A tin‑based perovskite solar cell with an inverted hole‑free transport layer to achieve high energy conversion efficiency by SCAPS device simulation

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Abstract
Organic–inorganic halide perovskite solar cells (PSCs) have received extensive research in the field of optoelectronic materials. The absorption layer widely used in PSCs is methylammonium lead trihalide (MAPbX3, X = Cl, Br, I), still, the toxicity of lead (Pb) restricts its development, tin-based perovskite MASnI3 has attracted much attention due to its sound absorption characteristics. In this work, the perovskite solar cell adopts an inverted HTL-free structure, and the one-dimensional solar cell capacitor simulator SCAPS-1D (Solar Cell Capacitance Simulator) was adopted for numerical simulation and found that FTO/CH3NH3SnI3/C60/Au structure PSCs also showed excellent photovoltaic performance. We studied the influence of the thickness of the absorber layer, the defect density, the doping concentration of different layers, and we also studied PSCs with two structures, upright (p-i-n) and inverted (n-i-p) under the same lighting conditions. The simulation results show that the optimized inverted HTL-free tin-based PSCs based on C60 is with inspiring performance: a short-circuit current density ($J_{SC}$) of 32.4566 mA/cm², Open circuit voltage ($V_{OC}$) of 0.8585 V, fill factor (FF) of 73.72% and power conversion efficiency (PCE) of 20.54%. Based on HTL-free, the inverted structure can realize the PSCs to the maximum extent to ensure the light intensity of the incident perovskite layer, and the light-induced carriers could be effectively collected, directly increase the number of excitable electron–hole pairs, showing better performance. Based on the inverted HTL-free tin-based PSCs, we also listed the PSCs performance parameters of different material ETL. This work provides new ideas for PSCs development in the future.

Keywords Tin‑based perovskite · Inverted structure · HTL ‑ free · SCAPS ‑ 1D
1 Introduction

In recent years, PSCs have attracted significant attention due to their simple structure (Laban and Etgar 2013; Mei et al. 2014), low preparation cost (Cai et al. 2017), suitable and adjustable band gap (Noh et al. 2013; Kulkarni et al. 2014), high extinction coefficient (Kim et al. 2012a, b; Gratzel 2014), bipolar carrier transmission characteristics (Stranks et al. 2013; Xing et al. 2013a, b) and flexible devices (Lin et al. 2017). Energy conversion efficiency increased from 3.8 (Akhiro et al. 2009) to 25.2% (Frost et al. 2014). Such a speed of development is unprecedented in the photovoltaic field. For PSCs with excellent performance, spiro-OMeTAD and PTAA are the most common HTL materials. Additives are also needed to enhance electrical conductivity/improve contact with the absorbent layer. However, these additives often have adverse effects. For example, 4-tert-butyl pyridine is corrosive and causes the decomposition of PSCs (Li et al. 2014). Lithium salts are very sensitive to water and cannot be used in humid environments (Liu et al. 2014). In addition, these hole transport layer materials are costly and not stable enough for long-term use. Based on this, HTL-free PSCs (Chen and Yang 2017, 2019; Maniarasu et al. 2018) have been developed, which can significantly save the cost of materials, simplify the production process and promote commercial development. As the electrodes of PSCs, ITO and FTO can directly contact the absorption layer. In addition, the inverted structure of PSCs (p-i-n) has the advantages of good stability and weak J-V hysteresis effect. At the same time, the inverted HTL-free PSCs ensure the light intensity of the incident perovskite layer to the greatest extent, showing better performance. The first reported inverted HTL-free PSCs structure is ITO/MAPbI$_3$/C$_{60}$/Ag, achieving a PCE of 5.4% (Hu et al. 2014). At present, the PCE of the device structure has attained a maximum of 20% (Wu et al. 2018), which has attracted more and more attention.

Although the current research on PSCs has achieved remarkable results, these perovskite materials used to absorb sunlight contain the toxic heavy metal lead, which is not friendly to the environment. This will undoubtedly limit the large-scale application of PSCs in the future, so there is an urgent need for development of new green and environmentally friendly lead-free PSCs. Tin-based perovskite has even better photoelectric properties than lead-based perovskites, such as high absorption coefficient, small exciton binding energy and high carrier mobility, etc., which is currently the strongest candidate (Yu et al. 2011; Chung et al. 2012; Chen et al. 2012; Xie et al. 2016). According to the Shockley-Queisser limit theory (Shockley and Queisser 1961), the highest efficiency of a single solar cell is 33% corresponding to an absorption band gap of 1.34 eV. The absorption band gap of lead halide perovskite is generally larger in the range of 1.5–1.8 eV, while that of tin-based perovskite is narrower in the scope of 1.3 eV, which is very close to the ideal value of 1.34 eV. Therefore, tin-based PSCs are expected to obtain higher short-circuit current density and reach the theoretical limiting conversion efficiency.

In this work, we propose to inverted HTL-free tin-based PSCs, use the one-dimensional simulation platform solar cell capacitor simulator SCAPS to simulate the characteristics of the device. The effects of the thickness, defect density and doping concentration of each layer were investigated comprehensively. Based on the physical parameters of each functional layer, the impact on the device were analyzed to determine the best material parameters and improve the performance of the device, which is helpful to realize simple device structure, reduce cost and simplify manufacturing process to promote commercial development.
2 Methodology

PSCs model is established in this work through theoretical methods to analyze the influencing factors of PSCs to optimize its performance, which is conducive to avoiding experiment duplication and reducing resource waste. In the process of simulating and optimizing solar cells, SCAPS-1D software developed by M. Burgelman of the University of Gent in Belgium is applied, which is suitable for affecting cells with various homojunction and heterojunction structures. Its basic principle is to solve the Poisson equation and current continuity equation under these constraints based on the established battery structure model and the material input parameters (Rai et al. 2020; Burgelman et al. 2000).

\[
\nabla \cdot \mathbf{E} \nabla \varphi = -q(p - n + N_D - N_A) \quad (1)
\]

\[-\nabla \cdot J_p = q(R - G) + q \frac{\partial p}{\partial t} \quad (2)
\]

\[-\nabla \cdot J_n = q(R - G) + q \frac{\partial n}{\partial t} \quad (3)
\]

By setting the material parameters and corresponding boundary conditions, the above equations are solved with SCAPS-1D software through numerical calculations to obtain the relevant characteristics of the solar cells. Where, \( \varphi \) is the electric potential, \( p \) and \( n \) are the concentration of free carrier holes and electrons, \( J_p \) and \( J_n \) are electron current density and hole current density, \( R \) and \( G \) are the recombination rate and generation rate of electron–hole pairs, \( N_A \) and \( N_D \) represent the acceptor and donor doping concentration.

The PCE, EQE, \( V_{OC} \), \( J_{SC} \) and FF mentioned in the article are important indicators of the performance of PSCs, and they are explained and formulated as follows:

Open circuit voltage \( V_{OC} \) (V) and short-circuit current density \( J_{SC} \) (mA/cm\(^2\)): The J-V corresponds to the voltage value when the current density is zero and the current density value when the voltage is zero, respectively.

Fill Factor (FF): represents the ability of the entire battery to continuously output power while operating, which is calculated as:

\[
FF = \frac{P_{Max}}{J_{sc} \times V_{oc}} = \frac{J_{Max} \times V_{Max}}{J_{sc} \times V_{oc}}
\]

Here, \( P_{Max} \) is the maximum output power of the battery, and \( J_{Max} \) and \( V_{Max} \) are respectively the corresponding current density and voltage value when the battery reaches the maximum output power.

Power Conversion Efficiency (PCE): refers to the ratio of the maximum output power of the device to the incident light illumination intensity, which is also the maximum input power, calculated by the formula:

\[
PCE = \frac{P_{Max}}{P_{in}} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\%
\]

External quantum efficiency EQE: refers to the ratio of the number of electrons produced by the battery after absorbing photons to the number of incident photons. The calculation formula is:
EQE = \frac{N_{\text{electron}}}{N_{\text{photon}}} = \frac{1240 \times J_{\text{sc}}}{\lambda \times P_{\text{in}}} \times 100\% \quad (6)

Here, \(N_{\text{electron}}\) is the number of electrons obtained, \(N_{\text{photon}}\) is the number of incident photons, \(J_{\text{sc}}\) is the short-circuit current density of the cell in the case of monochromatic light irradiation, and \(\lambda\) is the wavelength of the incident light.

### 2.1 Device structure and simulation parameters

The cell is composed of glass substrate/transparent conductive oxide (FTO)/absorption layer (CH\(_3\)NH\(_3\)SnI\(_3\))/electron transport layer (C\(_{60}\))/metal back contact (Au). As shown in Fig. 1a, inverted the HTL-free tin-based PSCs, the perovskite absorber layer is directly prepared on the top of the front electrode, and its difference from ordinary PSCs is that the holes are at the interface between the perovskite and the transparent anode, and the holes extracted from the perovskite move directly into the anode, as shown in Fig. 1b energy band structure. Exact parameter values are generally difficult to obtain, the parameters of FTO, ETL and perovskite absorption layer, and we have carefully selected relatively reasonable parameters based on the reported simulation literature and experimental studies of tin-based PSCs. Table 1 includes the basic physical and device parameter settings of each layer (Hao et al. 2014a, b; Lakhdar and Hima 2019; Minemoto and Murata 2014; Azri et al. 2019; Du et al. 2016; Anwar et al. 2017;). \(\varepsilon_r\) is the dielectric Permittivity, \(\chi\) is the electron affinity, \(E_g\) is the band gap energy, \(\mu_n\) and \(\mu_p\) are the electron mobility and hole mobility, and \(N_t\) is the defect density. The thermal velocities of the electrons and holes are set to 10\(^7\) cm/s. The defect state in the absorption layer is set to a neutral Gaussian distribution, and the characteristic energy is 0.1 eV, and the defect energy level is in the middle of the band gap. The trapping cross-section of electrons and holes in the absorption layer is 1 \(\times\) 10\(^{-15}\)cm\(^2\), and the trapping cross-section of electrons and holes in other layers is 2 \(\times\) 10\(^{-14}\)cm\(^2\). Considering the carrier recombination at the interface, an interface defect layer is added between the FTO/absorption layer and the absorption layer/electron transport layer. The energy distribution of the interface defect layer is set as a single neutral defect, and the trapping cross section of the defect is 1 \(\times\) 10\(^{-15}\)cm\(^2\), and the total defect

**Fig.1**  a Device structure; b Energy band structure
density is $1 \times 10^{18}$ cm$^{-3}$, which is located 0.6 eV above the top of the valence band. Table 2 lists the defect density inside and at the interface of the light-absorbing layer. In this simulation, the surface of each layer and the optical reflection of the interface between the layers are not considered.

### 2.2 Simulation analysis of the proposed device

According to the initial parameters given in Tables 1 and 2, Fig. 2 shows the calculated energy band diagram (a), current density–voltage (J-V) (b) and external quantum efficiency (EQE) (c). The reflection of each functional layer and interface and the additional series resistance caused by FTO or back contact are not considered. The energy band diagram in Fig. 2a, $E_v$ (eV), $F_p$ (eV), $F_n$ (eV), $E_c$ (eV) represent the highest energy level of the valence band, the hole Fermi level, and the electron Fermi level and the lowest energy level of the conduction band, respectively. Figure 2b is based on the initial parameters of the above Tables 1, 2, and it demonstrates that the simulated $V_{OC} = 0.9366$ V, $J_{SC} = 25.8907$ mA/cm$^2$, $FF = 70.83\%$, and $PCE = 17.18\%$, the result is close to the conclusion obtained by Manish Kumar et al. (Manish et al. 2020; Abdelaziz et al. 2020; Roy et al. 2020), which verifies the rationality of this work. The quantum efficiency (EQE) shown in Fig. 2c is also the

### Table 1 Basic parameters of each layer of the device

| Parameters                              | FTO          | MASnI$_3$ | C$_{60}$ |
|-----------------------------------------|--------------|-----------|----------|
| Thickness (nm)                          | 500          | 400       | 30       |
| Band gap, $E_g$ (eV)                    | 3.5          | 1.3       | 1.7      |
| Electron affinity, $\chi$ (eV)          | 4.0          | 4.17      | 3.9      |
| Dielectric permittivity, $\varepsilon_r$| 9            | 8.2       | 4.2      |
| CB effective density of states, $N_c$ (cm$^{-3}$) | $2.20 \times 10^{18}$ | $1.0 \times 10^{18}$ | $8 \times 10^{19}$ |
| VB effective density of states, $N_v$ (cm$^{-3}$) | $1.80 \times 10^{19}$ | $1.0 \times 10^{18}$ | $8 \times 10^{19}$ |
| Electron mobility, $\mu_n$ (cm$^2$/Vs)  | 20           | 1.6       | 0.08     |
| Hole mobility, $\mu_p$ (cm$^2$/Vs)      | 10           | 1.6       | 0.0035   |
| Shallow donor density $N_D$ (cm$^{-3}$)  | $1.00 \times 10^{19}$ | 0         | 0        |
| Shallow Acceptor density $N_A$ (cm$^{-3}$) | 0           | $1.0 \times 10^{17}$ | $1.0 \times 10^{18}$ |
| Defect density $N_t$ (cm$^{-3}$)         | $1.00 \times 10^{15}$ | $1.0 \times 10^{15}$ | $1.0 \times 10^{15}$ |
| Electron thermal velocity (cm/s)         | $10^7$       | $10^7$    | $10^7$   |
| Hole thermal velocity (cm/s)             | $10^7$       | $10^7$    | $10^7$   |

### Table 2 Defect density values inside the absorber layer and at interface of the device

| Parameters                              | FTO/CH$_3$NH$_2$SnI$_3$ | CH$_3$NH$_3$SnI$_3$/C$_{60}$ | CH$_3$NH$_2$SnI$_3$ |
|-----------------------------------------|--------------------------|--------------------------------|---------------------|
| Defect type                              | Neutral                  | Neutral                         | Neutral             |
| Capture cross section for electron and holes (cm$^{-2}$) | $1.00 \times 10^{-15}$ | $1.00 \times 10^{-15}$ | $2.00 \times 10^{-14}$ |
| Energetic distribution                   | Single                    | Single                          | Gaussian            |
| Energy level with respect to $E_v$       | 0.6                       | 0.6                             | 0.65                |
| Characteristic energy (eV)              | 0                         | 0                               | 0.1                 |
| Total density (cm$^{-3}$)               | $10^{18}$                 | $10^{18}$                       | $1.0 \times 10^{15}$ |
simulated result under the same parameters. Based on the analysis of the data shown in Fig. 2, the band gap of CH$_3$NH$_3$SnI$_3$ is 1.3 eV, which is narrower than the 1.55 eV of CH$_3$NH$_3$PbI$_3$, so that the absorption wavelength of tin-based perovskite is shifted to 950 nm. The range of the external quantum efficiency curve covers the entire visible spectrum, and the absorption from 350 to 880 nm is the strongest, exceeding 50%, which is consistent with the PCE spectrum measured in the literature (Hao et al. 2014a, b). The redshifted external quantum efficiency is more conducive to light absorption in the infrared wavelength range.

3 Results and discussion

The following results and discusses are based on the simulation results.

3.1 Effect of changing absorber thickness and doping concentration

For PSC, the spectral response of the device is highly dependent on the thickness of the absorption layer, which has a great influence on the overall performance of the device. The absorption layer thickness varies from 250 to 1000 nm, and other input parameters are shown in Table 1 and Table 2. First, J-V of devices with different absorption layer thickness...
is obtained, as shown in Fig. 3a. When the absorption layer is 700 nm and 1000 nm, their J-V curves almost coincide. As shown in the inset of Fig. 3c, d, \(V_{OC}\) increases as the thickness of the absorbing layer increases, and increases significantly before the thickness of the absorbing layer reaches 850 nm, after which the \(V_{OC}\) curve tends to be flat and even has a downward trend as the thickness of the absorbing layer continues to increase (More absorption layer thicknesses are not listed here). The carrier number of the perovskite absorption layer increases with the increase in thickness, and the PCE and short-circuit current density \(J_{SC}\) also increase. When the thickness reaches 850 nm, the curve tends to be flat. As the thickness of the perovskite absorption layer increases, the thicker perovskite absorption layer can absorb more photons and thus produce more excitons. However, excessive absorption layer thickness may lead to the increase of harmful recombination and diffusion length, and finally the PCE curve tends to flatten or even decline. Based on the above analysis, the optimal value of the absorption layer thickness is 850 nm. Figure 3b depicts the influence of the thickness change of the absorption layer on the EQE (%) changing with wavelength. As the thickness increases, more long-wave external quantum efficiency increases and the absorption becomes stronger, so the carrier extraction increases.

Tin-based PSCs are in an unfavorable self-doping process, and their unstable oxidation state \(Sn^{2+}\) is easily oxidized to a stable \(Sn^{4+}\) oxidation state at room temperature. In this work, the doping concentration of \(CH_3NH_3SnI_3\) absorption layer varies from 10^{13} to

![Graphs](image-url)
$10^{19}$ cm$^{-3}$. As shown in Fig. 4 a and d, when the doping concentration is between $10^{13}$ and $10^{16}$ cm$^{-3}$, $V_{OC}$, $J_{SC}$, FF and PCE tend to be stable. As the doping concentration increases, the built-in electric field of the perovskite layer is no longer enhanced and the separation of carriers slows down. But as the doping concentration continues to increase, when it exceeds $10^{16}$ cm$^{-3}$, as shown in Fig. 4b, the carrier recombination rate (R) of the battery increases significantly in this work, resulting in a higher Auger recombination rate, and PCE shows a downward trend. When the doping concentration reaches $10^{17}$–$10^{18}$ cm$^{-3}$, it is the top region of doping concentration, and the $V_{OC}$ reaches the peak. This concentration range has a good $V_{OC}$ without causing the electric field to decay. However, when the doping concentration of the top region is too high, it will cause serious doping effect. As a result of the serious adverse doping effect, it will cause the band gap of the absorption layer to shrink, resulting in a rapid decrease in $V_{OC}$. The optimized $V_{OC}$, $J_{SC}$, FF and PCE are 0.8522 V, 30.0242 mA/cm$^2$, 74.08% and 18.95% respectively when $N_A$ is $10^{16}$ cm$^{-3}$. Only the proper doping concentration can improve $J_{SC}$ and $V_{OC}$ well and increase the value of power conversion efficiency.

3.2 Effect of changing defect density ($N_t$)

To further improve the performance of the battery, the defect density of the perovskite layer is another important factor that needs to be considered. The tin-based perovskite film covering the electron transport layer was observed to have poor film quality, the recombination

![Fig. 4](image-url) Changing the doping concentration $N_A$: a J-V; b Recombination rate; c $V_{OC}$, $J_{SC}$; d FF, PCE
of carriers in the perovskite light absorption layer will dominate. The flawed quality film means that the perovskite absorption layer has a greater defect density \( (N_t) \). The effect of perovskite defects density on battery performance is studied based on Shockley–read–Hall composite model (SRH). The simulated defect is set to a neutral Gaussian distribution with a characteristic energy of 0.1 eV, which is located in the middle of the band gap. The SRH composite model is as follows:

\[
R_{SRH} = \frac{p_n - n_i^2}{\tau_p (n + n_i) + \tau_n (p + n_i)}
\]

where \( R_{SRH} \) is the rate of recombination, \( n \) and \( p \) are concentration of electrons and holes respectively and \( \tau_n \) and \( \tau_p \) are life time of these charge carriers. The parameters are modified by changing the defect density from \( 10^{13} \) to \( 10^{17} \text{ cm}^{-3} \). As shown in Fig. 5c, d, when the defect density is below \( 10^{15} \text{ cm}^{-3} \), the defect density does not have a great influence on PCE and other parameters. When \( N_t \) exceeds \( 10^{15} \text{ cm}^{-3} \), the density of defect states has a severe effect on PCE. In order to discuss the effect of defect state density on device performance in more detail, based on the Shockley–Read–Hall recombination model (SRH), as shown in Fig. 5b, we discussed the effect of defect state density on the recombination rate. When \( N_t \) is \( 10^{13} \text{ cm}^{-3} \), the recombination rate is almost zero. When \( N_t \) is \( 10^{15} \text{ cm}^{-3} \), the recombination rate starts to increase. When \( N_t \) is \( 10^{17} \text{ cm}^{-3} \), the recombination rate

![Fig. 5](image-url) Changing the defect density \( N_t \): a J-V; b Recombination rate; c \( V_{OC}, J_{SC} \); d FF, PCE
increases significantly. As the defect density increases, the performance begins to drop drastically. The reason is that defects are like recombination sites, which ultimately reduce the life of electrons and holes.

### 3.3 Effect of changing device structure

In the HTL-free perovskite structure, the inverted structure is adopted, which shows superior photovoltaic performance. In order to verify this, the two structures shown in Fig. 6a and b are modeled and analyzed. As shown in Fig. 6a, on the basis of adopting the upright structure (p-i-n), we conducted a modeling analysis of FTO/C$_{60}$/CH$_3$NH$_3$SnI$_3$/Au (parameters are shown in Table 1 and Table 2): the obtained PCE is 1.95%. With the parameters being unchanged, as shown in Fig. 6b, based on the inverted structure (n-i-p), we modeled and analyzed the FTO/CH$_3$NH$_3$SnI$_3$/C$_{60}$/Au structure, and obtained a PCE of 17.65%. Based on the above modeling of different structures, SCAPS analysis shows that the PCE
obtained by the inverted structure of HTL-free PSCs is larger than that obtained by the upright structure. We speculated that the light intensity of the incident perovskite layer could be retained to the maximum extent without the light blocking of C60, and the light-induced carriers could be effectively collected (Xing et al. 2013a, b; Stranks et al. 2013) due to their long life and excellent transmission characteristics, directly increase the number of excitable electron–hole pairs, showing better performance.

In order to verify this, we changed the thickness of the electron transport layer C60 of these two structures. Through the analysis, it was found that for the FTO/C60/CH3NH3SnI3/Au structure, when the thickness of the C60 is changed, the VOC, JSC, FF and PCE also undergo large fluctuations, as shown in Fig. 6c. With the increasing thickness of C60, it formed a light obstruction to the absorber layer, the light-induced carriers of the absorber layer cannot be collected effectively and the number of electron–hole pairs cannot be excited effectively, which is an important component of the performance of the whole device. And finally the PCE stabilized when the thickness of C60 was 150 nm, the attained result PCE of 4.05% is close to the PCE of 3.56% obtained by K. P. Marshall (Marshall et al. 2016), which verifies the validity of device modeling. For the FTO/CH3NH3SnI3/C60/Au structure, we found that when changing the thickness of different C60, the changes in VOC, JSC, FF and PCE are very small, as shown in Fig. 6d. The inverted structure makes C60 not obstruct the light from the absorption layer, the light-induced carriers can be effectively collected and the number of electron–hole pairs is effectively excited. At this point, the thickness of C60 has little effect on the device, and retains the light intensity incident on the perovskite layer to the greatest extent.

For PSCs with HTL, the superior performance of inverted HTL-free tin-based PSCs can also be found here. Himanshu Dixit et al. (Hd et al. 2019) used NiO as the hole transport layer to model and analyze the FTO/C60/CH3NH3SnI3/NiO/Au structure, and the final PCE was 9.99%, which is similar to the experimental results of Jokar et al. (Zhu et al. 2018; Liao et al. 2016; Jokar et al. 2018; Ke et al. 2018). Compared to the FTO/CH3NH3SnI3/Au structure, the obtained PCE is 17.65%, one of the reasons we give for this is that C60 does not form a light obstruction to the absorber layer. In addition, compared with the traditional perovskite solar cells, the FTO of the inverted HTL-free PSCs is in direct contact with CH3NH3SnI3, and the FTO is completely coated by the absorption layer film, reducing the probability of crystal cracks, cracks or pinholes in the perovskite layer. The photocurrent recombination between the two electrodes is reduced due to the reduction of pinholes (Bao et al. 2015). The work function of FTO is −4.4 eV and the HOMO level of CH3NH3SnI3 is −5.1 eV. From the energy level, FTO has high hole transport and collection efficiency for the device.

3.4 Effect of changing the doping concentration of FTO

For an inverted HTL-free tin-based PSC, the FTO directly contacts the perovskite layer. Therefore, it is of great significance to study the effect of FTO properties (such as doping concentration) on the performance of the device. Such detection helps to further control the physical parameters of FTO to improve the efficiency of the device. Figure 7 a b c show the curves of J-V and VOC, JSC, FF, PCE under different FTO doping concentration ND. When ND is greater than 1019 cm−3, the J-V curve becomes overlapping and fuzzy, the PCE values tend to stabilize and VOC reaches the top region of doping concentration at 1019 cm−3 with a good open circuit voltage. It is worth noting that as the doping concentration increases, the conductivity of FTO may inevitably increase due to the increase in carrier concentration,
and the strong absorption of these additional carriers reduces the visible light transmittance of FTO. The final optimized value \( N_D \) is determined as \( 10^{19} \text{ cm}^{-3} \), which was consistent with the results obtained by Like Huang et al. (Huang et al. 2016).

Based on the optimization analysis of the above-mentioned various layer parameters, the optimized values determined finally are shown in Table 4: the thickness of the absorption layer is 850 nm, the doping concentration is \( 1.00 \times 10^{16} \text{ cm}^{-3} \), and the defect density is \( 1.00 \times 10^{15} \text{ cm}^{-3} \). The FTO doping concentration is \( 1.00 \times 10^{19} \text{ cm}^{-3} \). The thickness of the ETL is 30 nm. Figure 8 shows the J-V diagram and external quantum efficiency (EQE) diagram obtained from the final optimized values (refer to Tables 1

### Table 3 Final parameter optimization values

| Optimized parameters | Thickness (nm) | Doping density (cm\(^{-3}\)) | Defect Density (Nt) (cm\(^{-3}\)) |
|----------------------|----------------|-----------------------------|----------------------------------|
| Absorber             | 850            | \( 1.00 \times 10^{16} \)   | \( 1.00 \times 10^{15} \)        |
| FTO                  | –              | \( 1.00 \times 10^{19} \)   | –                                |
| ETL                  | 30             | –                           | –                                |
A tin-based perovskite solar cell with an inverted hole-free... and Tables 2 for other parameters), where (Table 3) $V_{OC} = 0.8585 \text{ V}$, $J_{SC} = 32.4566 \text{ mA/cm}^2$, FF = 73.72%, and PCE = 20.54%.

### 3.5 Other ETL candidates

In addition to C60 as an electron transport layer, we use PCBM, CdS, IGZO, ZnO as candidates. Figure 9 shows the energy band structure diagram of the different ETL and the optimized J-V curve diagram. The main selection suggestions for parameters are shown in Table 4 (Lakhdar and Hima 2020; Azri et al. 2019; Lin et al. 2018). Table 5 summarizes the performance comparison of different ETL devices, including important parameters of $V_{OC}$, $J_{SC}$, FF and PCE. When C60 is used as ETL, PCE reaches 20.54%, PCBM also shows excellent photovoltaic performance, while other materials CdS, IGZO and ZnO show relatively weak photovoltaic performance.
3.6 Conclusion

In this work, the structure design of the proposed inverted HTL-free tin-based PSCs was simulated using SCAPS-1D software. After optimization, the \( V_{OC} \) was 0.8585 V, \( J_{SC} \) was 32.4566 mA/cm\(^2\), FF was 73.72%, and PCE was 20.45%. To optimize the structure, we separately changed the device parameters, and observed and analyzed their effects on the performance of PSCs. The simulation results show that when the thickness of the absorption layer is 850 nm, the growth of PCE tends to be stable, and the excessive thickness of the absorption layer will lead to the increase of the diffusion length and the harmful recombination increase. The doping concentration of the absorption layer reaches \( 10^{16} \) cm\(^{-3}\), the built-in electric field of the perovskite layer is no longer enhanced, and the separation of carriers becomes slower, and the carrier recombination rate (R) increases significantly. The greater the defect density of the absorber layer, the more significant the impact on the PSCs and the worse the performance, so the defect density should be reduced as much as possible. In the PSCs structure studied in this work, FTO will be in direct contact with perovskite layer, and it is very valuable to study the influence of FTO parameters on the device. When \( N_D \) is \( 10^{19} \) cm\(^{-3}\), the PCE value stabilizes, \( V_{OC} \) reaches the top region of doping concentration, and the open circuit voltage is good. We also used the same light conditions to study PSCs with two structures, upright (p-i-n) and inverted (n-i-p), and the results show that based of HTL-free, the inverted structure can realize the PSCs to the maximum extent to ensure the light intensity of the incident perovskite layer, and the light-induced carriers could be effectively collected, directly increase the number of excitable electron–hole pairs, showing better performance.

| Table 4 | The main parameters of other ETL candidates |
|---------|---------------------|
| Parameters | PCBML | CdS | IGZO | ZnO |
| Thickness (nm) | 30 | 30 | 30 | 30 |
| Band gap, \( E_g \) (eV) | 2.0 | 2.4 | 3.05 | 3.3 |
| Electron affinity, \( \chi \) (eV) | 3.9 | 4.2 | 4.16 | 4.1 |
| Dielectric Permittivity, \( \varepsilon_r \) (cm\(^2\)/Vs) | 3.9 | 10.0 | 10.0 | 9.0 |
| Electron/hole mobility, \( \mu_n/\mu_p \) (cm\(^2\)/Vs) | 0.2/0.2 | 100/25 | 15/0.1 | 100/25 |
| Doping (cm\(^{-3}\)) | \( 1.00 \times 10^{10} \) | \( 1.00 \times 10^{14} \) | \( 1.0 \times 10^{15} \) | \( 1.0 \times 10^{14} \) |
| Defect density \( N_t \) (cm\(^{-3}\)) | \( 1.00 \times 10^{15} \) | \( 1.00 \times 10^{15} \) | \( 1.0 \times 10^{15} \) | \( 1.0 \times 10^{15} \) |

| Table 5 | Performance comparison of different ETL devices |
|---------|---------------------|
| | \( V_{OC} \) (V) | \( J_{SC} \) (mA/cm\(^2\)) | FF (%) | PCE (%) |
| C\(_60\) | 0.8585 | 32.4566 | 73.72 | 20.54 |
| PCBM | 0.8759 | 29.4917 | 55.83 | 14.42 |
| CdS | 0.3411 | 31.3062 | 70.85 | 7.57 |
| IGZO | 0.2625 | 30.8498 | 65.25 | 5.28 |
| ZnO | 0.2640 | 31.0850 | 66.58 | 5.46 |
A tin-based perovskite solar cell with an inverted hole-free…

Author contributions LH Collected the data, Contributed data or analysis tools, Performed the analysis, Performed the computer simulations, Wrote the paper. TL Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper. XM Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper. JW Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper. XW Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper. GH Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper. HP Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper. XZ Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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