Supporting Information

Quantifying Efficiency Loss of Perovskite Solar Cells by a Modified Detailed Balance Model

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1. Supplementary Note 1−Device models for perovskite solar cells

The drift-diffusion model, circuit model and detailed balance model are three commonly-used theoretical models for investigating device physics of perovskite solar cells (PVSCs). Here, we briefly outline the three models.

a. Drift-diffusion model

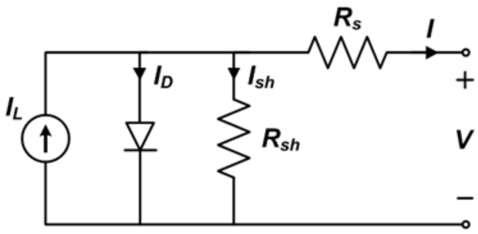
The drift-diffusion model is governed by the Poisson, drift-diffusion and continuity equations:

$$\begin{aligned} &\nabla\cdot(\varepsilon\nabla\psi)=-q(p-n)\\ &\frac{\partial n}{\partial t}=\frac{1}{q}\nabla\cdot\mathbf{J}_n+G-R\\ &\frac{\partial p}{\partial t}=-\frac{1}{q}\nabla\cdot\mathbf{J}_p+G-R \end{aligned} \tag{S1}$$

where $\mathbf{J}_\mathrm{n}=-q\mu_n n\nabla\psi+qD_n\nabla n$ and $\mathbf{J}_\mathrm{p}=-q\mu_p p\nabla\psi-qD_p\nabla p$ are the electron and hole current densities, respectively. The electron (hole) diffusion coefficient satisfies the Einstein relation $D_{n(p)}=\mu_{n(p)}\,k_BT/q$ and $\mu_{n(p)}$ is electron (hole) mobility. Furthermore, G is the generation rate, R is the recombination.

The drift-diffusion model can be used to study the carrier dynamics (transport, recombination and collection) in PVSCs and has the capability to gain the insight of device optimization. However, the predicted results are critically dependent on many empirically/experimentally determined parameters such as mobility, effective density of states, dielectric constant, band gap, work function, recombination rate, etc. In addition, the photon recycling effect cannot be trivially incorporated in this model. Due to a large variation of carrier density (on the magnitude of several orders) and high nonlinearity, a great number of computational techniques have been proposed to solve the drift-diffusion model. However, the retrieval of the simulation parameters from the drift-diffusion model is very difficult.

b. Circuit model



The PVSCs can be modeled by an equivalent circuit above. The current-voltage curve can be expressed by the Kirchhoff's current law for the output current I.

$$I = I_{ph} - I_D - I_{sh} \tag{S2}$$

Here, I_{ph} represents the photogenerated current in PVSCs and I_{sh} is the current flowing in the shunt resistance. I_D is the diode current that can be modeled by the Shockley's equation

$$I_D = I_0 \left[\exp\left(\frac{q(V + IR_s)}{nk_B T} \right) - 1 \right] \tag{S3}$$

where R_s and R_{sh} are the series and shunt resistances of PVSCs, respectively. n is the diode ideality factor. I_0 is the saturation current, k_BT is the thermal energy at the temperature T. Since the I_{sh}=(V+IR_s)/R_{sh}, the output current I of the PVSCs under the applied voltage V is:

$$I = I_{ph} - I_0 \left[\exp\left(\frac{q(V + IR_s)}{nk_B T} \right) - 1 \right] - \frac{V + IR_s}{R_{sh}} \tag{S4}$$

The circuit model provides a simple and fast approach to study the device physics of PVSCs. There are five parameters in the circuit model that needs to be retrieved from the experimental current density-voltage curve, including the saturation current I_0, ideality factor n, photogenerated current I_{ph}, series resistance R_s, and shunt resistance R_{sh}. As a result, the uniqueness of the retrieved parameters cannot be guaranteed. Moreover, the recombination mechanisms (e.g. radiative, trap-assisted, and Auger recombination) are implicitly involved in the ideality factor n. In sum, the circuit model can only give preliminary understandings of device physics in PVSCs.

c. Detailed balance model

The photocurrent is calculated as the difference between the photons absorbed by and the photons leaving from the PVSCs:

$$J = J_e(V) - J_{ph} \tag{S5}$$

where V is the applied voltage. J_e represents the current density corresponding to the radiative emission and J_{ph} is the photogenerated current due to the absorption of incident light in perovskite material

$$J_{ph} = q\int_0^\infty \alpha(\lambda, L) \frac{\Gamma(\lambda)\lambda}{hc_0} d\lambda \tag{S6}$$

where c_0 is the speed of light in air. Γ is the global AM 1.5G spectrum of Sun, λ is the wavelength, and q is the elementary charge. $\alpha(\lambda, L)$ is the absorptivity of the solar cell with an active layer thickness of L.

According to the detailed balance theory and Boltzmann statistics, the radiative current J_e can be expressed as

$$J_e = J_0 \left[\exp\left(\frac{qV}{k_B T} \right) - 1 \right] \tag{S7}$$

where J_0 is the radiative saturation current, which can be calculated by the blackbody radiation law.

$$J_0 = q\int_0^{\infty} \alpha(\lambda, L)\frac{\Gamma_0(\lambda)\lambda}{hc_0}d\lambda$$

$$\Gamma_0(\lambda) = \int_0^{2\pi} d\varphi\int_0^{\theta_m} S(\lambda)\cos(\theta)\sin(\theta)d\theta = \pi\sin^2\theta_m(\lambda)S(\lambda)$$

$$S(\lambda) = \frac{2hc_0^2}{\lambda^5}\frac{1}{\exp\left(\frac{hc_0}{\lambda k_B T}\right)-1} \tag{S8}$$

where $\Gamma_0(\lambda)$ is the blackbody emission spectrum of the solar cell and $S(\lambda)$ is the thermal radiance of the cell. θ_m is the maximum emission angle related to the angular restriction design.

The detailed balance model is an indispensible tool for predicting the efficiency limit of PVSCs. The model only considers the detailed balance between absorbed photons and emitted photons. However, for the practical PVSCs, the inclusions of the non-radiative recombination and the influence of carrier transport layers are important for understanding device physics qualitatively and unveiling energy loss quantitatively.

In our revised detailed balance model, we include the currents J_r and J_n induced by the radiative and non-radiative recombination, respectively. Moreover, we introduce the series resistance R_s that describes the ohmic loss from the contacts, carrier transport layers, and the hetero-junction interfaces between the perovskite and carrier transport layers. The introduced shunt resistance R_{sh} captures the defects and voids induced current leakage. The revised detailed balance model captures different recombination mechanisms, the influences of carrier transport layers and contacts, photon recycling effects, and optical effects (light trapping). Compared to the circuit model, only three parameters are needed to be extracted. Thus, it is a promising tool to photovoltaic science and engineering.

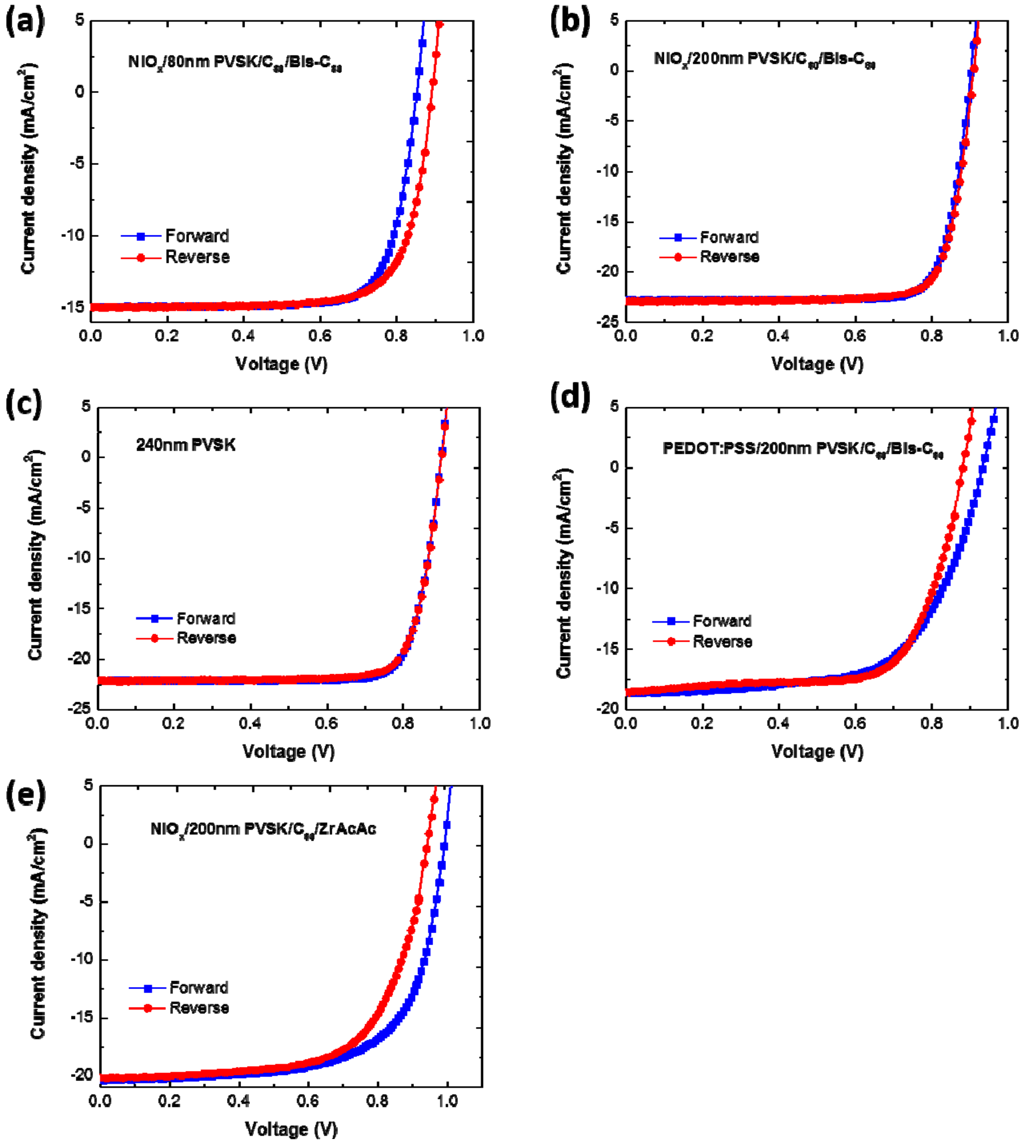


Figure S1. The *J-V* characteristics for perovskite solar cells with different perovskite thickness (a, b, and c) and carrier transport layers (b, d, and e) measured under different scan directions.

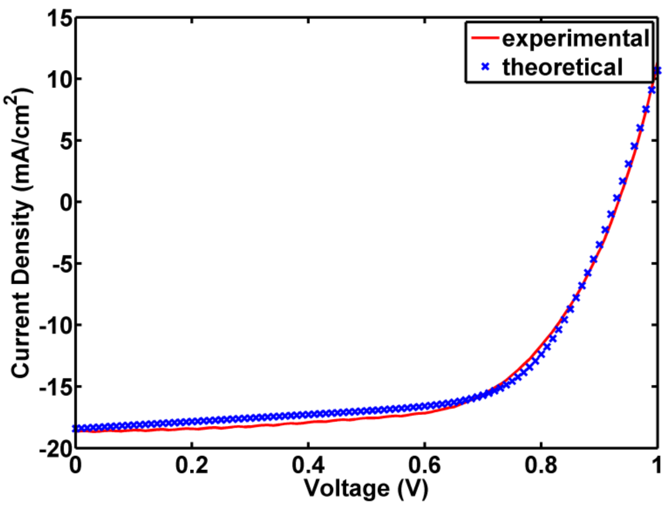


Figure S2. The theoretically fitted and experimentally measured *J-V* characteristics for perovskite solar cells incorporating PEDOT:PSS and Bis-C_{60} as the hole transport layer and interfacial layer, respectively. The device structure is given as: ITO/ PEDOT:PSS (40 nm)/ $CH_3NH_3PbI_3$ (200 nm)/ C_{60} (50 nm)/ Bis-C_{60} (10 nm)/ Ag (120 nm). The forward scanning is employed. The relative fitting error is 3.34%.

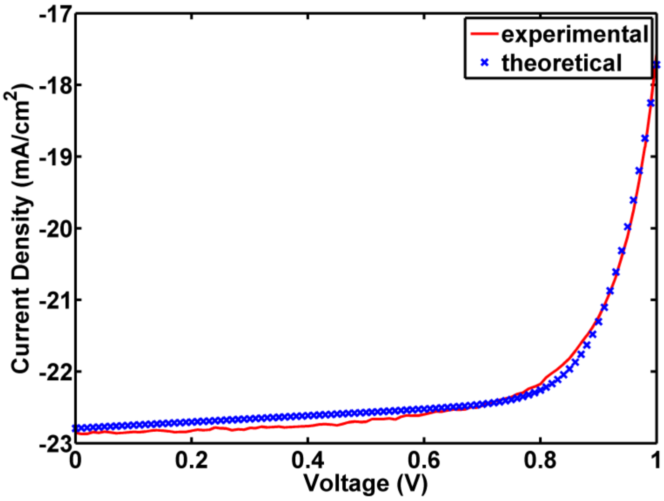


Figure S3. The theoretically fitted and experimentally measured *J-V* characteristics for the high-performance perovskite solar cell. The device structure is given as: ITO/ NiO_x (20 nm)/ $CH_3NH_3PbI_3(Cl)$ (300 nm)/ PCBM:C_{60} mixture (50 nm)/ Bis-C_{60} (10 nm)/ Ag (120 nm). The relative fitting error is 0.48%.