Unlocking the Potential of Selenium Solar Cells for Indoor and Tandem Photovoltaics Through Theoretical and Photoelectric Simulations

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Experimental Section

1. Computational Details

All density functional theory (DFT) calculations were conducted using the Vienna ab initio simulation package (VASP 6.3). The exchange-correlation interactions were simulated using the Perdew-Burke-Ernzerhof (PBE) functional, and the ion-electron interactions were described with the projector augmented wave (PAW) method. Since conventional density functional theory (DFT) calculations at the Perdew-Burke-Ernzerhof (PBE) level do not accurately account for nonlocal van der Waals forces, which can significantly affect the adsorption energies of small molecules, we incorporated dispersion corrections in our analysis. Therefore, the DFT-D3 method was utilized in this study to address these dispersion effects. The sampling of the Brillouin zone k-points for all periodic structures was performed using a Monkhorst-Pack grid with a $3 \times 3 \times 1$ mesh setup. A cutoff energy of 400 eV was selected to strike a balance between computational accuracy and efficiency. The convergence criteria were set to $0.05 \text{ eV} \text{ Å}^{-1}$ for force and 10^{-5} eV for energy. In the molecular dynamics (MD) simulations, the Andersen thermostat was employed to simulate the equilibrium dynamics within the NVT ensemble. After an initial equilibration period of 14 ps, the equilibrium dynamics were sustained for 1000 ps, with each time step set to 1 femtosecond.

The calculation of transition dipole moments was performed using CP2K with the TDDFT method. The TZVP-GTH basis set was employed, with the number of virtual orbitals set to 30. The lowest three excited states were computed, and the transition dipole moments between these states were processed using Multiwfn.

2. SCAPS-1D modeling principles are described in detail

$$N_{phot}(\lambda, x) = N_{phot0}(\lambda) \cdot T_{front}(\lambda) \cdot exp(-x\alpha(x)) \frac{1 + R_{back}(\lambda)exp(-2(d-x)\alpha(\lambda))}{1 - R_{back}(\lambda)R_{int}exp(-2d\alpha(\lambda))}$$
(1)

$$G(x) = \int_{\lambda_{min}}^{\lambda_{max}} G(\lambda, x) d\lambda = \int_{\lambda_{min}}^{\lambda_{max}} \alpha(\lambda, x) \cdot N_{phot}(\lambda, x) d\lambda$$
(2)

$$N_{peak} \times exp \left[-\left(\frac{E - E_t}{E_c}\right)^2 \right] N_{tot} = E_c N_{peak}$$
(3)

Equation (1) describes the photon density within the solar cell at various positions and wavelengths, while Equation (2) outlines the mechanism for carrier generation in a solar cell. Here, *d* represents the thickness of the layer, *x* is the positional parameter within each layer, $N_{phot}(\lambda, x)$ is the photon flux at each position within the cell, and $N_{phot0}(\lambda)$ is the incident photon flux. In the context of solar cell physics, $T_{front}(\lambda)$ and $R_{back}(\lambda)$ represent the transmittance of the front contact and the reflectance of the back contact, respectively. R_{int} is the reflectance within the interior of the solar cell, which can affect the overall light trapping and absorption. $\alpha(\lambda)$ is the absorption coefficient of each layer, which varies with wavelength and is a key factor in determining how much light is absorbed by each layer. $G(\lambda, x)$ is the generation rate of electron-hole pairs at position x within the cell, which is directly related to the light absorption and the subsequent creation of charge carriers that contribute to the cell's current. $\alpha(\lambda, x)$ is the light absorption coefficient at position x within the cell, indicating how the absorption capability changes with both wavelength and position within the cell. In the simulation, the type of defect is modeled as a Gaussian defect, and the distribution of these defects is described by equation (3). Here, E_t represents the trap level, E_c is the characteristic energy of the defect, N_{peak} is the energy density at the peak of the defect distribution, and N_{tot} is the total defect density. This Gaussian distribution helps to model the non-negligible carrier recombination that occurs due to the presence of defects in the solar cell material.

The calculations are concluded by resolving Poisson's equation and the continuity equations for both electrons and holes as follows:

$$\begin{pmatrix}
\frac{\partial}{\partial x} \left[\varepsilon_0 \varepsilon \frac{\partial \psi}{\partial x} \right] = -q \left[p - n + N_D^+ - N_A^- + P_t \right] \\
-\frac{\partial J_n}{\partial x} - U_n + G = \frac{\partial n}{\partial t} \\
-\frac{\partial J_p}{\partial x} - U_p + G = \frac{\partial p}{\partial t} \\
J_n = -\frac{\mu_n n \partial E_{Fn}}{q \quad \partial x} \\
J_p = -\frac{\mu_n p \partial E_{Fn}}{q \quad \partial x}
\end{cases}$$
(4)

Where ε_0 is the vacuum dielectric constant, ε is the relative dielectric constant, ψ is the electrostatic potential, q is the electron charge, p is the free hole concentration, nis the free electron concentration, P_t is the trapped hole concentration, N_t is the trapped electron concentration, N_D^+ is donor doping concentration, N_A^+ is the acceptor concentration, J_n is the electron current density. J_p is the hole current density, G is the formation rate, U_p is the hole recombination rate, U_n is the electron recombination rate, μ_n is the electron mobility, μ_p is the hole mobility, E_{Fn} is the electron quasi-Fermi level, E_{Fp} is the hole quasi-Fermi level. Poisson's equation describes the relationship between the charge carriers and the internal electric field within the solar cell, while the carrier transport equation models the distribution of carrier concentrations throughout the solar cell.

Shockley-Read-Hall (SRH) Recombination Model

$$R_{SRH} = \frac{np - n_i^2}{\tau_p \left(n + N_c e^{\frac{E_g - E_t}{K_B T}}\right) + \tau_n \left(P + N_v e^{\frac{E_t}{K_B T}}\right)}$$
(5)

Where R_{SRH} represents the recombination rate, *n* and *p* are the concentration of electrons and holes, E_t denotes the energy level of trap states, τ_n and τ_p are the lifetimes of electron and hole, respectively. Furthermore, the lifetime of the carriers can be calculated using the following:

$$\tau_{n,p} = \frac{1}{\sigma_{n,p} V_{th} N_t} \tag{6}$$

where $\sigma_{n,p}$ represents the capture cross-sectional area for electrons and holes, N_t is the density of trap sites and V_{th} shows the thermal velocity of mobile carriers.

3. Finite Element Analysis Method

The optical characteristics of Se solar cells are determined using established experimental thicknesses and material properties reported in previous studies. For each layer's material, the refractive index (n) and extinction coefficient (k) values are derived from either experimental measurements or simulated data found within the scientific literature.¹ The Se solar cells consist of a glass substrate containing FTO (500 nm), ETL (50 nm), Se (1000 nm), and Au (100 nm). We have implemented optical simulations based on the finite element method (FEM). Solving Maxwell's equations enables us to

acquire spatial electromagnetic field data for coupled frequency-domain analyses. In our approach, we utilize two sets of Floquet periodicity indices to enforce periodic boundary conditions. Additionally, we incorporate Perfectly Matched Layers (PML) to serve as absorbing boundary conditions in our three-dimensional simulations. The standard AM1.5G solar spectrum, which spans from 300 to 700 nm, is used to simulate solar irradiance, aligning with the absorption wavelength of 1.85 eV for selenium. In the process of calculating device reflection, the interface between the two media is considered as an integrated entity. Reflectance is calculated by integrating the reflected energy flux over the incident energy flux. The absorption and reflection spectra are determined using wave equation theory. The wave equations for the electric and magnetic fields are as follows:

$$\nabla \times (\mu^{-1} \nabla \times E) - k_0^2 \left(\varepsilon - \frac{J\sigma}{\omega \varepsilon} \right) E = 0$$
(7)

$$\nabla \times \left(\left(\varepsilon - \frac{I\sigma}{\omega\varepsilon}\right)^{-1} \nabla \times H\right) - k_0^2 \mu H = 0$$
(8)

Among them, k_0 is the initial velocity of wave propagation, ω is the angular frequency, ε is the dielectric constant related to the wavelength, σ is the electrical conductivity of the material, μ is the magnetic permeability of the material, E is the electric field strength, and H is the magnetic field strength.

$$J = \int_{300}^{700} \frac{q\lambda}{hc} A(\lambda) \phi_{AM.1.5G}(\lambda) d\lambda$$
⁽⁹⁾

where q is the electron charge, c is the speed of light in vacuum, h is Planck's constant, λ is an incident wavelength, $\phi_{AM1.5G}(\lambda)$ is the standard solar spectral irradiance under AM1.5G. A(λ) represents the absorption efficiency of the Se layer.

4. Light intensity dependence of V_{oc}

The diode ideality factor (η) is a crucial parameter for analyzing the carrier recombination mechanisms in thin film solar cells. Values of η close to 1 indicate that band-to-band recombination is predominant, while values of η approaching 2 suggest that non-radiative recombination, such as Shockley-Read-Hall (SRH) recombination, is the dominant process. The most reliable method for determining the η value involves examining the variation of the diode current with the intensity of incident light, which is a common approach in characterizing solar cells and diode behavior. The relationship between and light intensity (I) can be shown empirically as follows:

$$V_{oc} = E_g + \left(\eta \frac{kT}{q}\right) ln(\frac{I}{I_o})$$
(10)

In this context, E_g represents the band gap of the absorbing material, q denotes the elementary charge, and I_0 is the reference intensity, which is 1000 W m⁻². Nonetheless, the intricate interactions among various recombination processes in this simulation result in multiple linear segments, complicating the interpretation of the results. Within the range of 100 W m⁻² (0.1 Sun) to 1000 W m⁻² (1 Sun), the slope for $\eta kT/q$ for the baseline device and the optimized device is 0.056 and 0.046, respectively. These slopes correspond to η values of 1.79 and 1.45, respectively. Consequently, the optimized device shows a decrease in non-radiative (SRH) recombination, which is beneficial for enhancing carrier lifetimes and overall device performance.



Figure S1. The absorption coefficients of light in all directions of the material. (a) Se chain structure. (b) Se chain structure with defect. (c) Se chain structure with interstitial Se.



Figure S2. Band offset values and device band positions under three different electron

transport layers (ETLs). (a) Band offset values under three different ETLs. (b) Device band positions under the TiO₂ layer. (c) Device band positions under the SnO₂ layer. (d) Device band positions under the ZnO layer.



Figure S3. Device performance changes with the thickness of the Se absorbing layer (200~2000 nm). (a) PCE (%), (b) V_{OC} (V), (c) J_{SC} (mA/cm²), (d) FF (%).



Figure S4. Refractive index data (n, k) for each layer required for optical simulation:

(a) TiO_2 , (b) Se, (c) ZnO, (d) SnO_2 , (e) Au, and (f) FTO.



Figure S5. Band offset values and device band positions under three different hole transport layers (HTLs). (a) Band offset values under three HTLs. (b) Device band positions under the Spiro-OMeTAD layer. (c) Device band positions under the Cu_2O layer. (d) Device band positions under the MoO_x layer.



Figure S6. Performance parameters of the device with a hole transport layer: (a) PCE (%), (b) V_{OC} (V), (c) J_{sc} (mA/cm²), (d) FF (%).



Figure S7. Performance parameters of the device without a hole transport layer: (a) PCE (%), (b) V_{oc} (V), (c) J_{sc} (mA/cm²), (d) FF (%).



Figure S8. Interface defect density of TiO₂/Se: (a) PCE (%), (b) V_{oc} (V), (c) J_{sc} (mA/cm²), (d) FF (%).



Figure S9. Interface defect density on Se/MoO_x: (a) PCE (%), (b) V_{oc} (V), (c) J_{sc} (mA/cm²), and (d) FF (%).



Figure S10. (a) Photogenerated carrier generation rate at different positions of the device, (b) Recombination current under different defect concentrations at the upper and lower interfaces of the device.



Figure S11. Influence of conduction band offset on device performance: (a) PCE (%), (b) V_{oc} (V), (c) J_{sc} (mA/cm²), (d) FF (%).



Figure S12. Influence of valence band offset on device performance: (a) PCE (%), (b) V_{oc} (V), (c) J_{sc} (mA/cm²), and (d) FF (%).



Figure S13. Internal recombination rates of the devices under different (a) conduction band offset values and (b) valence band offset values.



Figure S14. (a) Original device with Mott-Schottky; (b) Optimized device with Mott-Schottky.



Figure S15. (a) Comparison of electrochemical impedance spectra between the original and optimized devices; (b) Comparison of activation energy between the original and optimized devices.



Figure S16. Comparison of open-circuit voltage versus light intensity between the original and optimized devices.



Figure S17. Se-CIGS tandem device structure. (a) Se-CIGS Device current density matching under varying top cell thickness, and (b) optimal EQE of series-connected devices.



Figure S18. Se-Perovskite (1.25 eV) device structure. (a) Device current density matching under varying top cell thickness, and (b) optimal EQE of series-connected devices.

i	j	Х	Y	Ζ	Diff.(eV)
0	1	-0.36	-0.95	-0.02	0.06
0	2	2.00	0.76	0.15	0.19
0	3	-1.91	0.66	0.11	0.27
1	2	2.70	-0.52	0.59	0.13
1	3	3.41	5.21	2.02	0.21
2	3	-2.05	-6.73	-2.24	0.08

Table S1. Transition dipole moment, excitation energy (Diff.) from ground state to excited state of 500 ps.

Table S2. Transition dipole moment, excitation energy (Diff.) from ground state to excited state of 550 ps.

i	j	X	Y	Z	Diff.(eV)
0	1	0.76	2.49	0.67	0.11
0	2	-0.33	0.43	0.01	0.12
0	3	-0.80	-0.82	-0.03	0.18
1	2	-0.85	0.19	-0.22	0.02
1	3	-2.70	-7.21	-2.29	0.08
2	3	-1.29	-0.69	-0.31	0.06

i	j	Х	Y	Ζ	Diff.(eV)
0	1	-0.66	0.72	-0.04	0.11
0	2	0.75	0.05	0.08	0.24
0	3	-0.42	-0.72	0.32	0.29
1	2	2.61	6.37	1.65	0.14
1	3	-13.66	-20.96	-7.50	0.18
2	3	-0.04	-0.95	-0.39	0.04

Table S3. Transition dipole moment, excitation energy (Diff.) from ground state to excited state of 600 ps.

Table S4. Transition dipole moment, excitation energy (Diff.) from ground state to excited state of 650 ps.

i	j	Х	Y	Z	Diff.(eV)
0	1	0.93	-0.96	-0.01	0.14
0	2	-1.77	0.74	-0.38	0.18
0	3	0.02	0.25	-0.06	0.23
1	2	-4.24	-1.88	-1.93	0.04
1	3	-1.33	-3.16	-1.38	0.09
2	3	-2.46	0.60	0.14	0.04

i	j	Х	Y	Ζ	Diff.(eV)
0	1	0.89	0.12	0.63	0.06
0	2	-1.47	-0.74	0.34	0.12
0	3	0.96	3.34	0.42	0.19
1	2	2.88	-3.03	-0.98	0.06
1	3	0.60	-1.44	-0.54	0.13
2	3	-6.78	-6.28	-2.03	0.07

Table S5. Transition dipole moment, excitation energy (Diff.) from ground state to excited state of 700 ps.

Table S6. Comparison of Specific Performance Parameters Between ExperimentalResults and Simulation Results

Work Mode	$J_{ m SC}({ m mA/cm^2})$	$V_{\rm OC}({ m V})$	FF (%)	PCE (%)
Experiment	10.90	0.89	54.50	5.30
Simulation	11.07	0.90	52.94	5.31

					Spiro-		
Parameters	TiO ₂	SnO ₂	ZnO	Se	OMeTA	Cu ₂ O	MoO _x
					D		
L (nm)	30	30	30	1000	200	200	200
$E_{g}(eV)$	3.2	3.5	3.47	1.85	3.17	2.17	3
X(eV)	4.1	4	4.3	3.93	2.05	3.2	2.5
\mathcal{E}_r	9	9	9	7.43	3	7.11	12.5
$N_{\rm c}~({\rm cm}^{-3})$	2.2×10 ¹⁸	2.2×10 ¹⁷	2×10 ¹⁸	8.8×10 ¹⁹	2.2×10 ¹⁸	2.2×10 ¹⁸	1.8×10 ¹⁹
$N_{\rm v}$ (cm ⁻³)	1×10 ¹⁹	2.2×10 ¹⁶	1.8×10^{20}	1.6×10 ²⁰	1.8×10 ¹⁹	1.8×10 ¹⁹	2.2×10 ¹⁸
μ_n (cm ² .V ⁻¹ .	20	20	100	5 010-1	2.10-4	20	25
s ⁻¹)	20	20	100	5.8×10 ⁻¹	2×104	20	25
$u_p (cm^2.V^{-1}.$	10	10	25	4.4×100	2.410-4	00	100
s ⁻¹)	10	10	25	4.4×10°	2×10 4	80	100
$N_{\rm d}~({\rm cm}^{-3})$	1×10 ¹⁸	1×10 ¹⁷	1×10 ¹⁸	-	-	-	
$N_{\rm a}$ (cm ⁻³)	-	-	-	1×10 ¹⁵	1×10 ¹⁸	1×10 ¹⁸	1×10 ¹⁸
$N_{\rm t}$ (cm ⁻³)	1×10 ¹⁵	1×10 ¹⁵	1×10 ¹⁵	1.4×10 ¹⁶	1×10 ¹⁵	1×10 ¹⁵	1×10 ¹⁵
References	2		2	3	4	5	3

Table S7. Specific parameters required for each layer in the simulation.

Parameters	Perovskite/ETL	HTL/Perovskite	
Defect type	Neutral	Neutral	
Capture cross section of	1 × 10-19	1×10-19	
electrons (cm ²)	1^10	1~10 **	
Capture cross section of	1×10-19	1×10-19	
holes (cm ²)	1^10	1/10	
Reference for defect energy	above the highest F	above the highest F	
level E_t	above the ingliest L_v	above the highest L_{v}	
Energy concerning	0.6	0.6	
reference (eV)			
Total density (cm ⁻³)	1×10^{10}	1×10 ¹⁰	

Table S8. Specific parameters required for the interface composite in the simulation.

Device starstore	Light	V _{OC}	T	EE(0/)	PCE	Deferences
Device structure	condition	(V)	$J_{ m SC}$	FF (%)	(%)	References
$ETO/TO S_{CMA}/Au$	ANT 1-5	0.00	13.60	50.00	7 20	6
F10/110 ₂ /Se (CMA)/Au	AIVI 1.3	0.90	(mA/cm ²)	39.00	7.20	, , , , , , , , , , , , , , , , , , ,
FTO/TiO ₂ /Se (CMA)/Au	1000 lux	0.77	112 (µA/cm ²)	63.90	18.00	6
ITO/PEDOT:		0.04			2 0 0	7
PSS/Se/PCBM/Ag	AM 1.5	0.84	$9.61(mA/cm^2)$	47.80	3.90	7
		0.00	10.00	52 40	5 20	8
F1O/ZnMgO/Se/MoOx/Au	AM 1.5	0.99	(mA/cm ²)	52.40	5.20	0
ITO/SnO ₂ /Se/P5NH/Ag	AM 1.5	0.85	8.99 (mA/cm ²)	56.00	4.30	9
ITO/SnO ₂ /Se/P25NH/Ag	AM 1.5	0.73	8.12 (mA/cm ²)	57.60	3.40	9

Table S9. Summary of the reported efficiency comparisons based on different device structures.

 Table S10. Summary of the performance of the devices with various electron transport

 layers.

Electron	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA/cm ²)	FF (%)	PCE (%)
transport layer				
TiO ₂	1.02	17.03	72.12	12.59
SnO_2	1.02	16.96	72.45	12.60
ZnO	0.93	16.91	68.93	10.87

Hole transport	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA/cm^2})$	FF (%)	PCE (%)
layer				
Control	1.02	17.03	72.12	12.59
Spiro-OMeTAD	1.07	17.05	71.89	13.17
Cu ₂ O	1.19	17.18	75.08	15.44
MoO _x	1.19	17.31	77.23	16.01

Table 11. Summary of the performance of the devices with various hole transport layers under standard sunlight.

Table S12. Summary of the performance of the devices with various hole transport layers under indoor lighting.

Hole transfer layer	$V_{\rm OC}$ (V)	$J_{ m SC}~(\mu m A/cm^2)$	FF (%)	PCE (%)
Control	0.77	112.20	63.90	18.00
Spiro-OMeTAD	0.80	114.04	64.05	19.57
Cu ₂ O	0.86	115.38	69.98	23.37
MoO _x	0.87	116.20	71.24	24.10

Device				
Structure	$V_{\rm OC}(\mathbf{V})$	$J_{\rm SC}$ (mA/cm ²)	FF (%)	PCE (%)
Se/GIGS	1.87	17.24	73.00	23.56
Se/Perovskite (1.25eV)	2.01	17.24	70.90	24.60

Table S13. Specific Performance Comparison of Tandem Devices with Selenium,CIGS, and Perovskite.

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