be -3.74 eV.

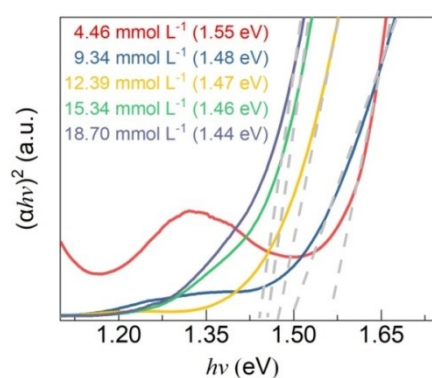


Figure S7. Tauc plot of the annealed Sb₂(S,Se)₃ films with different concentration of SU. As the concentration of SU increases from 4.46 mmol L⁻¹ to 18.70 mmol L⁻¹, the bandgap of the film decreases from 1.546 eV to 1.443 eV.

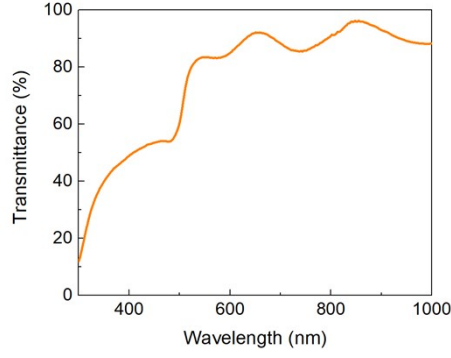


Figure S8. The transmittance spectra of CdS/FTO.

Table S1. The PL bandgap, optical bandgap and Stokes shift of the crystallized $\text{Sb}_2(\text{S,Se})_3$ film with different concentration of SU.

Concentration of SU	PL (eV)	UV (eV)	Stokes Shift (eV)
4.46 mmol L ⁻¹	1.441	1.546	0.105
9.34 mmol L ⁻¹	1.422	1.483	0.061
12.39 mmol L ⁻¹	1.393	1.473	0.080
15.34 mmol L ⁻¹	1.381	1.466	0.085
18.70 mmol L ⁻¹	1.365	1.443	0.078

Table S2. The detail device parameters of the champion device.

Method	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)	R _s (Ω cm ²)	R _{sh} (Ω cm ²)	Ref.
CBD	0.625	22.98	57.6	8.27	6	273	This work 7
HT	0.670	23.7	66.8	10.7	4.3	957.8	

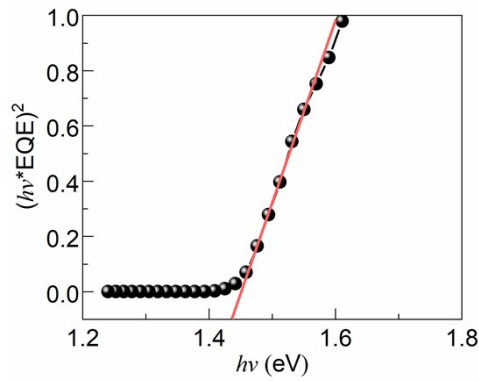


Figure S9. The bandgap (~1.44 eV) of $\text{Sb}_2(\text{S,Se})_3$ film with 9.34 mmol L⁻¹ SU obtained from EQE data. The band gap of $\text{Sb}_2(\text{S,Se})_3$ film with 9.34 mmol L⁻¹ SU calculated by EQE is approximately 1.44 eV and is similar to the bandgap from Tauc plot.

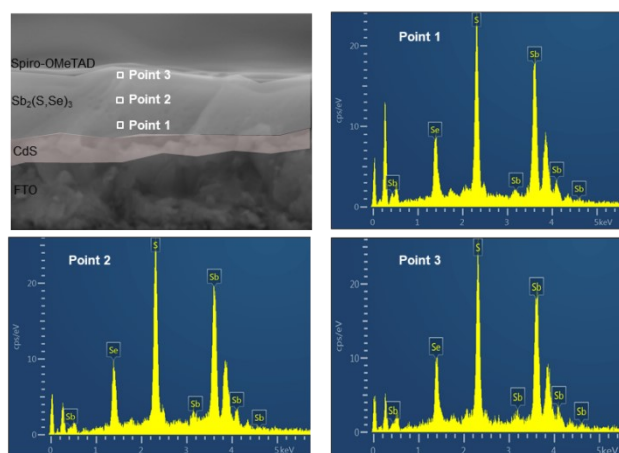


Figure S10. EDS element content in different points of the champion device. According to the Figure S9, the content of Sb, S and Se in the film is about 52.22-52.97 At%, 39.36-39.66 At% and 7.67-8.12 At% respectively. Taking the EDS accuracy into account, the distribution of S and Se in the film was difficult to distinguish. Therefore, we consider that $\text{Sb}_2(\text{S,Se})_3$ film prepared by CBD method is uniform inside.

Table S3. Content of Sb,S,Se in different points of the champion device.

Position	Sb (At%)	S (At%)	Se (At%)
Point 1	52.97	39.36	7.67
Point 2	52.66	39.62	7.72
Point 3	52.22	39.66	8.12

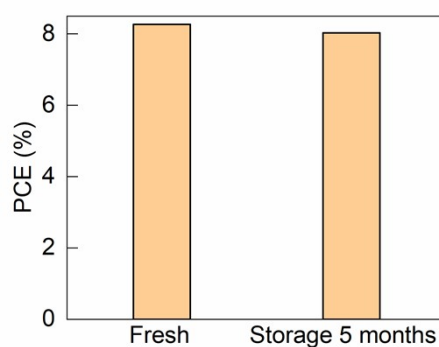


Figure S11. The device stability of $\text{Sb}_2(\text{S,Se})_3$ solar cells. The unencapsulated device merely degraded from 8.27% to 8.03% after storing in the ambient for 5 months, and exhibited excellent long-term storage stability.

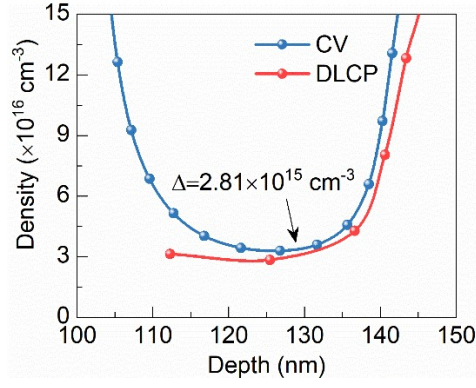


Figure S12. The C-V and DLCP characterization of $\text{Sb}_2(\text{S,Se})_3$ solar cells. The blue dot line is the curve of defect density with depth testing by C-V. The red dot line is the curve of defect density with depth testing by DLCP. The interface defect density is $2.81 \times 10^{15} \text{ cm}^{-3}$.

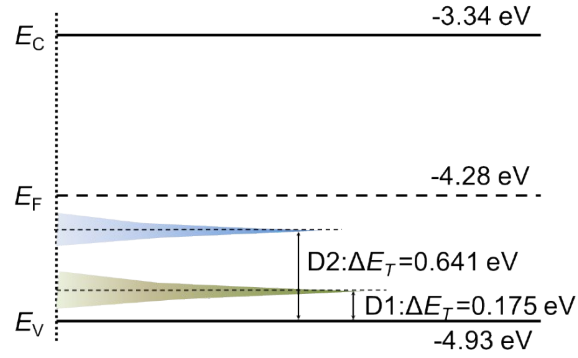
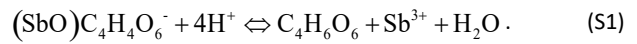
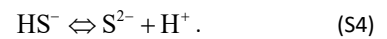
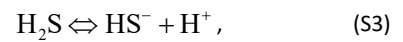
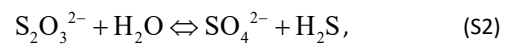


Figure S13. A schematic of the energy states and defect levels of $\text{Sb}_2(\text{S,Se})_3$ film with 9.34 mmol L^{-1} SU. The defect energy levels of $\text{Sb}_2(\text{S,Se})_3$ film were 0.175 eV and 0.641 eV corresponding to D1 and D2, respectively. The defect densities of D1 and D2 were calculated from the integral area of Gaussian distribution, where N_t of D1 and D2 were $9.27 \times 10^{15} \text{ cm}^{-3}$ and $4.89 \times 10^{15} \text{ cm}^{-3}$, respectively. The defect energy levels of $\text{Sb}_2(\text{S,Se})_3$ thin film were depicted in here.

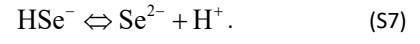
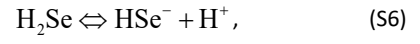
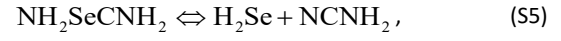
Chemical reaction during the CBD process: The chemical process of CBD $\text{Sb}_2(\text{S,Se})_3$ film is complicated. First, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$ is dissolved and hydrolyzed to release Sb^{3+} , which plays the role of antimony source. The hydrolysis process can be expressed by Equation (S1),



Then $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is dissolved and hydrolyzed to provide S^{2-} , which plays the role of sulfur source. This process can be expressed by Equation (S2-S4),



Subsequently, $\text{NH}_2\text{SeCNH}_2$ (SU), the selenium source, is dissolved and generate Se^{2-} through multi-stage decomposition, which can be expressed by Equation (S5-S7),



Eventually, Sb^{3+} , S^{2-} , and Se^{2-} synergistically react to form $\text{Sb}_2(\text{S},\text{Se})_3$ film according to Equation (S8),

