Supplementary Information

All-inorganic Sb₂S₃-based Two-terminal Tandem Solar Cells Enable

over 10.9% Efficiency Employing a Concise Interconnection Layer

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Experiment and Simulation Section

Preparation of CdS:In ETL: The CdS:In layer was deposited by the chemical bath deposition (CBD) method directly onto Glass/FTO substrates. The F-doped SnO₂ (FTO) substrates were purchased from Advanced Election Technology Co., Ltd. The square resistance of $<10 \Omega$ sq⁻¹ and transmittance of >83% was employed as the transparent conducting electrodes. For the CBD and CdCl₂ post-treatment process, refer to our previous work for details.¹

*Preparation of Sb*₂*S*₃ *Absorber and SJSC Fabrication:* The Sb₂S₃ films were synthesized by a hydrothermal method. For the *Sb*₂*S*₃ absorber deposition and post-annealing process, refer to the previous work for details.¹ It is noteworthy that, in this study, deposition time was set at 3/3.5/4/4.5/5 h to obtain different thickness Sb₂S₃ layers. Finally, the typical structure of a Sb₂S₃ SC, Glass/FTO/CdS:In/Sb₂S₃/Spiro-OMeTAD /Au, was completed by spinning a layer of Spiro-OMeTAD as HTL followed by thermal annealing in air (~100 °C) for 10 min. For the optimal structure, Glass/FTO/CdS:In/Sb₂S₃/PbS-EDT/Au, two layers of PbS QDs (1st exciton peak at 888 nm) were treated with EDT ligand (PbS-EDT) acting as the HTL. Please refer to the previous work for details of PbS QD synthesis method.² After HTL fabrication, the Au electrodes were deposited by thermal evaporation (~60 nm with a deposition rate of 0.5 Å/s). The active area of the device was 0.04 cm² as defined by the mask.

Preparation of Sputtered ZnO Film: The magnetron sputtering (MS) was performed using the JCP500 high vacuum multi-target magnetron sputtering coating system. A 99.9% pure zinc oxide from Zhongnuo New Material Company served as the sputtering target. The standard preparation procedure involved maintaining the sample substrate at 25 °C, adjusting the sputtering power to 100 W (2.19 W cm⁻²), employing an oxygen and argon mixture (O₂:Ar = 3:97/1:99) as the sputtering gas, and controlling the chamber pressure at 2.7 Pa throughout the sputtering process. The deposition rate and time during this procedure were approximately 1 Å/s and 15 min, respectively. *Preparation of PbS QD Absorber and SJSC Fabrication:* The ZnO thin film as ETL was prepared according to the above ZnO deposition method. The absorber was fabricated by spin-coating the PbS-halide QD ink onto the ZnO thin film. For the PbS QD synthesis (1st exciton peak at 1290 nm) and ligand exchange process, please refer to the previous work for details.² Following a solution-phase ligand exchange in a solvent system of DMF and octane, the PbS-IBr (PbI₂ and PbBr₂ capped PbS QDs) solution with a concentration of 350 mg mL⁻¹ in a 7:3 N-butylamine:DMF solvent, was

spin-coated onto the ZnO film at 2500 rpm for 45 s. Subsequently, the film was annealed at 90 °C for 10 min, and the absorber film naturally cooled to below 40 °C. The entire process was conducted in a nitrogen atmosphere glove box. Following this, two layers of PbS QDs (1st exciton peak at 880 nm) were treated with EDT ligand (PbS-EDT) acting as the HTL followed by thermal evaporation of the Au electrode (~60 nm with a deposition rate of 0.5 Å/s). The active area of the device was 0.04 cm² as defined by the mask.

Preparation of ICL and 2T-TSC Fabrication: The preparation of the front and rear subcells refers to the corresponding fabrication of SJSCs. For fabrication of ICL as PbS-EDT/Au/ZnO, a 40 nm PbS-EDT layer was coated on top of the Sb₂S₃ layer within the front subcell. Then 1 nm Au was deposited by thermal evaporation (a deposition rate of 0.05 Å/s) followed by MS-ZnO (80 nm) deposition process. For fabrication of ICL as PbS-EDT/Au/SnO₂/ZnO, a 15 nm SnO₂ layer was introduced between 1 nm Au and ZnO layers. The SnO₂ layer was prepared at 85 °C by ALD method with a chamber pressure of 900 Pa, using tetrakis(dimethylamino)tin(IV) (TDMASn) as Sn source and H₂O as oxygen source. The ALD flow was repeated with a water source pulse time of 0.1 s, a carrier gas flow rate of 100 sccm, a purge time of 10 s. The subsequent fabrication of rear subcell was the same as the deposition method for PbS QD SJSCs.

2D-FDTD Simulations: (1) Material Addition: Imported the n/k values of each material measured by the ellipsometer into the material database. Set the optical properties of the three-dimensional materials through data fitting. (2) Simulation Region Setting³: Set periodic boundary conditions for the simulation region, and set the incident direction of light source as PML (perfectly matched layer) boundaries. To reduce simulation time, the simulation area could be limited close to the light source and the cell bottom. (3) Light Source Addition⁴: Set a plane wave light source which was processed by continuous wave (CW) normalization. The software automatically injected the light source calculated based on the class Gaussian-shaped pulse to simulate AM 1.5G solar radiation spectrum. (4) TSC Structure Model Creation: The device structure was defined as TCO (650 nm)/CdS:In (60 nm)/Sb₂S₃/PbS-EDT (40 nm)/Au (1 nm)/ZnO (80 nm)/PbS QDs (340 nm)/PbS-EDT (40 nm). Set the absorber thickness of the two subcells as sweeping variables. Defined the global variables for thickness in the overall model and introduced global variables into the structure group. Modelled each layer of the cell, setting the simulation length and width of each layer to 2 µm. (5) Simulation

Grid Setting: Set the grid according to the precision and resolution requirements. Since the thickness of the Au (1 nm) was much smaller than other layers, refined the grid here to more accurately represent the Au parasitic absorption. (6) Analysis Group Addition⁵: Added exciton generation rate analysis groups to both subcells and used the formula to calculate the J_{sc} output values of the two subcells and the absorption rate for different wavelength. (7) Monitor Addition: Set a frequency monitor near the light source and linear monitors along the direction of light propagation inside the TSC to provide feedback on changes in the light field within the TSC. (8) Sweep Parameter Setting: Set the sweep thickness of the subcells and performed nested sweeps to obtain the subcell J_{sc} . (9) Result Analysis: Imported the sweep result of J_{sc} matrix into MATLAB to obtain min { J_{sub1} , J_{sub2} }, and output the J_{sc} of the 2T-TSC.

The relevant physical equations underlying the simulation process are as follows³⁻⁵:

$$J_{sc} = q \int_{\lambda}^{\lambda_{max}} F_{1.5}(\lambda) \cdot EQE(\lambda) \cdot d\lambda$$
⁽¹⁾

$$P_{abs}(x,\lambda) = \frac{1}{2} c \varepsilon_0 \alpha n |E(x)|^2$$
⁽²⁾

$$\alpha = \frac{4\pi k}{\lambda} \tag{3}$$

Here, q is the unit charge, $F_{1.5}(\lambda)$ is the number of absorbed photons under simulated AM1.5G standard solar irradiation, λ is the wavelength, c is the light speed, ε_0 is the vacuum permittivity, α is the absorption coefficient, E(x) is the optical field, n is the refractive index, k is the extinction coefficient, and x is the spatial coordinate perpendicular to the direction of the absorption layer as set in the simulation.

Characterization: The SEM (FEI Nova NanoSEM450) characterization was utilized to observe the cross-sectional morphology of SCs. The optical absorbance of films was checked by UV-Vis spectrophotometer (PerkinElmer Instruments, Lambda 950 using integrating sphere). The KPFM was measured by conductive atomic force microscopy (SPM9700). The cross-section samples used for TEM were prepared by a focus ion beam system (FIB, FEI Helios). And the internal crystal lattice fringe information and elemental depth EDX of TSC were collected by TEM (JEOL JEM-NEOARM, 200 kV). The J-V curves were measured under a simulated AM1.5G (100 mW cm⁻²) illumination from a 450 W xenon lamp (Oriel, Model 9119, Newport) combined with a source meter (Keithley 2400) at 25 °C in the air. The light intensity was calibrated with a standard Si solar cell

(Oriel, Model 91150V, Newport). The EQE curves were obtained by a QE-R (Enlitech Co., Ltd.). For TSC EQE measurement, the probe light spot covered the full device active area. The bottom PbS QD cell was measured by saturating the top Sb_2S_3 cell using a blue flashlight with 460 nm peak emission to maintain short circuit conditions. For the front cell measurement, a NIR flashlight with 850 nm peak emission was used. The TPC curves were measured by a system consisting of 530 nm monochromatic light, function generator, and oscilloscope. The EIS results were obtained by a CHI1000c multichannel electrochemistry workstation (Chenhua, Co., China). The refractive index and extinction coefficient of each layer of film are measured by ellipsometry system (SOPRA GES-5E).



Fig. S1. (a) The storage stability of the $S-Sb_2S_3$ and $E-Sb_2S_3$ solar cells exposed to the ambient air. (b) Surface KPFM mapping of Sb_2S_3 layer.



Fig. S2. Energy band diagrams of the 2T-TSCs.



Fig. S3. TEM analysis. (a-e) The TEM EDX mapping of TSC. STEM images of (f) P2, (g) P3, and (h) P1 ICL interfaces marked in Figure 4e.



Fig. S4. STEM analysis. STEM lattice fringe information of (a) P2, (b) P3, and (c) P1 ICL interfaces marked in Figure 4i.



Fig. S5. The relationship between the absorption spectra of Sb_2S_3 and PbS QDs and the standard solar radiation spectrum.



Fig. S6. Wavelength dependent refractive index (n) and extinction coefficient (k) values of functional layers.



Fig. S7. SEM analysis. Cross-sectional SEM images of (a-e) Sb_2S_3 front cells with different absorber thickness and (f) PbS QD rear sub-cell.



Fig. S8. Performance parameter comparison of Sb_2S_3 subcells with different absorber thickness. There are 17 devices for each type in (a-d) and the box lines indicate the standard deviation, and the centre represents the mean value.



Fig. S9. Characterization of device performance. (a) The optimum performance of 2T-TSC and the corresponding subcells. (b) J-V curves of 2T-TSCs with or without SnO₂ layer in ICL. (c) EQE spectra and integrated J_{sc} curves of champion Sb₂S₃ SJSC and PbS QD SJSC.



Fig. S10. Performance parameter comparison box plots of 2T-TSCs with different ICL schematics. There are 28 devices for each type in (a-d) and the box lines indicate the standard deviation, and the center represents the mean value.



Fig. S11. (a) The maximum power point tracking of the PbS QD SJSC. (b, c) Storage stability of the PbS QD SJSC (b) and the 2T-TSC(c).

Devices		V _{oc} (V)	$J_{\rm sc}$ (mA/cm ²)	FF (%)	PCE (%)
Sb ₂ S ₃ SJSC	F. to R.	0.699	17.60	63.62	7.82
	R. To F.	0.691	17.72	63.62	7.79
PbS SJSC	F. to R.	0.470	32.07	65.46	9.87
	R. To F.	0.477	31.76	64.86	9.84
2T-TSC	F. to R.	1.128	15.52	62.38	10.92
	R. To F.	1.122	15.68	61.93	10.90

Table S1. The forward-reverse scan photovoltaic parameters of subcells and 2T-TSC measured underAM1.5G illumination.

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