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Modelling and loss analysis of meso-structured perovskite solar cells

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A mathematical model for meso-structured perovskite solar cells is derived and calibrated towards measured intensity dependent current-voltage characteristics. This steady-state device model describes the transport of free carriers, carrier recombination and optical generation. The optical part considers internal transmission, reflection, and absorption of light, using a transfer matrix approach. The carrier recombination in the form of radiative, Auger and Shockley-Read-Hall mechanisms is accounted for inside the perovskite capping layer, as well as interfacial recombination between the perovskite and electron/hole-transporting layers. After calibration by best-fitting the unknown parameters towards intensity dependent current-voltage measurements of an in-house fabricated meso-structured perovskite solar cell, we identify the dominant recombination mechanisms and their locations inside the cell. A subsequent loss analysis indicates that, in our fabricated solar cell, the interfacial recombination between the perovskite/mesoporous titanium dioxide within the mesoporous absorber layer constitutes the main loss channel. This interfacial recombination accounts for up to 46% of all recombination losses at maximum power, thereby exceeding the recombination inside the perovskite capping layer with 31% loss. Furthermore, the thickness of the perovskite capping layer and the mesoporous layer is varied by means of simulation between 50 and 500 nm, in order to predict the optimum device geometry for the calibrated recombination parameters. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4986115>]

I. INTRODUCTION

A major milestone in the development and pursuit of high-efficiency photovoltaic devices was the conceptualisation of the perovskite solar cell (PSC) by Miyasaka *et al.*¹ in 2009. They incorporated the organic-inorganic lead halide perovskite compounds $\text{CH}_3\text{NH}_3\text{PbI}_3$ as visible-light sensitizers in the form of nanoparticles coating on the surface of a mesoporous metal oxide film with 3.8% conversion efficiency. Miyasaka's PSCs, however, suffered from degradation due to the dissolution of the perovskite layer by the liquid electrolyte. Kim *et al.*² achieved in 2012 for almost 10% efficiency when spiro-MeOTAD was adopted to replace the liquid electrolyte in an analogy of the solid-state-dye-sensitized solar cell. In the same year, Lee *et al.*³ obtained an efficiency of 10.9% by replacing the mesoporous n-type titanium dioxide (TiO_2) with insulating aluminium oxide. This discovery laid the foundation for the development of planar PSCs by realizing that a mesoporous metal oxide is no longer necessary in the structure of PSCs. Since then, the efficiency has been consistently improved, reaching 22.1% in 2016.⁴

In general, PSCs have the advantage of low-cost fabrication,⁵ tunable optoelectronic properties such as broad optical absorption spectra, and high incident photo-to-electron conversion efficiency.⁶

In tandem with the material development for PSCs, mathematical modelling has come to play an important role in elucidating the device physics, unveiling its intrinsic material properties and predicting the device performance. Sun *et al.*⁷ obtained an analytical solution of “n-i-p” or “p-i-n” type cells with the assumption of an constant electric field and no recombination within the active layer. Agarwal *et al.*,⁸ Liu *et al.*,⁹ and Yang *et al.*¹⁰ investigated one-dimensional (1D) planar-type PSCs in terms of recombination, thickness and defect density of the perovskite layer, the fill factor and the origin of the high open-circuit voltage. Fu *et al.*¹¹ and Zhou *et al.*¹² extended the studies to a two-dimensional planar configuration, revealing the impact of carrier diffusion length on power conversion efficiency. Yang *et al.*¹³ adopted an effective-medium approach for the photoactive layer and studied the dominant types of recombination in mesoporous PSCs. Wu *et al.*¹⁴ demonstrated the electron concentration of TiO_2 nanowires can influence the cell performance in mesoporous PSCs. Minemoto and Murata¹⁵ added the interfacial recombination in their work; however, the bulk recombination was not considered. Wang *et al.*¹⁶ and Foster *et al.*¹⁷ further included both the bulk and interfacial recombination in their model, but Wang *et al.* cannot differentiate the types of recombination mechanisms at the interface and Foster *et al.* excludes the Auger and Shockley-Read-Hall (SRH) recombination

mechanisms. Based on Foster's formulation, Zhou *et al.*¹⁸ implemented a model with non-uniform generation, and both the radiative and SRH recombination mechanisms. Its drawback is the lack of internal light reflection. In the aforementioned mathematical models, no one has considered radiative, Auger and SRH recombination mechanisms at the bulk and also the interfacial recombination together, as well as at the same time taken internal light reflection into consideration.

Snaith *et al.*¹⁹ demonstrated that the presence of an anomalous hysteresis in the current-voltage (I-V) characteristics of PSCs is possibly due to large defect density, ferroelectric properties and excess ions in the perovskite material. Azpiroz *et al.*²⁰ and Domanski *et al.*²¹ attributed the origin of hysteresis effect to ionic migration within the bulk and charge accumulation at the interfacial contacts. Based on this, Richardson *et al.*²² and O'Kane *et al.*²³ modelled the hysteresis behaviour in planar PSCs by taking the ionic migration into consideration with the assumption of linear electric potential in the perovskite. We do not include ionic migration in our study.

In view of the dominant types of recombination mechanism in PSCs, we continue the development of mathematical modelling for PSCs by firstly deriving a device model for meso-structured PSCs with (1) the effect of light reflection included; (2) radiative, Auger and SRH recombination mechanisms at the bulk and the interfacial recombination together considered. We first calibrate and validate the resulting model with in-house fabricated solar cells by reproducing measured intensity dependent current-voltage curves at three different illumination levels. Using the mathematical framework developed, we then identify the dominant recombination mechanisms and their location within the solar cell. Last, a corresponding loss analysis framework developed for meso-structured PSCs is carried out, thereby quantifying the potential efficiency improvement if the device geometry is changed, i.e., we vary the thickness of the perovskite capping layer as well as the thickness of the mesoporous absorber layer of the PSCs.

II. EXPERIMENTS

A meso-structured PSC with an efficiency of 12.0% was fabricated according to the procedure outlined in Fu *et al.*²⁴

We used FTO glass as the cathode for the collection of electrons inside the cell. On top of it, a compact layer of TiO₂ was deposited and this layer acts as the electron-transporting layer. Subsequently, 30 nm TiO₂ nanoparticle paste was spin-coated onto the FTO to get a mesoporous TiO₂ film. When the PbI₂ solution was mixed with CH₃NH₃I solution onto the mesoporous film, CH₃NH₃PbI₃ was formed inside the pores of the TiO₂ mesoporous film, as well as on top of this film. Spiro-MeOTAD was afterwards spin-coated to form the hole-transporting layer onto the existing layer, which is denoted as the perovskite capping layer. Last, gold, the anode layer for the collection of holes, was deposited by thermal evaporator through a metallic mask to define the area of the solar cell. A detrimentally low shunt resistance was observed in this device, likely because of an incomplete coverage of the perovskite material above the TiO₂ mesoporous film. Thus, a shunting pathway has formed as a result of direct interfacial contact between the TiO₂ mesoporous film and the Spiro-MeOTAD.

Figure 1(a) shows a cross-sectional image of our fabricated meso-structured PSC from a field emission scanning electron microscope (SEM) (instrument JOEL JSM-7600F). The thickness of each layer, l , is estimated from the SEM image as follows: 110 nm for gold; 268 nm for Spiro-MeOTAD; 176 nm for perovskite capping layer; 345 nm for mesoporous layer; 480 nm for FTO. The thickness of the TiO₂ compact layer is too small to be estimated from the SEM image and hence is assumed to be in the range of 50–80 nm.

A series of I-V curves were measured under three different illumination intensities, namely, 0.3 sun, 0.5 sun and 1 sun, of an AAA graded solar simulator (Newport 91190A) with a 450 W xenon lamp (model 81172, Oriel). The reference cell for calibration was a certified Oriel PN91150V silicon solar cell. I-V scans were carried out in both the forward scan (FS) and the backward scan (BS), with a rate of 0.1 Vs⁻¹. Figure 2 shows the I-V measurement in both directions. Here, we quantified the hysteresis effect in the I-V curves by defining a hysteresis index ($\mathcal{H}$) according to the literature²⁵ as

FIG. 1. (a) A SEM image of the fabricated meso-structured PSC; (b) Schematics of the meso-structured PSC with six layers (thickness labelled l^A , l^H , l^P , l^M , l^E and l^C) and five interfaces (labelled I, II, III, IV and V). The materials used in each layer are: gold for the anode (A); Spiro-MeOTAD for the hole-transporting layer (H); CH₃NH₃PbI₃ for the perovskite capping layer (P); an intermixture of mesoporous CH₃NH₃PbI₃ and mesoporous TiO₂ for the mesoporous layer (M); compact TiO₂ for the electron transporting layer (E); FTO for the cathode (C).

FIG. 2. Measured (symbols) and fitted using two-diode model (lines) current-voltage curves of our processed meso-structured PSC under a spectral AM 1.5 solar illumination. Three different illumination intensities are used for training sets, i.e., 0.3 sun (left and right pointing green filled triangle), 0.5 sun [left and right pointing red filled triangle] and 1 sun (left and right pointing blue filled triangle), respectively. (►) indicates the forward scan and (◄) the backward scan.

$$\mathcal{H} = \left| \frac{j_{BS}^{\text{expt}}(0.6V_{oc}) - j_{FS}^{\text{expt}}(0.6V_{oc})}{j_{BS}^{\text{expt}}(0.6V_{oc})} \right|, \quad (1)$$

where j_{BS}^{expt} and j_{FS}^{expt} are the measured current density in BS and FS, respectively, V_{oc} is the open-circuit voltage. A $\mathcal{H}$ value of 1 indicates the cell has hysteresis as high as the photocurrent, while a $\mathcal{H}$ value of 0 corresponds to no significant hysteresis. The $\mathcal{H}$ values in our I-V measurement are 0.002, 0.025 and 0.101 at 0.3 sun, 0.5 sun and 1 sun, respectively. It indicates that the hysteresis effect in our cell increases with an increase in the illumination intensity and no significant hysteresis at 0.3 sun and 0.5 sun. The FS I-V curves were chosen for our model calibration and validation later.

III. MATHEMATICAL FORMULATION

We first consider that the meso-structured PSC can be modelled with six layers and five interfaces, as illustrated in Fig. 1(b). Since $\text{CH}_3\text{NH}_3\text{PbI}_3$ is formed inside the pores of TiO_2 mesoporous film and also on top of this film, we formulate a mesoporous layer and a perovskite capping layer separately, the former consists of mesoporous $\text{CH}_3\text{NH}_3\text{PbI}_3$ and mesoporous TiO_2 whereas the latter consists of compact $\text{CH}_3\text{NH}_3\text{PbI}_3$ only. Since the mesoporous layer is a composite of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and TiO_2 , we use effective medium approximations to model its macroscopic properties. Our device model comprises two main parts.

The first part treats the optical components of the model, including internal transmission, reflection and absorption of light and is modelled with the well-established transfer matrix method.^{26,27} The average size of TiO_2 nanoparticle in this experiment is about 30 nm and the pore scale of perovskite in the mesoporous layer is taken to have similar or even smaller size. Yin *et al.*²⁸ used volume averaging theory to predict the behavior of the optical properties of nanocomposite materials. The typical length scale of the system is much

smaller than the wavelength of light range from 300 to 820 nm and the Debye length is estimated to be 125 nm according to the definition given by Ref. 29. This Debye length is large compared to the size of the microstructure, around 30 nm, whence volume averaging theory can be applied to obtain effective optical properties. The effective-medium refractive index depends not only on the refractive index of perovskite and TiO_2 but also on their extinction coefficients. The same holds for the effective-medium extinction coefficient.

The second part which is the electrical components of the model describes generation, recombination and transport of the charge carriers. At interface I and IV, the electric potential and the electron/hole concentration are defined, while at interface II and III, the continuity of electric potential and the electric field are enforced, leading to a corresponding jump of electron/hole flux and of the electron/hole concentration, see Foster *et al.*¹⁷ The net recombination for electrons and holes inside the perovskite capping layer consists of three terms, namely, radiative recombination, Auger recombination and SRH recombination, respectively. An effective recombination term describes the net recombination of electrons and holes inside the mesoporous layer. This term includes radiative, Auger and SRH recombination within the perovskite material itself, as well as the recombination occurring at the interface between the perovskite and the mesoporous TiO_2 .

The main characteristics and assumption for our model are as follows:

- (1) The three-dimensional structure of the meso-structured PSC is reduced into a 1D effective-medium geometry in the x-direction, under the condition that the electron/hole flux in both y- and z-direction vanishes. The contacts at the anode and cathode are assumed to be equipotential.
- (2) A 1D effective-medium approach describes the generation and recombination within the mesoporous layer.
- (3) Interfacial recombination is explicitly considered at interface II. At this interface, two possible ways of recombination are postulated: either one electron from the perovskite capping layer recombines at the interface with one hole from the hole-transporting layer; or one electron and one hole from the perovskite capping layer recombine at the interface. No interfacial recombination is assumed to take place at interface III and IV, because these two interfaces are of the same material, respectively.
- (4) The anode and cathode are the current collectors. They are assumed to behave ohmically.
- (5) The effective Debye length inside the mesoporous layer is assumed large compared to the fine scale morphological structure of the mesoporous layer.²⁹

A. Governing equations

In this paper, the superscripts A, H, P, M, E and C denote properties associated with the anode, hole-transporting layer, perovskite capping layer, mesoporous layer, electron-transporting layer and cathode, respectively.

In the hole-transporting layer, we solve the conservation equation for holes coupled with the Poisson equation

$$\nabla \cdot \mathbf{J}_h^H = 0, \quad (2)$$

$$\nabla^2 \psi^H = -\frac{e}{\varepsilon^H} (C_h - N_a^{H-}), \quad (3)$$

where C_h is the hole concentration, $\mathbf{J}_h^H$ is the hole flux in the hole-transporting layer, ψ^H is the electric potential in the hole-transporting layer, e is the elemental charge, ε^H is the permittivity of hole-transporting layer, and N_a^{H-} is the ionized acceptor impurity concentration in the hole-transporting layer.

In the electron-transporting layer, we consider the conservation equation of electrons and the Poisson equation

$$\nabla \cdot \mathbf{J}_e^E = 0, \quad (4)$$

$$\nabla^2 \psi^E = \frac{e}{\varepsilon^E} (C_e - N_d^{E+}), \quad (5)$$

where C_e is the electron concentration, $\mathbf{J}_e^E$ is the electron flux in the electron-transporting layer, ψ^E is the electric potential in the electron-transporting layer, ε^E is the permittivity of electron-transporting layer, and N_d^{E+} is the ionized donor impurity concentration in the electron-transporting layer.

In the perovskite capping layer, we solve for conservation of holes and electrons as well as the Poisson equation

$$\nabla \cdot \mathbf{J}_h^P = G^P - R^P, \quad (6)$$

$$\nabla \cdot \mathbf{J}_e^P = G^P - R^P, \quad (7)$$

$$\nabla^2 \psi^P = \frac{e}{\varepsilon^P} (C_e - C_h), \quad (8)$$

where $\mathbf{J}_h^P$ and $\mathbf{J}_e^P$ are the hole and electron fluxes in the perovskite layer, respectively, ψ^P is the electric potential in the perovskite layer, ε^P is the permittivity of perovskite, G^P is the generation rate of electrons and holes from optical calculation, and R^P is the net recombination rate for electrons and holes inside this layer.

Similarly in the mesoporous layer, which is treated as an effective medium layer, we solve for conservation of holes and electrons as well as the Poisson equation

$$\nabla \cdot \mathbf{J}_h^M = G^M - R^M, \quad (9)$$

$$\nabla \cdot \mathbf{J}_e^M = G^M - R^M, \quad (10)$$

$$\nabla^2 \psi^M = \frac{e}{\varepsilon^M} (C_e - C_h), \quad (11)$$

where $\mathbf{J}_h^M$ and $\mathbf{J}_e^M$ are the hole and electron fluxes in the mesoporous layer, respectively, ψ^M is the electric potential in the mesoporous layer, ε^M is its effective permittivity defined by Eq. (44), G^M and R^M are the generation rate and net recombination rate for electrons and holes inside this layer.

B. Boundary conditions

At the interface V between the electron-transporting layer and the cathode, without loss of generality we set the

electric potential as zero; the electron concentration is given by

$$\psi^E|_V = 0, \quad (12)$$

$$C_e|_V = N_c^E \exp\left(\frac{\chi_e^E - W^A}{k_B T}\right) \exp\left(\frac{eV_{bi}}{k_B T}\right), \quad (13)$$

where N_c^E is the effective conduction band density of states in the electron-transporting layer, χ_e^E is the absolute value of electron affinity in the electron-transporting layer, W^A is the work function of the anode, V_{bi} is the built-in potential, k_B is the Boltzmann constant and T is the absolute temperature.

At the interface I between the hole-transporting layer and the anode, the electric potential and hole concentration is given by

$$\psi^H|_I = V_{ap} - V_{bi}, \quad (14)$$

$$C_h|_I = N_v^H \exp\left(\frac{W^C - \chi_h^H}{k_B T}\right) \exp\left(\frac{eV_{bi}}{k_B T}\right), \quad (15)$$

where V_{ap} is the applied voltage, N_v^H is the effective valance band density of states in the hole-transporting layer, W^C is the work function of the cathode, χ_h^H is the absolute value of ionization potential in the hole-transporting layer.

At the interface II between the hole-transporting layer and the perovskite capping layer, the continuity of electric potential, electric displacement and electric flux take the form

$$\psi^H|_{II} = \psi^P|_{II}, \quad (16)$$

$$\varepsilon^H \nabla \psi^H|_{II} \cdot \mathbf{e}_x = \varepsilon^P \nabla \psi^P|_{II} \cdot \mathbf{e}_x, \quad (17)$$

$$(\mathbf{J}_h^P|_{II} - \mathbf{J}_e^P|_{II}) \cdot \mathbf{e}_x = \mathbf{J}_h^H|_{II} \cdot \mathbf{e}_x, \quad (18)$$

$$\mathbf{J}_e^P|_{II} \cdot \mathbf{e}_x = R_{II}, \quad (19)$$

where R_{II} is the interface net recombination rate at the interface II defined as

$$R_{II} = S_{eff} \left[(C_{e,s}^P C_{h,s}^H - C_i^P C_i^H) + (C_{e,s}^P C_{h,s}^P - C_i^P C_i^P) \right], \quad (20)$$

in which S_{eff} is the effective surface recombination velocity at the interface II, $C_{e,s}^P$ and $C_{h,s}^H$ are the interface electron and hole concentrations of the perovskite capping layer, respectively, $C_{h,s}^H$ is the interface hole concentration of the hole-transporting layer, C_i^P and C_i^H are the intrinsic carrier densities of the perovskite capping layer and the hole-transporting layer, respectively. In addition, the ratio of the hole concentrations at interface II can be formulated in terms of the jumps in the ionization potential¹⁷ as

$$\frac{C_h|_{II}}{C_h|_{II+}} = \frac{N_v^P}{N_v^H} \exp\left(\frac{\chi_h^H - \chi_h^P}{k_B T}\right), \quad (21)$$

where N_v^P is the effective valance band density of states and χ_h^P is the absolute value of the ionization potential in the perovskite capping layer.

At the interface III between the perovskite capping layer and the mesoporous layer, the continuity of electric potential, electric displacement and electric flux have the form

$$\psi^M|_{\text{III}} = \psi^P|_{\text{III}}, \quad (22)$$

$$\varepsilon^M \nabla \psi^M|_{\text{III}} \cdot \mathbf{e}_x = \varepsilon^P \nabla \psi^P|_{\text{III}} \cdot \mathbf{e}_x, \quad (23)$$

$$(\mathbf{J}_e^M|_{\text{III}} - \mathbf{J}_e^P|_{\text{III}}) \cdot \mathbf{e}_x = (\mathbf{J}_h^M|_{\text{III}} - \mathbf{J}_h^P|_{\text{III}}) \cdot \mathbf{e}_x = 0, \quad (24)$$

and the ratio of the electron concentration at interface III can be formulated in terms of the jumps in the electron affinity¹⁷

$$\frac{C_e|_{\text{III}+}}{C_e|_{\text{III}-}} = \frac{N_c^P}{N_c^M} \exp\left(\frac{\chi_e^P - \chi_e^M}{k_B T}\right), \quad (25)$$

where N_c^P and N_c^M are the effective conduction band density of states in perovskite and mesoporous layer, respectively. χ_e^P and χ_e^M are the absolute values of electron affinity in perovskite and mesoporous layer, respectively.

At the interface IV between the mesoporous layer and the electron-transporting layer, the continuity of electric potential, electric displacement and electric flux have the form

$$\psi^M|_{\text{IV}} = \psi^E|_{\text{IV}}, \quad (26)$$

$$\varepsilon^M \nabla \psi^M|_{\text{IV}} \cdot \mathbf{e}_x = \varepsilon^E \nabla \psi^E|_{\text{IV}} \cdot \mathbf{e}_x, \quad (27)$$

$$(\mathbf{J}_e^M|_{\text{IV}} - \mathbf{J}_e^E|_{\text{IV}}) \cdot \mathbf{e}_x = \mathbf{J}_h^M|_{\text{IV}} \cdot \mathbf{e}_x = 0. \quad (28)$$

C. Constitutive relations

We define the hole and electron fluxes in the different layers as follows:

$$\mathbf{J}_h^i = -C_h \mu_h^i \nabla \psi^i - D_h^i \nabla C_h, \quad (29)$$

$$\mathbf{J}_e^j = C_e \mu_e^j \nabla \psi^j - D_e^j \nabla C_e, \quad (30)$$

where the superscripts i and j denote the layer ($i = \{H, P, M\}$ and $j = \{E, P, M\}$); μ_h^i and μ_e^j are the mobilities of holes and electrons in layer i and j , respectively, and D_h^i and D_e^j are the diffusion coefficients defined by Einstein's relation

$$D_h^i = \mu_h^i \frac{k_B T}{e}, \quad (31)$$

$$D_e^j = \mu_e^j \frac{k_B T}{e}. \quad (32)$$

The generation rate terms G^k in the perovskite capping layer and the mesoporous layer, as stated in Eqs. (6), (7), (9), and (10) are equated by calculating the effective optical electric field component of each layer with transfer matrix methodology and using volume averaging theory in order to obtain an effective medium refractive index and extinction coefficient in case of modelling the mesoporous layer M as

$$G^k = \frac{\theta^k}{h\nu} Q^k, \quad (33)$$

where superscript $k = i \cap j = \{P, M\}$, θ is the quantum efficiency of free charge generation, h is Planck's constant, ν is the frequency of incident wave, Q is the time average of the energy dissipated per second in layer k at normal incidence defined by²⁶

$$Q^k = 2\pi\nu\varepsilon_0\eta_{eff}^k\kappa_{eff}^k|\mathbf{E}_{eff}^k|^2, \quad (34)$$

in which ε_0 is the permittivity of free space, $\mathbf{E}_{eff}$ is the effective optical electric field, η_{eff} and κ_{eff} are the effective-medium refractive index and extinction coefficients, respectively, defined by volume averaging theory³⁰ as

$$\eta_{eff}^2 = \frac{1}{2} \left(X + \sqrt{X^2 + Y^2} \right), \quad (35)$$

$$\kappa_{eff}^2 = \frac{1}{2} \left(-X + \sqrt{X^2 + Y^2} \right), \quad (36)$$

where

$$X = \phi^k \left[(\eta^P)^2 - (\kappa^P)^2 \right] + (1 - \phi^k) \left[(\eta^E)^2 - (\kappa^E)^2 \right], \quad (37)$$

$$Y = 2\phi^k\eta^P\kappa^P + 2(1 - \phi^k)\eta^E\kappa^E, \quad (38)$$

and ϕ^k is the porosity of layer k defined as

$$\phi^k = \frac{\text{volume of perovskite inside layer } k}{\text{volume of layer } k}. \quad (39)$$

It is obvious that $\phi^P = 1$. η^P and κ^P are the optical properties of the perovskite material, η^E and κ^E are the optical properties of electron-transport layer. In Eq. (33), $\frac{Q}{h\nu}$ gives the number of photons of a given energy incident on the layer k . When it multiplies by θ , it gives the number of electrons and holes generated. In Eqs. (34)–(36), volume averaging theory is used to model the effective medium optically.

In the perovskite capping layer, the net recombination term R^P for electrons and holes in Eqs. (6) and (7) is defined by³¹

$$\begin{aligned} R^P = & B_{rad}^P \left[C_e C_h - (C_i^P)^2 \right] \\ & + \left(A_{e,Aug}^P C_e + A_{h,Aug}^P C_h \right) \left[C_e C_h - (C_i^P)^2 \right] \\ & + \frac{C_e C_h - (C_i^P)^2}{\tau_{e,SRH}^P (C_h + C_{h,t}) + \tau_{h,SRH}^P (C_e + C_{e,t})}, \end{aligned} \quad (40)$$

where B_{rad}^P is the radiative recombination coefficient, $A_{e,Aug}^P$ and $A_{h,Aug}^P$ are the Auger recombination coefficients for two-electron collisions and two-hole collisions, respectively, $\tau_{h,SRH}^P$ and $\tau_{e,SRH}^P$ are the SRH recombination lifetime for hole and electron capture by the trap, respectively. $C_{h,t}$ and $C_{e,t}$ are the values of hole and electron density, respectively, when the hole or electron Fermi level is equal to the trap level,

$$C_{h,t} = C_i^P \exp\left(\frac{E_i - E_t}{k_B T}\right), \quad (41)$$

$$C_{e,t} = C_i^P \exp\left(\frac{E_t - E_i}{k_B T}\right), \quad (42)$$

where E_i is the intrinsic potential energy related to C_i^P and E_t is the energy of trap state in the band gap.

In the mesoporous layer, the net recombination term R^M for electrons and holes in Eqs. (9) and (10) is defined by

$$R^M = D_{eff}^M [C_e C_h - (C_i^M)^2], \quad (43)$$

where D_{eff}^M is the effective recombination coefficient and C_i^M is the intrinsic carrier density in the mesoporous layer.

The effective permittivity ϵ^M in Eq. (11) for the mesoporous layer is taken as the volume average of the permittivities from the perovskite and the electron-transporting layers

$$\epsilon^M = \phi^M \epsilon^P + (1 - \phi^M) \epsilon^E. \quad (44)$$

The total current density j_{tot} flowing through the solar cell is

$$j_{tot} = e [-(C_h \mu_h^m + C_e \mu_e^m) \nabla \psi^m - D_h^m \nabla C_h + D_e^m \nabla C_e], \quad (45)$$

where superscript $m = i \cup j = \{H, P, M, E\}$.

For our loss analysis, we also define the following parameters: the radiative (j_{rad}^P), Auger (j_{Aug}^P) and SRH (j_{SRH}^P) recombination current from the perovskite capping layer as

$$j_{rad}^P = \int_{C+I^E+I^M}^{C+I^E+I^M+I^P} B_{rad}^P [C_e C_h - (C_i^P)^2] dx, \quad (46)$$

$$j_{Aug}^P = \int_{C+I^E+I^M}^{C+I^E+I^M+I^P} (A_{e,Aug}^P C_e + A_{h,Aug}^P C_h) [C_e C_h - (C_i^P)^2] dx, \quad (47)$$

$$j_{SRH}^P = \int_{C+I^E+I^M}^{C+I^E+I^M+I^P} \frac{C_e C_h - (C_i^P)^2}{\tau_{e,SRH}^P (C_h + C_{h,t}) + \tau_{h,SRH}^P (C_e + C_{e,t})} dx, \quad (48)$$

respectively; the recombination current j_{prv}^M from the perovskite material within the mesoporous layer from the recombination current in the perovskite capping layer by means of their volume ratio as

$$j_{prv}^M = \frac{I^M \phi^M}{I^P} (j_{rad}^P + j_{Aug}^P + j_{SRH}^P); \quad (49)$$

the recombination current j_{int}^M at the perovskite/TiO₂ interface as

$$j_{int}^M = \int_{C+I^E}^{C+I^E+I^M} D_{eff}^M [C_e C_h - (C_i^M)^2] dx - j_{prv}^M; \quad (50)$$

the recombination current j_{II} at the interface II between the perovskite capping layer and the hole-transporting layer as

$$j_{II} = R_{II}; \quad (51)$$

the total recombination current j_{rec} as

$$j_{rec} = j_{rad}^P + j_{Aug}^P + j_{SRH}^P + j_{prv}^M + j_{int}^M + j_{II}. \quad (52)$$

Furthermore, the efficiency of a solar cell, η_{sc} , is determined as the fraction of incident power which is converted into electricity and is defined as

$$\eta_{sc} = \frac{V_{oc} I_{sc} \mathfrak{F}}{P_{in}},$$

where I_{sc} is the short-circuit current, $\mathfrak{F}$ is the fill factor and P_{in} is the input power.

IV. NUMERICS

The system of non-linear ordinary differential equations for the dependent variables—concentration of holes C_h , concentration of electrons C_e , and electric potential ψ —was solved numerically with the commercial finite-element solver COMSOL MULTIPHYSICS 5.2a.³² The direct solver PARDISO was selected as the nonlinear solver with a relative convergence tolerance of 10^{-6} . A typical run for one solution required around 4 s (wall-clock time) with around 8×10^3 degrees of freedom on a deca-core 3.1 GHz workstation with 512 GB RAM.

The generation rate of electrons and holes within a wavelength range from 300 to 820 nm was obtained from a code written by McGehee *et al.*³³ based on the transfer matrix method. After importing the generation rate profile inside COMSOL, a cubic spline interpolation was performed. Further, the refractive index and extinction coefficients for each layer of the solar cell were obtained from ellipsometric measurements by Snaith *et al.*³⁴

V. CALIBRATION AND VALIDATION

As aforementioned, the FS I-V curves from our experiments show a non-negligible shunt resistance in our device, as we can observe from Fig. 2: at an illumination intensity of 1 sun, there is a visible drop of the current density of 1.3 mA cm^{-2} when the applied voltage is ranging from 0 to 0.6 eV. This shunt resistance is likely due to a direct contact of the TiO₂ mesoporous film to the Spiro-MeOTAD, thereby providing an alternative path for the light-generated current inside the solar cell. As our mathematical model does not include shunt-resistance, we need to eliminate this influence of the shunt resistance in the measured FS I-V curves. Miyano *et al.*³⁵ demonstrated the I-V curve of a PSC can be phenomenologically well described by a two-diode model. Thus, we employed the two-diode model in order to convert our measured FS I-V curves in Fig. 2 to “shunt-free” I-V curves in Fig. 3. The two-diode model can be written in the form as

$$j_{tot}^{2d}(V_{ap}) = j_{photo} - j_{01} \exp \left[\frac{e(V_{ap} + j_{tot}^{2d} R_s)}{k_B T} \right] - j_{02} \exp \left[\frac{e(V_{ap} + j_{tot}^{2d} R_s)}{2k_B T} \right] - \frac{V_{ap} + j_{tot}^{2d} R_s}{R_{sh}}, \quad (53)$$

where j_{tot}^{2d} is the current density of the two-diode model, j_{photo} is the photogenerated current density, j_{01} and j_{02} are the reverse saturation currents of diode 1 and 2, respectively, R_s is the series resistance and R_{sh} is the shunt resistance. In Fig. 2, the FS I-V curve at an intensity of 0.3 sun was the first training set for calibrating the parameters j_{01} , j_{02} , R_s and R_{sh} in the two-diode model by solving a non-linear fitting problem in the least-squares sense similar to Eqs. (56) and (57). The remaining training sets were the FS I-V curves at intensities of 0.5 and 1 sun for calibrating R_s and R_{sh} by taking the values of j_{01} and j_{02} from the first calibration at 0.3 sun. The calibrated R_s and R_{sh} in each of the sets are different,

FIG. 3. Simulated (lines) and shunt-corrected measured (symbols) current-voltage curves for our in-house processed meso-structured PSC under an AM 1.5 spectral solar illumination: three different illumination intensities are used, i.e., the training set is at 0.3 sun (▼), and two test sets are at 0.5 sun (■) and 1 sun (▲).

possibly because of their dependence on light intensity. The values of the parameters for two-diode model can be found in Table I. The maximum relative error between I-V curves from two-diode model and FS experimental measurement is 8%, 9%, and 5% at 1 sun, 0.5 sun and 0.3 sun, respectively, when the last six data points are not taken into consideration.

We introduce a shunt-resistance correction factor for the current as

$$\Delta j^{\text{corr}}(V_{ap}) = -j_{\text{tot}}^{\text{2d}} + \lim_{R_{sh} \rightarrow \infty} j_{\text{tot}}^{\text{2d}}, \quad (54)$$

and subsequently the current density from shunt-resistance correction, $j_{\text{tot}}^{\text{corr}}$, can be evaluated as

$$j_{\text{tot}}^{\text{corr}}(V_{ap}) = j_{\text{FS}}^{\text{expt}} + \Delta j^{\text{corr}}. \quad (55)$$

There are a total of 36 parameters required for our mathematical model. Table II shows those which are either directly measured, i.e., the thickness of the various layers is determined by means of SEM, or which have been accurately measured elsewhere and are thus taken from literature. However, there are 7 more parameters, i.e., the recombination parameters for the perovskite capping layer, the mesoporous layer and at the interface II— B_{rad}^P , $A_{e,\text{Aug}}^P$, $A_{h,\text{Aug}}^P$, $\tau_{e,\text{SRH}}^P$, $\tau_{h,\text{SRH}}^P$, D_{eff}^M , S_{eff} —which are less well known due to experimental difficulties in measuring them directly. Based on the work of Agarwal *et al.*,⁸ we assume $A_{e,\text{Aug}}^P = A_{h,\text{Aug}}^P$ and $\tau_{e,\text{SRH}}^P = \tau_{h,\text{SRH}}^P$ as a first approximation. This helps in reducing the unknown parameters for calibration from 7 to 5. In order to determine them, the corresponding parameters in

TABLE I. Two-diode model parameters. All values are fitted.

Parameters	Values (0.3 sun)	Values (0.5 sun)	Values (1 sun)
j_{01} (mA cm ⁻²)	2.8×10^{-22}	2.8×10^{-22}	2.8×10^{-22}
j_{02} (mA cm ⁻²)	5.9×10^{-12}	5.9×10^{-12}	5.9×10^{-12}
R_s (Ωcm ²)	13.7	14.8	9.9
R_{sh} (Ωcm ²)	848	907	245

TABLE II. Mathematical model non-calibrated parameters.

Parameters	Values	References
T	298 K	...
ϕ^M	0.3	36
ϵ^H	$3\epsilon_0$	17
ϵ^E	$9\epsilon_0$	15
ϵ^P	$6.5\epsilon_0$	17
μ_h^H	$5.6 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	37
μ_e^E	$6 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	38
μ_h^P	$5 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	39
μ_e^P	$5 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	39
μ_h^M	$1 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	13
μ_e^M	$1 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	13
N_a^{H-}	$3 \times 10^{24} \text{ m}^{-3}$	9
N_d^{E+}	0 m^{-3}	Estimated ^a
W^C	4.2 eV	8
W^A	5.1 eV	9
χ_h^H	5.22 eV	2
χ_e^E	4 eV	2, 40
χ_h^P	5.43 eV	2, 40
χ_e^P	3.93 eV	2, 40
N_c^P	$2.2 \times 10^{24} \text{ m}^{-3}$	15
N_c^E	$1 \times 10^{25} \text{ m}^{-3}$	14
N_c^M	$1 \times 10^{25} \text{ m}^{-3}$	Estimated ^b
N_v^P	$1.8 \times 10^{25} \text{ m}^{-3}$	15
N_v^H	$1 \times 10^{26} \text{ m}^{-3}$	14
E_t	5.27 eV	41
l^H	268 nm	Estimated ^c
l^P	176 nm	Estimated ^c
l^M	345 nm	Estimated ^c
l^E	50 nm	Estimated ^c

^aNo additives added in the electron-transporting layer.

^bSame as N_c^E as electrons go to TiO₂ in mesoporous layer.

^cSEM image.

our mathematical model were calibrated against our shunt-corrected measured FS I-V data at illumination intensities of 0.3 sun as the training set and subsequently validated at 0.5 and 1 sun as the test sets.

Calibration of these parameters was performed by solving a non-linear curve-fitting problem in the least-squares sense in MATLAB R2015a;⁴² i.e., we can find the parameters

$$\Phi = (B_{\text{rad}}^P, A_{e,\text{Aug}}^P, A_{h,\text{Aug}}^P, \tau_{e,\text{SRH}}^P, \tau_{h,\text{SRH}}^P, D_{\text{eff}}^M, S_{\text{eff}}) \quad (56)$$

that best fit the expression

$$\min_{\Phi} \|\mathbf{I}(\Phi, V_{ap}) - \mathbf{I}^{\text{corr}}(V_{ap})\|^2, \quad (57)$$

where $\mathbf{I}$ and $\mathbf{I}^{\text{corr}}$ are vectors that contain simulated and shunt-corrected measured FS current densities at various applied voltage, V_{ap} , respectively. We adapted heuristically these 7 parameters with a constraint in three orders of magnitude from the initial condition for the least-squares minimization. We found the set of parameters with the summed square of residuals within 1. The values of calibrated parameters can be found in Table III. The first 5 parameters are in the range of reported values⁸ and their values differ by one order of magnitude.

TABLE III. Mathematical model calibrated parameters.

Parameters	Values	References
B_{rad}^P	$3.4 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$	Fitted
$A_{e,Aug}^P$	$3.6 \times 10^{-39} \text{ m}^6 \text{ s}^{-1}$	Fitted
$A_{h,Aug}^P$	$3.6 \times 10^{-39} \text{ m}^6 \text{ s}^{-1}$	Fitted
$\tau_{e,SRH}^P$	$2.1 \times 10^{-7} \text{ s}$	Fitted
$\tau_{h,SRH}^P$	$2.1 \times 10^{-7} \text{ s}$	Fitted
D_{eff}^M	$6.4 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$	Fitted
S_{eff}	$2.3 \times 10^{-27} \text{ m}^4 \text{ s}^{-1}$	Fitted

The maximum relative error between I-V curves from the mathematical model and the shunt-corrected FS measurement is 6% at 0.3 sun. This error is 16% and 18% at 0.5 and 1 sun, respectively. Overall, comparatively good agreement was obtained as shown in Fig. 3. The validation at 0.5 sun and 1 sun in Fig. 3 shows that our mathematical model is able to capture the cell behaviour in the FS I-V measurement and a hysteresis model is required in future for capturing the BS I-V behaviour. In addition, in Fig. 2, we observe that hysteresis is not a leading-order effect at 0.3 sun and 0.5 sun.

VI. PLOTS OF POTENTIAL AND CARRIER CONCENTRATIONS

We examine the local behaviour of the dependent variables, namely, electric potential and carrier concentrations, at the condition of short-circuit current for the mathematical model. As only the hole and electron are considered in the hole-transporting and electron-transporting layers, respectively, we speculate that the right hand side of their Poisson equations in Eqs. (3) and (5) has a larger order of magnitude than the ones in the perovskite capping layer and the mesoporous layer. As a result, both the hole-transporting and electron-transporting layers have a higher non-linear electric potential in comparison with the other two layers. This simulated electric potential profile in Fig. 4 corresponds well with our speculation and also suggests there is a significant space charge effect in the hole-transporting and electron-transporting layers. In Fig. 4, the electric potential is approximately linear in the perovskite capping layer and the

FIG. 4. Distribution of electric potential in the meso-structured PSC at an illumination intensity of 1 sun at short-circuit current.

mesoporous layer due to a reduction in the space charge effect by the screening effect from the opposite carriers. Since there is no carrier generation in the hole-transporting and electron-transporting layers, the drift fluxes inside Eqs. (2) and (4) have to be counter-balanced by their respective diffusion fluxes. A consequence of this is huge carrier concentration gradient in the hole-transporting and electron-transporting layers. This is confirmed by the simulated concentration profile in Fig. 5.

VII. LOSS ANALYSIS AND DISCUSSION

Recombination losses inside the solar cell are crucial to the cell performance because they affect both the current collection as well as the forward bias injection current. It is necessary to quantify these recombination losses as it aids in evaluating the importance of each loss mechanism within the cell and consequently allows to estimate the potential efficiency improvement if some parameters such as the thickness are changed. After calibration and validation towards the intensity dependent I-V measurements, we extract the percentage of each recombination loss under open-circuit and maximum power condition, for our in-house fabricated PSC, by dividing j_{rad}^P , j_{Aug}^P , j_{SRH}^P , j_{prv}^M , j_{int}^M , and j_{II} with j_{rec} . Figure 6 illustrates the corresponding loss analysis at an open-circuit voltage of 1.08 V and at a maximum power voltage of 0.79 V, respectively.

At open circuit, the recombination losses are listed in descending order: 38% for the recombination at perovskite/TiO₂ interface in the mesoporous layer; 21% for the radiative recombination in the perovskite capping layer; 17% for the recombination from the perovskite material within the mesoporous layer; 14% for the recombination at perovskite capping layer/hole-transporting layer interface; 7% and 3% for the Auger and SRH recombination in the perovskite capping layer. The total recombination inside the mesoporous layer is 55%, which is significant over the total recombination from the perovskite capping layer of 31%.

Radiative recombination is the dominant recombination within the perovskite capping layer, whereas the dominant

FIG. 5. Distribution of electron (—) and hole (---) concentrations in the meso-structured PSC at an illumination intensity of 1 sun at short-circuit current.

FIG. 6. Percentage contribution of various recombination loss channels: (a) under open-circuit condition; (b) under maximum power condition.

recombination from the mesoporous layer occurs at the perovskite/TiO₂ interface. Only in case, all recombination inside the perovskite material is added up, this is 48% and substantially more than the interfacial recombination from the mesoporous layer. Analyzing a single recombination loss channel, recombination at the perovskite/TiO₂ interface within the mesoporous layer is by far the most dominant recombination loss at open-circuit.

Similarly, at maximum power, the recombination losses are as follows: 46% for the recombination at perovskite/TiO₂ interface in the mesoporous layer; 22% for the radiative recombination in the perovskite capping layer; 20% for the recombination from the perovskite material within the mesoporous layer; 8% for the SRH recombination in the perovskite capping layer; 3% for the recombination at perovskite capping layer/hole-transporting layer interface; 1% for the Auger recombination in the perovskite capping layer.

The interfacial recombination from the mesoporous layer dominates over all other recombination loss channels. Now the total recombination inside the perovskite material adds up to 51%, which is slightly above the interfacial recombination from the mesoporous layer with 46%. As we can see, the recombination percentage from the perovskite capping layer remains unchanged at both the open-circuit and maximum power, while the interfacial recombination within the mesoporous layer increases by 8% from open-circuit to maximum power. We suggest that this is due to the interfacial potential barrier formed between the perovskite and the TiO₂. There is experimental evidence^{43,44} showing the existence of such a interface potential barrier at the perovskite/TiO₂ interface, and this could hinder the electron transporting process and result in a higher recombination at the interface and further influence the efficiency of those TiO₂-based PSCs.

In summary, the dominant type of recombination takes place inside the meso-structured layer, i.e., at the interface between the perovskite and the mesoporous TiO₂. This is the case for maximum power as well as for open-circuit conditions, if the perovskite bulk recombination inside the mesoporous layer and inside the perovskite capping layer is

counted separately. Therefore, our results imply that careful surface engineering of mesoporous TiO₂ is important for device performance—this is in accordance with the experimental work by Ramakrishna *et al.*⁴⁵ and Tan *et al.*⁴⁶

VIII. PREDICTION OF OPTIMUM DEVICE GEOMETRY

We proceed to study how the thickness of the various layers affects the device performance, i.e., η_{sc} . We want to answer the question if the layer thicknesses are optimally chosen, considering the given recombination channels. The thickness of the perovskite capping layer and of the mesoporous layer is most critical inside the device because most generation and recombination of electrons/holes occurs within these two layers. This reduces the study for thickness variation into (i) studying the thickness variation of the perovskite capping layer, (ii) studying the thickness variation of the mesoporous layer and (iii) investigating this firstly one at a time and finally simultaneously together. We expect our experimental thickness to be more or less close to the optimal thickness, as an experimental thickness optimization has been undertaken beforehand, in order to achieve the best efficiency.

Figure 7 shows the predicted efficiency potential by varying the thickness of the perovskite capping layer and the mesoporous layer one at a time. When the thickness of the perovskite capping layer is changed, the thickness of the mesoporous layer is fixed at the experimental length, and vice versa. Simulating a thickness variation of the perovskite capping layer, a maximum efficiency is predicted at the thickness of 160 nm, which is close to the experimental value of 176 nm. This indicates that the chosen thickness of the perovskite capping layer in our experiment has been well-optimised. On the other hand, simulating a thickness variation of the mesoporous layer, two different maxima for the solar cell efficiency show up, i.e., a local maximum at a thickness of 300 nm and a global one at a thickness of 120 nm. Obviously, the experimental value of 345 nm is a local-optimised condition and there is a possibility to increase the solar cell efficiency by significantly reducing the thickness of the mesoporous layer. From a morphological

FIG. 7. Predicted efficiency potentials in terms of (a) the thickness of the perovskite capping layer and (b) the thickness of the mesoporous layer. The shunt-corrected experimental efficiency is 14.05%, indicated by a square (■).

control point of view, an underlying meso-structured perovskite layer is required in order to grow a high-quality perovskite capping layer.⁴⁷ Given the finding that the interfacial recombination within the meso-structured perovskite layer is the most dominant source of recombination, however, its thickness should be minimized.

Subsequently, we investigate the efficiency potential by varying both the thicknesses of perovskite capping layer and mesoporous layer simultaneously. The result is illustrated in a 2D contour plot in Fig. 8. As we can see, there are multiple local maxima and the predicted global maximum efficiency of 14.4% is located at a perovskite capping layer thickness of 200 nm and a mesoporous layer thickness of 90 nm. According to our simulation, there is room for an absolute efficiency improvement of about 0.35% by slightly increasing the perovskite capping layer thickness from 176 nm to 200 nm and significantly decreasing the thickness of the mesoporous layer from 345 nm down to 90 nm. Furthermore, we notice that the area with relative higher efficiency is located in the middle to right-bottom of Fig. 8 whereas the thickness of the mesoporous layer is relatively lower than the

FIG. 8. Simulated efficiency potential by varying the thickness of perovskite capping layer and the thickness of mesoporous layer simultaneously. The colourbar indicates the efficiency. The horizontal and vertical dotted lines indicate the cross sections which are shown in Figs. 7(a) and 7(b), respectively. The square (■) indicates the shunt-corrected experimental efficiency and the triangle (▲) indicates the simulated maximum efficiency.

experimental value. This supports our aforementioned loss analysis result, stating that the dominant recombination comes from the interface between the perovskite and the TiO₂ within the mesoporous layer. When its thickness is decreased, the corresponding interfacial area will be decreased as well, thereby resulting a suppression in the interfacial recombination within the mesoporous layer, and thus increasing the resulting solar cell efficiency.

IX. CONCLUSIONS

This work derives a mathematical formulation of perovskite device model, which is able to describe intrinsic solar cell physics such as free charge carrier generation, carrier transport and recombination within the bulk, as well as at the interfaces. Our device model has been calibrated and validated with an in-house fabricated meso-structured PSC device, using intensity dependent I-V measurements at 0.3 sun, 0.5 sun and 1 sun illuminations. Furthermore, a loss analysis for meso-structured PSC has been developed, showcasing the various recombination channels inside the perovskite solar cells. According to our loss analysis, the dominant type of recombination for our cell takes place at the interface between the perovskite and the TiO₂ within the mesoporous absorber layer of the solar cell. This is the case for maximum power condition, as well as for open-circuit condition. Moreover, inside the perovskite capping layer, as a consequence of its direct band gap, radiative recombination dominates over Auger and SRH recombination. Our study also indicates that the thicknesses of the perovskite capping layer and the mesoporous layer can be optimized towards maximum device performance by a significant reduction in the mesoporous layer thickness and a slight increment in the perovskite capping layer thickness.

X. OUTLOOK

Our developed device model is able to compare the different device performance of a planar-structured PSC towards a meso-structured PSC. A corresponding device calibration for comparing these two types of perovskite solar cell is currently on-going. Furthermore, an extension of this work aims at a three-dimensional explicit modelling of the meso-structured layer, in order to validate the 1D effective-medium approach presented in this paper. We can also derive functional forms of the effective material properties and examine the relation between macroscopic and nanoscopic quantities.

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NOMENCLATURE

$A_{e,Aug}$	Auger recombination coefficients for two-electron collisions, $m^6 s^{-1}$
$A_{h,Aug}$	Auger recombination coefficients for two-hole collisions, $m^6 s^{-1}$
B_{rad}	radiative recombination coefficient, $m^3 s^{-1}$
C_e	electron concentration, m^{-3}
$C_{e,s}$	interface electron concentration, m^{-3}
$C_{e,t}$	electron density when the electron Fermi level is equal to the trap level, m^{-3}
C_h	hole concentration, m^{-3}
$C_{h,s}$	interface hole concentration, m^{-3}
$C_{h,t}$	hole density when the hole Fermi level is equal to the trap level, m^{-3}
C_i	intrinsic carrier densities, m^{-3}
D_{eff}	effective recombination coefficient, $m^3 s^{-1}$
D_i	diffusion coefficient of species i , $m^2 s^{-1}$
e	elementary charge, C
E_c	LUMO energy level, eV
E_{eff}	optical electric field, $V m^{-1}$
E_F	Fermi energy level, eV
E_i	intrinsic potential energy, eV
E_t	energy of trap state, eV
E_v	HOMO energy level, eV
$\mathcal{F}$	fill factor
G	generation rate of electrons and holes, $m^{-3} s^{-1}$
h	Planck's constant, J s
$\mathcal{H}$	hysteresis index
I_{sc}	short-circuit current, $mA cm^{-2}$
J_i	flux of species i , $m^{-2} s^{-1}$
j_{photo}	photogenerated current density, $mA cm^{-2}$
j_{tot}	current density, $mA cm^{-2}$
j_{BS}^{xpt}	measured current density in backward scan, $mA cm^{-2}$
j_{FS}^{xpt}	measured current density in forward scan, $mA cm^{-2}$

j_{tot}^{corr}	current density from shunt-resistance correction, $mA cm^{-2}$
j_{tot}^{2d}	current density from the two diode model, $mA cm^{-2}$
j_{Aug}^p	Auger recombination current density, $mA cm^{-2}$
j_{rad}^p	radiative recombination current density, $mA cm^{-2}$
j_{SRH}^p	SRH recombination current density, $mA cm^{-2}$
j_{prv}^M	recombination current density from perovskite in mesoporous layer, $mA cm^{-2}$
j_{int}^M	recombination current density from the perovskite/TiO ₂ interface, $mA cm^{-2}$
j_{II}	recombination current density at interface II, $mA cm^{-2}$
j_{rec}	total recombination current density, $mA cm^{-2}$
j_{01}	reverse saturation currents of diode 1, $mA cm^{-2}$
j_{02}	reverse saturation currents of diode 2, $mA cm^{-2}$
k_B	Boltzmann constant, $J K^{-1}$
l	layer thickness, nm
N_c	effective conduction band density of states, m^{-3}
N_v	effective valance band density of states, m^{-3}
N_a^{H-}	ionized acceptor impurity concentration in H , m^{-3}
N_d^{E+}	ionized donor impurity concentration in E , m^{-3}
P_{in}	input power, W
Q	time average of the energy dissipated per second, $J m^{-3} s^{-1}$
R	net recombination rate of electrons and holes, $m^{-3} s^{-1}$
R_s	series resistance, Ωcm^2
R_{sh}	shunt resistance, Ωcm^2
S_{eff}	effective surface recombination velocity, $m^4 s^{-1}$
T	absolute temperature, K
V_{ap}	applied voltage, V
V_{bi}	built-in potential, V
V_{oc}	open-circuit voltage, V
W	work function, eV
ΔE_f	quasi-fermi level splitting, eV
Δj^{corr}	shunt-resistance correction factor, $mA cm^{-2}$

Greek

ϵ_0	permittivity of free space, Fm^{-1}
ϵ	permittivity of material, Fm^{-1}
η	refractive index
η_{sc}	solar cell efficiency
θ	quantum efficiency
κ	extinction coefficient
μ_i	mobility of species i , $m^2 V^{-1} s^{-1}$
ν	frequency of incident wave, s^{-1}
ϕ	porosity
$\tau_{e,SRH}$	SRH recombination lifetime for electron, s
$\tau_{h,SRH}$	SRH recombination lifetime for hole, s
χ_e	absolute value of electron affinity, eV
χ_h	absolute value of ionization potential, eV
ψ	electric potential, V
Ψ	absolute value of electric potential in the vacuum near the surface, V

Superscript

A	anode
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C cathode
 E electron-transporting layer
 H hole-transporting layer
 M mesoporous layer
 P perovskite capping layer

APPENDIX: DERIVATION OF EQS. (13), (15), (21), AND (25)

We derive the Eqs. (13), (15), (21), and (25):

From Fig. 9, the built-in potential, V_{bi} , which measures the electric potential difference between the anode and the cathode, is defined by

$$V_{bi} = \frac{W^A - W^C}{e}. \quad (A1)$$

The hole concentration at interface I is given by

$$\begin{aligned} C_h|_I &= N_v^H \exp\left(\frac{E_v^H - E_F}{k_B T}\right) \\ &= N_v^H \exp\left(\frac{-e\Psi^H - \chi_h^H + W^A + e\Psi^A}{k_B T}\right) \\ &= N_v^H \exp\left(\frac{-\chi_h^H + W^C + eV_{bi}}{k_B T}\right) \\ &= N_v^H \exp\left(\frac{W^C - \chi_h^H}{k_B T}\right) \exp\left(\frac{eV_{bi}}{k_B T}\right), \end{aligned} \quad (A2)$$

where Eq. (A1) is used in the third step.

The electron concentration at interface V is given by

$$\begin{aligned} C_e|_V &= N_c^E \exp\left(\frac{E_F - E_c^E}{k_B T}\right) \\ &= N_c^E \exp\left(\frac{-W^C - e\Psi^C + e\Psi^E + \chi_e^E}{k_B T}\right) \\ &= N_c^E \exp\left(\frac{eV_{bi} - W^A + \chi_e^E}{k_B T}\right) \\ &= N_c^E \exp\left(\frac{\chi_e^E - W^A}{k_B T}\right) \exp\left(\frac{eV_{bi}}{k_B T}\right), \end{aligned} \quad (A3)$$

where Eq. (A1) is also used in the third step.

FIG. 9. Schematic representation of band bending diagram for meso-structured PSC at short-circuit without illumination¹⁷ where E_v^H , E_c^P , and E_v^M are the HOMO energy levels in the hole-transporting layer, perovskite capping layer and mesoporous layer, respectively, E_c^E , E_c^P , and E_c^M are the LUMO energy levels in the electron-transporting layer, perovskite capping layer and mesoporous layer, respectively. Ψ^A , Ψ^H , Ψ^P , Ψ^M , Ψ^E , Ψ^C are the absolute values of electric potential in the vacuum near the surface in respective layers.

The ratio of hole concentration at interface II is given by

$$\begin{aligned} \frac{C_h|_{II-}}{C_h|_{II+}} &= \frac{N_v^P \exp\left(\frac{E_v^P - E_F}{k_B T}\right)}{N_v^H \exp\left(\frac{E_v^H - E_F}{k_B T}\right)} \\ &= \frac{N_v^P}{N_v^H} \exp\left(\frac{E_v^P - E_F - E_v^H + E_F}{k_B T}\right) \\ &= \frac{N_v^P}{N_v^H} \exp\left(\frac{-e\Psi^P - \chi_h^P + e\Psi^H + \chi_h^H}{k_B T}\right) \\ &= \frac{N_v^P}{N_v^H} \exp\left(\frac{\chi_h^H - \chi_h^P}{k_B T}\right). \end{aligned} \quad (A4)$$

The ratio of electron concentration at interface III is given by

$$\begin{aligned} \frac{C_e|_{III+}}{C_e|_{III-}} &= \frac{N_c^P \exp\left(\frac{E_F - E_c^P}{k_B T}\right)}{N_c^M \exp\left(\frac{E_F - E_c^M}{k_B T}\right)} \\ &= \frac{N_c^P}{N_c^M} \exp\left(\frac{E_F - E_c^P - E_F + E_c^M}{k_B T}\right) \\ &= \frac{N_c^P}{N_c^M} \exp\left(\frac{e\Psi^P + \chi_e^P - e\Psi^M - \chi_e^M}{k_B T}\right) \\ &= \frac{N_c^P}{N_c^M} \exp\left(\frac{\chi_e^P - \chi_e^M}{k_B T}\right). \end{aligned} \quad (A5)$$

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