Electronic Supplementary Information

Decrystallization of $CH_3NH_3PbI_3$ perovskite crystals via polarity dependent localized charges

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To estimate electron and hole densities inside $MAPbI_3$ layer, the structure is simplified as shown in Supplementary Fig.1. All the layers are ideally uniform along y-direction for building 1D simple model. Thus, we considered carrier densities as a function of thickness displacement along x-direction. Additionally, we assumed that there is no ion migration, no trap-assisted recombination and no photon recycling because those are not dominant under one sun illumination conditions (mainly generation and dynamics of charge carriers). Consequently, we considered light absorption (photo-carrier generation), radiative recombination, carrier diffusion and carrier drift inside $MAPbI_3$ perovskite layers by utilizing its physical properties according to the references [ref].

First, the carrier transport model is regarded as the following Boltzmann transport equations.

$$J_e = -q\mu_e n_e \nabla\varphi_{F,e} \quad \text{Eq 1}$$

$$J_h = -q\mu_h n_h \nabla\varphi_{F,h} \quad \text{Eq 2}$$

Where q is the elementary charge, μ_e and μ_h are the mobility of electron and hole, n_e and n_h are the density of electron and hole, $\varphi_{F,e}$ and $\varphi_{F,h}$ are the quasi Fermi level of electron and hole, respectively.

The quasi Fermi level is given by

$$\varphi_{F,e} = E_{CB} + V - \frac{kT}{q} ln\frac{n_e}{N_0} \quad \text{Eq 3}$$

$$\varphi_{F,h} = E_{VB} + V + \frac{kT}{q} ln\frac{n_h}{N_0} \quad \text{Eq 4}$$

Where E_{cb} and E_{vb} are the energy level of conduction band and valence band, V is the electrostatic potential, k is Boltzmann's constant, T is the temperature, N_0 is the total density of state

$$\therefore J_e = -q\mu_e n_e\left(\frac{dV}{dx} - \frac{kT}{q}\frac{1}{n_e}\frac{dn_e}{dx}\right) = -q\mu_e n_e\frac{dV}{dx} + \mu_e kT\frac{dn_e}{dx}$$

Accordingly, the current density of electrons and holes (J_e and J_h) could be calculated as follows.

… Eq 5

$$\therefore J_h = -q\mu_h n_h\left(\frac{dV}{dx} + \frac{kT}{q}\frac{1}{n_h}\frac{dn_h}{dx}\right) = -q\mu_h n_h\frac{dV}{dx} - \mu_h kT\frac{dn_h}{dx}$$

… Eq 6

The first term is associated with carrier drift, and the second one is corresponding to carrier diffusion by density difference.

To calculate carrier densities, the continuity equation of carriers is required. Considering carrier generation (G) and carrier recombination (R), the continuity equation of electrons and holes are expressed as the following equations.

$$\frac{dn_e}{dt} = \frac{1}{q}\frac{dJ_e}{dx} + G - R \qquad \text{Eq 7}$$

$$\frac{dn_h}{dt} =- \frac{1}{q}\frac{dJ_h}{dx} + G - R \qquad \text{Eq8}$$

Recombination R is calculated by following a Langevin process as expressed in Eq. 9, and generation G is calculated according to the reference [ref].

$$R = L\frac{q(\mu_e + \mu_h)}{\varepsilon_0\varepsilon_r}n_e n_h \qquad \text{Eq 9}$$

Finally, we can obtain the continuity equation of carrier in the 1D model by using Eq, 5-9, as shown in below.

$$\frac{dn_h}{dt} =- \frac{1}{q}\frac{dJ_h}{dx} + G - R = \mu_h n_h\frac{d^2V}{dx^2} + \mu_h\frac{dn_h}{dx}\frac{dV}{dx} + \frac{\mu_h kT}{q}\frac{d^2n_h}{dx^2} - L\frac{q(\mu_e + \mu_h)}{\varepsilon_0\varepsilon_r}n_e n_h + G$$

$$\frac{dn_e}{dt} = \frac{1}{q}\frac{dJ_e}{dx} + G - R =- \mu_e n_e\frac{d^2V}{dx^2} - \mu_e\frac{dn_e}{dx}\frac{dV}{dx} + \frac{\mu_e kT}{q}\frac{d^2n_e}{dx^2} - L\frac{q(\mu_e + \mu_h)}{\varepsilon_0\varepsilon_r}n_e n_h + G$$

Eq 10

Eq 11

At the steady-state, the time derivative of carrier density is zero ($dn_e/dt=dn_h/dt=0$). Therefore, Eq 10 and 11 could be simplified more.

$$\frac{\mu_e kT}{q}\frac{d^2n_e}{dx^2} = \mu_e n_e\frac{d^2V}{dx^2} + \mu_e\frac{dn_e}{dx}\frac{dV}{dx} + L\frac{q(\mu_e + \mu_h)}{\varepsilon_0\varepsilon_r}n_e n_h - G \qquad \text{Eq 12}$$

$$\frac{\mu_h kT}{q}\frac{d^2n_h}{dx^2} =- \mu_h n_h\frac{d^2V}{dx^2} - \mu_h\frac{dn_h}{dx}\frac{dV}{dx} + L\frac{q(\mu_e + \mu_h)}{\varepsilon_0\varepsilon_r}n_e n_h - G$$

Eq 13

Potential terms can be solved from poisson equation of Gauss law.

$$\nabla^2 V = -\frac{q}{\varepsilon_0 \varepsilon_r}(n_h - n_e)$$

Poisson equation

Poisson equation in 1D model $\frac{d^2V}{dx^2} = -\frac{q}{\varepsilon_0 \varepsilon_r}(n_h - n_e)$

Finally, the continuity equation of electrons and holes at the steady-state are obtained as a function of electron and hole densities and thickness displacement x as the following equations.

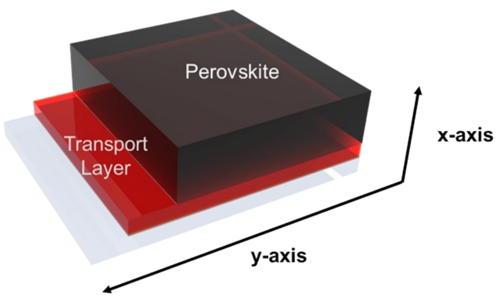
$$\therefore \frac{\mu_e kT}{q}\frac{d^2 n_e}{dx^2} = \frac{q\mu_e}{\varepsilon_0\varepsilon_r}\left(n_e^2 - n_e n_h\right) + \mu_e \frac{dn_e}{dx}\frac{q}{\varepsilon_0\varepsilon_r}\left(\int (n_e - n_h)dx - E_{x0}\right) + L\frac{q(\mu_e + \mu_h)}{\varepsilon_0\varepsilon_r}n_e n_h - G$$

Eq 14

$$\therefore \frac{\mu_h kT}{q}\frac{d^2 n_h}{dx^2} = \frac{q\mu_h}{\varepsilon_0\varepsilon_r}\left(n_h^2 - n_e n_h\right) - \mu_h \frac{dn_h}{dx}\frac{q}{\varepsilon_0\varepsilon_r}\left(\int (n_e - n_h)dx - E_{x0}\right) + L\frac{q(\mu_e + \mu_h)}{\varepsilon_0\varepsilon_r}n_e n_h - G$$

Eq 15

To solve equation 14 and 15 for calculating electron and hole densities inside three kinds of half devices, four boundary conditions regarding densities at edges (x=0 and 500 nm) are required. At the interface of the electron transport layer, electron density is considered to be zero based on experimental results of PL measurement (Most of carriers are quenched by charge selective layer). On the other hand, hole density is zero at the interface of the hole transport layer. Moreover, since there is no carrier diffusion at the boundary, density difference is regarded to be zero. Finally, we defined boundary conditions for the ETL/$MAPbI_3$, the HTL/$MAPbI_3$, and the glass/$MAPbI_3$ devices as shown in Supplementary Fig 2



Supplementary Information Figure 1. Simplified 1-d model for Transport Layer/Perovskite using in this calculation

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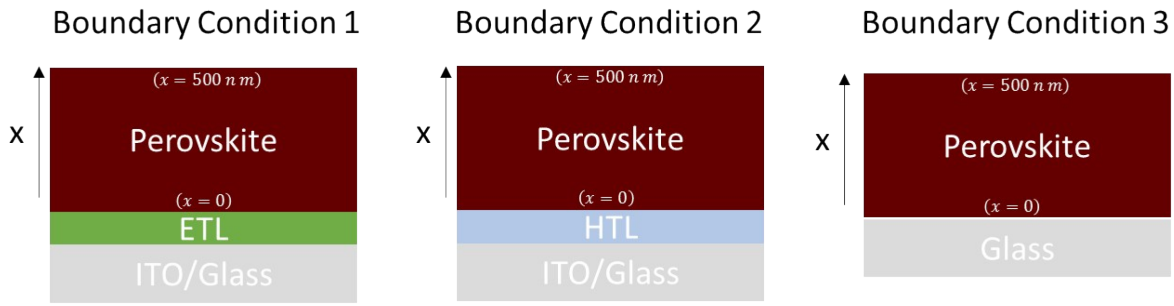

Boundary Condition 1:

$$n_e(x=0)=0$$
$$\frac{dn_h}{dx}(x=0)=0$$
$$\frac{dn_e}{dx}(x=5\times10^{-5}\,cm)=0$$
$$\frac{dn_h}{dx}(x=5\times10^{-5}\,cm)=0$$

Boundary Condition 2:

$$n_h(x=0)=0$$
$$\frac{dn_e}{dx}(x=0)=0$$
$$\frac{dn_e}{dx}(x=5\times10^{-5}\,cm)=0$$
$$\frac{dn_h}{dx}(x=5\times10^{-5}\,cm)=0$$

Boundary Condition 3:

$$\frac{dn_e}{dx}(x=0)=0$$
$$\frac{dn_h}{dx}(x=0)=0$$
$$\frac{dn_e}{dx}(x=5\times10^{-5}\,cm)=0$$
$$\frac{dn_h}{dx}(x=5\times10^{-5}\,cm)=0$$

Supplementary Information Figure 2. Boundary conditions for ETL/$MAPbI_3$, the HTL/$MAPbI_3$, and the glass/$MAPbI_3$ devices to solve equation 14 and 15.

We could obtain numerical solutions for simultaneous equations 14 and 15 by using MATLAB.

Parameter values for the model are shown in Supplementary Table.1

Parameter	Unit	Value
Q (unit charge)	C	1.6×10^{-19}
μ_e (electron mobility)	$cm^2V^{-1}s^{-1}$	5
μ_h (hole mobility)	$cm^2V^{-1}s^{-1}$	3
k (Boltzmann Constant)	JK^{-1}	1.38×10^{-23}
T (Temperature)	K	300
L (Recombination constant)		10^{-5}
ε_0 (Vacuum Permittivity)	$CV^{-1}cm^{-1}$	8.854×10^{-10}
ε_r (Relative Permittivity)		60
G (Carrier Generation)		1.7×10^{21}
α (absorption coefficient)	cm^{-1}	1.48×10^{4}