Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials

Modeling, Monte Carlo simulation on photon regeneration effects of perovskite $FAPbI_3$ for photovoltaic applications

Hengbin Xu[1], Xiangfu Wang[1,2*]

[1]*College of Electronic and Optical Engineering & College of Flexible Electronics (Future Technology), Nanjing University of Posts and Telecommunications, Nanjing, 210023, China*

[2]*Anhui Province Key Laboratory of Environment-friendly Polymer Materials, Anhui University, Hefei 230601, China*

*Corresponding authors

E-mail address: xfwang@njupt.edu.cn (Wang)

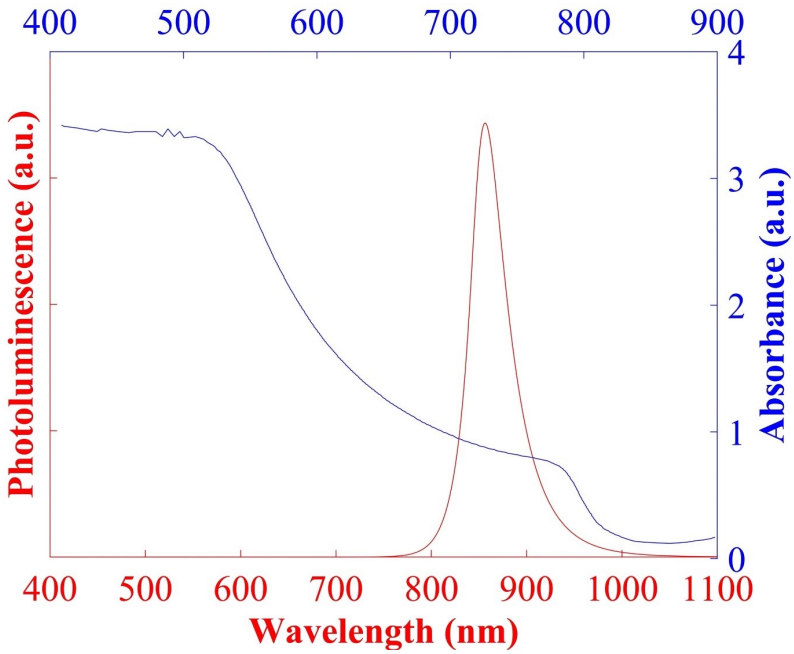

Fig.S1. UV-Vis absorption and PL spectra of $FAPbI_3$ film with d = 480nm at an excitation wavelength λ_e of 460nm.

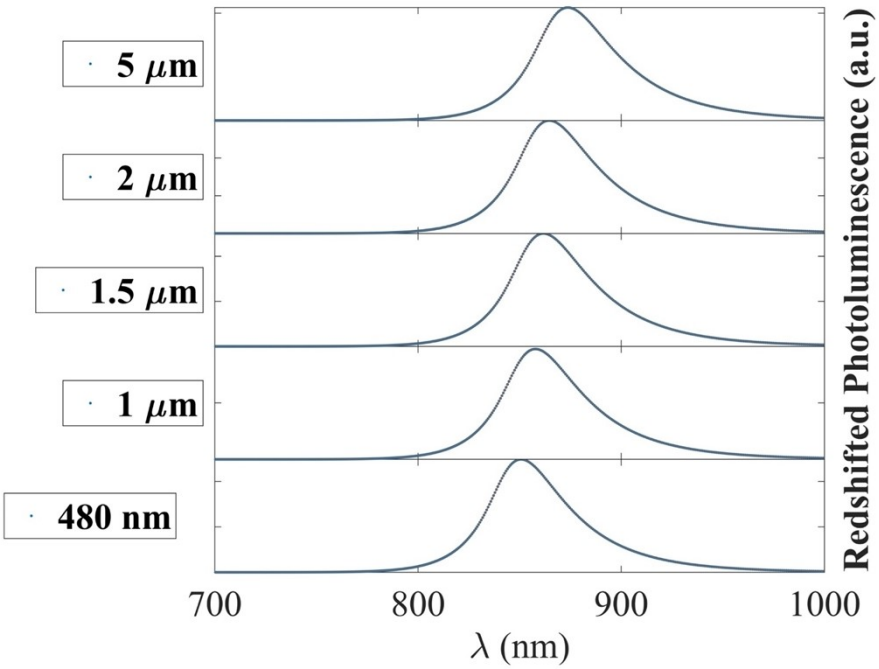

Fig.S2. The spectral redshift of $FAPbI_3$ film when λ_e = 460nm.

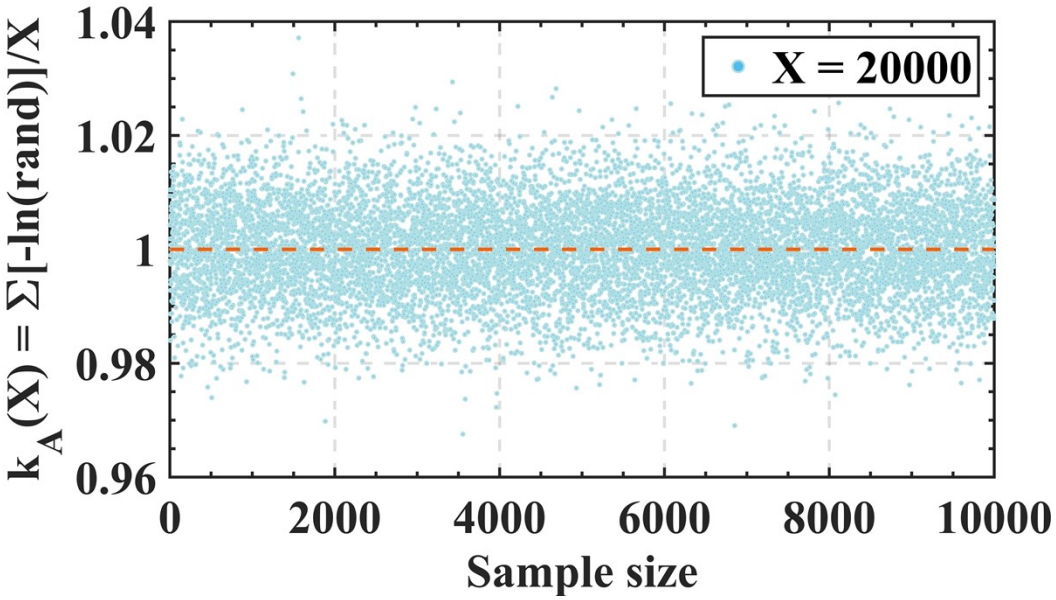

Fig.S3. Distribution of $k_A(X)$ when X = 20000 and sample size is 10000.

1. Redshift of the PL spectrum

As an intrinsic material, $FAPbI_3$ satisfies the condition of symmetric quasi-Fermi level splitting from the intermediate gap. Under this condition, the expression for the PL intensity (I_{PL}) has been proved by a previous theory [1]:

$$I_{PL}(E) = \frac{2\pi E^2}{h^3 c^2}(f_v - f_c)\frac{1 - \exp\left[-\alpha_{0K}(E)d\right]}{\exp\left(\frac{E - \Delta\mu}{k_B T}\right) - 1} \tag{1}$$

where h is the Planck constant, E is the photon energy, f_v is the occupation probability of valence band, f_c is the occupation probability of conduction band, $\Delta\mu$ is the measurement of quasi-Fermi-level splitting, $\alpha_{0K}(E)$ is the absorption coefficient accounting for the joint density of state (DOS):

$$\alpha_{0K}(E) = \frac{\alpha(E)}{(f_v - f_c)} \tag{2}$$

where $\alpha(E)$ represents the relationship between the absorption coefficient and E, which can be obtained from the data in the absorption spectrum. The excitation

wavelength λ_e used for the simulations was 460 nm, which is consistent with previous experiments [2] to obtain accurate UV-vis absorption and PL spectra of $FAPbI_3$ films (Figure.S1). On the premise of intrinsic material, (f_v - f_c) can be written as:

$$f_v - f_c = 1 - \frac{2}{\exp\left(\frac{E - \Delta\mu}{2k_B T}\right) + 1} \tag{3}$$

According to the above equations, we get the redshift of the PL spectrum, as shown in Fig.S2. The spectrum (Fig.S1) plotted by numerical calculations is very close to the PL spectrum measured by Lu et al [2]. This also proves the feasibility and correctness of the above calculations.

2. Calculation of some parameter values

2.1 Calculation of the absorption coefficient α

According to the Lambert-Beer law, the relationship between the absorption coefficient α and absorbance A is:

$$A = \varepsilon c d = \alpha M c d \tag{4}$$

where ε is the molar absorption coefficient, c is the substance concentration, d is the layer thickness, M is the molar mass. And the molar mass can be calculated by the following equation:

$$M = \frac{m}{n} = \frac{m}{cV} = \frac{\rho}{c} \tag{5}$$

where n is the amount of substance and ρ is the density of matter. Since the values of the parameters in Eq.4 are not easily accessible to us, we simplify Eq.4 by bringing in Eq.5 and end up with the following expressions:

$$\alpha = \frac{A}{\rho d} \tag{6}$$

We obtain the value of A for a specific wavelength of photons from the absorption spectrum, said spectrum being obtained with an effective light-receiving area (ELA) of $0.27 cm^2$ and a layer thickness of 480nm [2]. Then, we can obtain the value of α.

2.2 Calculation of the diffusion coefficient *D*

Since the Maxwell-Boltzmann distribution is followed in non-degenerate semiconductors, the non-equilibrium carrier mobility μ conforms to the Einstein relation that:

$$\frac{D}{\mu} = \frac{k_B T}{q} \tag{7}$$

where D is the coefficient of diffusion, k_B is the Boltzmann constant, T is the thermodynamic temperature, q is the charge.

2.3 Calculation of the recombination probability γ

Since $FAPbI_3$ is a direct-gap semiconductor material [3], the radiative recombination probability γ_r is usually higher than the non-radiative recombination probability γ_{nr}, both of them constitute the recombination probability γ which is determined by:

$$\gamma = \frac{k}{\Delta n} = \frac{k_r + k_{nr}}{\Delta n} = \gamma_r + \gamma_{nr} = \frac{1}{\tau} \tag{8}$$

where k is the recombination rate, Δn is the excess electron concentration produced by light injection, k_r is the radiative recombination rate, k_{nr} is the non-radiative recombination rate. According to the definition of internal photoluminescence quantum yield (QY_i), QY_i can be written as the ratio of k_r to k:

$$QY_i = \frac{k_r}{k} = \frac{\frac{k_r}{\Delta n}}{\frac{k}{\Delta n}} = \frac{\gamma_r}{\gamma} \tag{9}$$

and γ_r is:

$$\gamma_r = \gamma QY_i = \frac{QY_i}{\tau} \tag{10}$$

3. Constraints-Analysis

3.1 Carrier lifetime

According to the previous experimental results, the average carrier lifetime τ_0 in $FAPbI_3$ material is about 512ns [4], and the photocarrier lifetime τ_e has been proved to conform to the τ_0-related distribution [5] that:

$$\tau_e = -\tau_0 \ln(rand) \tag{11}$$

3.2 Bandgap & cutoff wavelength

Bound electrons can only change to free electrons when they absorb energy above the bandgap E_g, and the experimentally measured bandgap of $FAPbI_3$ material is about 1.52eV [24]. The cutoff wavelength λ_c corresponding to E_g can be calculated by the following equation:

$$\lambda_c = \frac{\hbar c}{E_g} \tag{12}$$

If photon wavelength $\lambda > \lambda_c$, this photon will not be absorbed.

3.3 Boundary conditions

For the $FAPbI_3$ film in vacuum in our simulation, we will describe the boundary conditions from the following three perspectives:

(1) Judgement of hitting the boundary or not

By comparing the ideal-position of the particle with the boundary coordinates, we can make a preliminary judgment on whether the particle collides with the top or bottom interfaces:

$$\begin{cases} d \le z^{ide} & hit\ the\ top\ interface \\ 0 < z^{ide} < d & without\ hitting\ boundary \\ z^{ide} \le 0 & hit\ the\ bottom\ interface \end{cases} \tag{13}$$

When a photon satisfies $z_p^{ide} \in (0, d)$ or the particle is a carrier, the z^{ide} is its actual-position z^{act} in this simulation. However, when the particle collides with the boundary, we need to calculate the maximum number of times N_{bm} that it is theoretically possible to hit the boundary.

(2) Number of times of collision to the boundary

In our simulation, no matter what kind of motion, it all can be written as:

$$z^{ide} = z' + l^{ide} cos\psi \tag{14}$$

where l^{ide} is a full step size, ψ is a random angle in the range $[0, \pi]$. To calculate the N_{bm}, the two cases of hitting the top and bottom interfaces need to be discussed separately, but their calculation procedures are very similar. Here, we take the top interface as an example:

The distance from the starting position to the top is:

$$z_{tt} = d - z' \tag{15}$$

And z^{ide} minus z_{tt} leaves a distance of z_{rest}, then we round and remainder the result of (z_{rest} / d):

$$\begin{cases} N_{bm} = \left[\frac{z_{rest}}{d}\right] \\ \Delta z = z_{rest} - N_{bm} d \end{cases} \tag{16}$$

Based on the parity of N_{bm}, we can calculate the position after all successful reflections:

$$z_f = \begin{cases} d - \Delta z\,, & N_{bm}\ is\ odd \\ \Delta z\,, & N_{bm}\ is\ even \end{cases} \tag{17}$$

In terms of the carriers, the z_f is considered to be the z^{act}. But for photons, only after a series of Fresnel formulas judgments, the z_f can be seen as the z^{act}.

(3) Judgments by Snell's law and Fresnel formulas

When a photon hits the interface, the incident angle θ_i and refractive angle θ_r will meet the Snell's law:

$$n_1 sin\theta_i = n_0 sin\theta_r \tag{18}$$

where n_1 is the refractive index of $FAPbI_3$ material, which is about 2.6 obtained from a previous study [11], and n_0 is the refractive index of air. Again, we will take the top interface as an example:

The trajectories of the incident, reflected and refracted rays are all in the same plane of photon motion, such that, no matter how many times the photon hits the boundary, the equation between the deflection angle θ and the incident angle θ_i is:

$$\begin{cases} \theta_r = \arcsin\left(n_1 sin\theta_i\right) \\ \theta_i = \theta \end{cases} \tag{19}$$

The critical angle θ_c can be calculated by the Snell's law:

$$\theta_c = \arcsin\left(\frac{n_0}{n_1}\right) \tag{20}$$

If $\theta_i \in (\theta_c, \pi/2)$, the total internal reflection (TIR) will occur.

If $\theta_i \in (0, \theta_c)$, then we need to calculate the internal reflection coefficient $R(\theta_i)$ for subsequent judgments. According to the Fresnel formulas, $R(\theta_i)$ is:

$$R(\theta_i) = \frac{1}{2}\left\{\left[\frac{\sin(\theta_i - \theta_r)}{\sin(\theta_i + \theta_r)}\right]^2 + \left[\frac{\tan(\theta_i - \theta_r)}{\tan(\theta_i + \theta_r)}\right]^2\right\} \tag{21}$$

and

$$\begin{cases} rand > R(\theta_i), & photon\ transmitted \\ rand \le R(\theta_i), & photon\ reflected \end{cases} \tag{22}$$

In the case of multiple collisions, since θ_i remains constant, we assume that:

$$\eta_1 = \{rand_1 \le R(\theta_i)\}$$

$$\eta_2 = \{rand_2 \le R(\theta_i)\}$$

...

$$\eta_{N_{bm}} = \{rand_{N_{bm}} \le R(\theta_i)\}$$

$$\Omega = \{\eta_1, \eta_2, \ldots \eta_{N_{bm}}\} \tag{23}$$

where event η_k represents the reflection of a photon after its k-th collision to the boundary, $rand_1 \ldots rand_k$ denotes k uncorrelated random numbers, and the most collision events that can be achieved in a single step constitute the sample space Ω. Only when the reflection occurs in all collision events, can the photon finally stay in the $FAPbI_3$ film. On this condition, the final-position is equal to its actual-position:

$$\begin{cases} \bigcap_{k=1}^{N_{bm}} \eta_k = 1, & z_f = z^{act} \\ \bigcap_{k=1}^{N_{bm}} \eta_k = 0, & photon\ transmitted \end{cases} \tag{24}$$

3.4 Simulation time

In the simulation, the calculation method of time t always follows:

$$t = \frac{d^{act}}{v} \tag{25}$$

where d^{act} represents the actual-distance traveled by the particle. The actual-distance of photon's motion is recorded as l^{act}, and the actual-distance for carrier is L^{act} which meets:

$$L^{act} = L^{ide} = L \tag{26}$$

The calculation of l^{act} can be divided into two categories:

(1) Photon does not hit the boundary or Photons hits the boundary but eventually stay in the film

Under these circumstances, we can draw the same conclusion as L^{act}:

$$l^{act} = l^{ide} = l \tag{27}$$

(2) Photon eventually transmits from the film

It is necessary to use the circular structure to obtain the corresponding number of times $k = k_0$ when η_k is firstly equal to 0, and the l^{act} (take the first collision to the top as an example) is:

$$l^{act} = \frac{z_{rest}}{cos\theta} + (k_0 - 1)\frac{d}{cos\theta} \tag{28}$$

According to the refractive index of the $FAPbI_3$ material, it is not difficult for us to calculate the velocity of photons v_p. In our simulation, carriers are considered to follow the Maxwell's velocity distribution law and the carrier velocity v_c is sampled as $2.618*10^5$ m/s.

4. Discussion on the correlation between I_{PR} and A_{CL}

When the layer thickness is constant, Fig.4(b) shows the variation of I_{PR} and A_{CL} with QY_i, where I_{PR} is proportional to the radiative recombination probability γ_r. According to the formula for γ_r (Eq.10 in SI), the expression of I_{PR} can be written as:

$$I_{PR} = k_I \frac{QY_i}{\tau_{avg}} \tag{29}$$

where k_I is a value independent of QY_i and τ. According to the analysis of Fig.4(a), we can obtain the following expressions:

$$I_{PR} = k_I(P_{esc}, \alpha)\frac{QY_i}{\tau_{avg}} = k_I(d)\frac{XQY_i}{\sum_{j=1}^{X}\tau_j} \tag{30}$$

According to the analysis in Fig.4(a), we can look for a connection between A_{CL} and material parameters with the help of I_{PL}:

$$\begin{aligned} A_{CL} &= \frac{(1+I_{PR})\sum_{i=1}^{X}\left[-\tau_0 \ln(rand_i)\right]}{X\tau_0} \\ &= \frac{\sum_{i=1}^{X}\left[-\ln(rand_i)\right]}{X}\left[1 + k_I(d)\frac{XQY_i}{\sum_{j=1}^{X}\tau_j}\right] \\ &= k_A(X)\left[1 + k_I(d)\frac{XQY_i}{\sum_{j=1}^{X}\tau_j}\right] \end{aligned} \tag{31}$$

When $QY_i = 0$, the radiative recombination probability of photocarriers is 0 at this time, the total number of new photons produced N_{np} is 0, the number of cycle elements in a total cycle n is 0, therefore the corresponding I_{PR} is always 0, as shown in Fig.4(b). Also, since all incident photons produce only one pair of carriers, a round of total

photon cycle always contains only one lifetime element, i.e., $\tau = \tau_e$, and the value of $(\tau/\tau_0)_{avg}$ is about 1 , as shown in Fig.4(b).

When $QY_i = 0$, Eq.31 can be written as:

$$A_{CL} = k_A(X) \tag{32}$$

The distribution of $k_A(X)$ when $X = 10000$ and the sample space is 10000 is shown in Fig.S3, from which we can find that: as X is larger, the mean value of $k_A(X)$ is closer to 1, which is consistent with our simulation results and further validates Eq.31.

When QY_i increases, the carrier of either lifetime has an increased γ_r compared to the original one. When the value of X is large enough, the average value of N_{np} increases, which makes the probability of a new photon regeneration cycle occurring higher, and the value of n_{avg} increases, as shown in Fig.4(b). Accordingly, A_{CL} increases slowly, but this increase is less clearly reflected in Fig.4(b) due to the instability of the fluctuation amplitude.

5. Table of parameter values

Name	Value	Unit
Temperature (T)	298.15	K
Boltzmann constant (k_B)	$8.617*10^{-5}$	eV/K
Planck constant (h)	$6.63*10^{-34}$	J*s
Electron charge (q_e)	$1.6*10^{-19}$	C
Bias voltage (V)	1.4	V
PN junction thickness ($d_{p,n}$)	$3*10^{-6}$	cm

Thickness of $FAPbI_3$ layer (d) [2]	480	nm
Refractive index of $FAPbI_3$ [11]	2.6	--
Internal photoluminescence quantum yield (QY_i)	0.7	--
Excitation wavelength (λ_{ex}) [2]	460	nm
Irradiance of sunlight (I) [2]	100	mW/cm^2
Effective light-receiving area (S) [2]	0.27	cm^2
Intrinsic carrier density (n_i) [10]	$2.3*10^5$	cm^{-3}
Coefficient of diffusion (D)	0.5	cm^2/s
First-order SRH recombination rate constant (k_1) [10]	$2*10^5$	s^{-1}
Internal radiative recombination rate constant (k_2^{int}) [10]	$2*10^{-10}$	$cm^{-3}*s^{-1}$
Third-order Auger recombination rate constant (k_3) [10]	10^{-28}	cm^6/s
Average carrier lifetime of $FAPbI_3$ (τ_0) [4]	512	ns
Forbidden band width of $FAPbI_3$ (E_g) [2]	1.52	eV
Quasi-Fermi energy level splitting (QFLS, $\Delta\mu$) [12]	1.28	eV
Acceptor or donor concentration in the PN junction (N)	$1.1*10^5$	cm^{-3}
n-i-p type FA^+ PSC: glass / ITO / SnO_2 / $FAPbI_3$ / Spiro-OMeTAD /Au [2]		
Refractive index of glass substrate (SLS glass) for	1.52	--

visible wavelengths		
Refractive index of conductive light-transmitting film (ITO) at 460 nm excitation wavelength	1.91	--
Refractive index of ETL (SnO_2)	1.997	--
Thickness of ETL (SnO_2) [2]	20	nm
Refractive index of HTL (Spiro-OMeTAD)	1.744	--
Thickness of HTL (Spiro-OMeTAD) [2]	200	nm
Short-circuit current density (J_{sc}) [2]	24.4	mA/cm^2
Fill factor (FF) [2]	81.3	%
p-i-n type MA^+ PSC: glass / ITO / PEDOT:PSS / $MAPbI_3$ / $PC_{61}BM$ / Au [7]		
Refractive index of glass substrate (SLS glass) for visible wavelengths	1.52	--
Refractive index of conductive light-transmitting film (ITO) at 460 nm excitation wavelength	1.91	--
Refractive index of HTL (PEDOT:PSS) at 460 nm excitation wavelength [6]	1.60	--
Thickness of HTL (PEDOT:PSS) [7]	200	nm
Refractive index of $MAPbI_3$ at 460 nm excitation wavelength [8]	2.35	--
Average carrier lifetime of $MAPbI_3$ [9]	100	ns
Forbidden band width of $MAPbI_3$	1.55	eV

Thickness of $MAPbI_3$ [7]	300	nm
Refractive index of ETL ($PC_{61}BM$) at 460 nm excitation wavelength [6]	1.61	--
Thickness of ETL ($PC_{61}BM$) [7]	200	nm
Short-circuit current density (J_{sc}) [7]	20.9	mA/cm^2
Fill factor (FF) [7]	79	%

6. Monte Carlo simulation code (MATLAB) for photon regeneration effects in $FAPbI_3$ layers (excluding HTL, ETL) in vacuum

```
%{
ASSUMPTIONS:
(1) The distribution of light in the model is assumed to be static.
(2) Scattering losses and polarization of light are neglected in the calculations.
(3) The FAPbI_{3} film is considered to be an isotropic intrinsic semiconductor
material.
(4) Under room temperature and low-level injection conditions, the FAPbI_{3} film
can be regarded as a non-degenerate semiconductor.
%}

function [mean_ratio] = tau_air(X, d, n, n0, alpha, tau0, D, QY1)
% X is the number of incident photons in simulation.
% d is the thickness of the FAPbI3 layer (nm).
% n is the absolute refractive index of FAPbI3.
```

```
% n0 is the relative refractive index of the medium (vacuum) around FAPbI3 layer.

% alpha is the absorption coefficient of FAPbI3.

% tau0 is the average lifetime of experimentally measured carriers (ps).

% D is the diffusion coefficient of FAPbI3 material (cm^2/s).

% QYi the internal photoluminescence quantum yield



t = 0;

% Initial time of the simulation

Tau = zeros(X, 1);

Ione_s = zeros(X, 1);

% Define an empty set of specified size to reduce computing time.

for i = 1:X

    ii = 500;

    % Upper limit of the number of photon regeneration cycles in FAPbI3 materials

    j = 1;

    % Counter of photon regeneration cycles

    z = 0;

    % Initial position

    theta1 = rand*pi;

    % Initial emission angle

    h = 4.136*10^(-15);

    % Planck's constant (eV*s)
```

```
c = 2.998*10^8;

% Speed of light (m/s)

v_p = (c*10^9*10^(-12))/n;

% Photon velocity in FAPbI3 material (nm/ps)

k = 8.617*10^(-5);

% Boltzmann's constant (eV/K)

T = 298.15;

% The standard temperature assumed in the simulation (K)

E_g = 1.52;

% Forbidden band width of FAPbI3 material (eV)

alpha1 = alpha;

sig_tau = 0;

% sig_tau is the sum of all derived carrier lifetimes generated by each single photon,

% not the sum of all carrier lifetimes for the entire simulated process.


%% PHOTON MOTION

while(ii > 0)

    z1 = z;

    % Save information about the position of the photon at the previous moment.

    alpha2 = alpha1;

    % Record the last absorption coefficient.

    l = -log(rand)/alpha2;
```

```
% Initial absorption distance
theta2 = theta1;
if(l <= 0)
    continue
else
    z2_theo = z1+l*cos(theta2);
    % Information on the ideal position of the photon at the next moment.
    if(z2_theo >= d)
        % Photon hitting the top interface of the FAPbI3 material
        p_x0 = d-z1;
        p_x1 = l*cos(theta2);
        p_x2 = p_x1-p_x0;
        p_x3 = mod(p_x2, d);
        n_abs1 = fix(p_x2/d);
        k3 = (sin(theta2)*n)/n0;
        if((k3 < -1) || (k3 > 1))
            % total internal reflection (TIR)
            if(n_abs1 == 0)
                % Photons are absorbed by the FAPbI3 material after only one
reflection.
                t = t + (l/v_p);
                z2 = d - p_x3;
```

```
                else
                    % Photons undergo more than one reflection process before being
absorbed.
                    t = t + (l/v_p);
                    if(mod(n_abs1, 2) == 1)
                        z2 = d - p_x3;
                    else
                        z2 = p_x3;
                    end
                end
            else
                photon_ref_angle = asin(k3);
                % Refraction angle
                floor_ref = 1/2*((sin(theta2-
photon_ref_angle)^2)/(sin(theta2+photon_ref_angle)^2))+...
                    ((tan(theta2-photon_ref_angle)^2)/(tan(theta2+photon_ref_angle)^2));
                % Fresnel coefficient
                Judge1 = rand;
                if(Judge1 >= floor_ref)
                    % Refraction occurs when photon first reaches the top interface
                    t = t + ((p_x0/cos(theta2))/v_p);
                    Tau(i, 1) = sig_tau;
```

```
                Ione_s(i, 1) = t;
                break
            else
                % The photon is reflected at the top interface for the first time
                % and continues to propagate in the medium.
                if(n_abs1 == 0)
                    t = t + (l/v_p);
                    z2 = d - p_x3;
                else
                    % Photons will reach the material boundary more than once.
                    for photon_i1 = 1:n_abs1
                        Judge_photon_i1 = rand;
                        res1 = (Judge_photon_i1 < floor_ref);
                        RES1 = zeros(1, n_abs1);
                        RES1(photon_i1) = res1;
                        % Storage of judgment results, where the elements are
logical values
                    end
                    if(mean(RES1) ~= 1)
                        % Refraction occurs in the case where the photon
reaches the boundary
                        K0 = find(RES1 == 0, 1);
```

```
                    t = t + K0*((p_x0/cos(theta2))/v_p);
                    Tau(i, 1) = sig_tau;
                    Ione_s(i, 1) = t;
                    break
                else
                    t = t + (l/v_p);
                    if(mod(n_abs1, 2) == 1)
                        z2 = d - p_x3;
                    else
                        z2 = p_x3;
                    end
                end
            end
        end
    end
elseif(z2_theo <= 0)
    % Photon hitting the bottom interface of the FAPbI3 material
    down_theta = pi-theta2;
    % Incidence angle
    p_x4 = z1;
    p_x5 = l*cos(down_theta);
    p_x6 = p_x5-p_x4;
```

```
                p_x7 = mod(p_x6, d);
                n_abs2 = fix(p_x6/d);
                k4 = (sin(down_theta)*n)/n0;
                if((k4 < -1) || (k4 > 1))
                    if(n_abs2 == 0)
                        t = t + (l/v_p);
                        z2 = d - p_x7;
                    else
                        t = t + (l/v_p);
                        if(mod(n_abs2, 2) == 1)
                            z2 = d - p_x7;
                        else
                            z2 = p_x7;
                        end
                    end
                else
                    down_ref_angel = asin(k4);
                    down_ref = 1/2*((sin(down_theta-
down_ref_angel)^2)/(sin(down_theta+down_ref_angel)^2))+...
                        ((tan(down_theta-
down_ref_angel)^2)/(tan(down_theta+down_ref_angel)^2));
                    Judge2 = rand;
```

```
if(Judge2 >= down_ref)
    t = t + ((p_x4/cos(down_theta))/v_p);
    Tau(i, 1) = sig_tau;
    Ione_s(i, 1) = t;
    break
else
    if(n_abs2 == 0)
        t = t + (l/v_p);
        z2 = d - p_x7;
    else
        for photon_i2 = 1:n_abs2
            Judge_photon_i2 = rand;
            res2 = (Judge_photon_i2 < down_ref);
            RES2 = zeros(1, n_abs2);
            RES2(photon_i2) = res2;
        end
        if(mean(RES2) ~= 1)
            K1 = find(RES2 == 0, 1);
            t = t + K1*((p_x4/cos(down_theta))/v_p);
            Tau(i, 1) = sig_tau;
            Ione_s(i, 1) = t;
            break
```

```
                else
                    t = t + (l/v_p);
                    if(mod(n_abs2, 2) == 1)
                        z2 = d - p_x7;
                    else
                        z2 = p_x7;
                    end
                end
            end
        end
    end
else
    % Photon does not collide with the FAPbI3 material interface and continue
to propagate through the material.
    z2 = z2_theo;
    t = t + l/v_p;
end


%% CARRIER MOTION
tau = -tau0*log(rand);
% Generation of carriers with random lifetimes (ps)
if(tau <= 0)
```

```
            continue
        else
            sig_tau = sig_tau + tau;
            Gama = t/tau;
            % Chance of recombination of non-equilibrium carriers in t.
            %%
            % The carriers assumed in this simulation do not move on the surface of
the material
            % and reflect when they reach the boundary.
            t3 = tau;
            % A recombination event occurs only when the time t is greater than tau,
            % and no new random recombination distances are generated until then.
            v_carrier = (2.618*10^5)*10^9*10^(-12);
            % The rate of average electron motion obtained by sampling using Monte
Carlo simulation.
            dif_avg = ((D*10^2)*tau)^0.5;
            % Mean free path of carriers (nm)
            del_t = (dif_avg/v_carrier);
            % del_t is the time taken for the carriers to travel the distance dif_avg in
the material,
            % i.e. the time taken to reach the recombination position (if they can be
recombined).
```

```
theta_c = rand*pi;
% Angle between the direction of carrier motion and z-axis
combination_judge = rand;
radiation_judge = rand;
if (combination_judge <= Gama)
    % Recombination occurs
    t = t+t3+del_t;
    % When carriers are recombined, their lifetime is counted in the total
lifetime,
    % and if recombination does not occur, the carrier lifetime is uncertain.
    if (radiation_judge <= QYi)
        % Radiative recombination occurs
        z3_theo = z2 + dif_avg * cos(theta_c);
        % z-coordinate of the ideal position of the carriers where radiative
recombination occurs
        if(z3_theo >= d)
            c_x0 = d-z2;
            c_x1 = dif_avg*cos(theta_c);
            c_x2 = c_x1-c_x0;
            c_x3 = mod(c_x2, d);
            n_dif1 = fix(c_x2/d);
            if(mod(n_dif1, 2) == 0)
```

```
        z3 = d - c_x3;
    else
        z3 = c_x3;
    end
    j = j+1;
    ii = ii-1;
    % Radiative recombination occurs, end of one photon
regeneration cycle.
elseif(z3_theo <= 0)
    theta_pic = pi-theta_c;
    c_x4 = z2;
    c_x5 = dif_avg*cos(theta_pic);
    c_x6 = c_x5 - c_x4;
    c_x7 = mod(c_x6, d);
    n_dif2 = fix(c_x6/d);
    if(mod(n_dif2, 2) == 1)
        z3 = d - c_x7;
    else
        z3 = c_x7;
    end
    j = j+1;
    ii = ii-1;
```

```
else
    z3 = z3_theo;
    j = j+1;
    ii = ii-1;
end

%% NEW PHOTON MOTION
del_u = 1.28;
% Quasi-Fermi energy level splitting (QFLS,Δμ) (eV)
syms x;
double E;
J_em = 17.39*10^(-3)*10^4;
% Electroluminescence current density (A/m^2)
k0 = 1000000000000000*1739^(1/2)*10000^(1/6)*exp(-1/2);
% The sign of k0 can be either positive or negative.
% k1 = -(exp(-1/2)*((62494443*10^(27/28)*33^(1/28))/25000)^(1/2))/2;
k2 = (9194277161966095*log(10000^(1/3)))/18014398509481984;
% k3 = (4597138580983047*log((10^(27/28)*33^(1/28))/10))/36028797018963968;
% k0,k1,k2,k3 are the PL spectral coefficients obtained by MATLAB curve fitting.
```

```
E_pr = linspace(0, 2, 5000);
Q1 = 1/(max((((2*pi).*E_pr.^2)./(h^3*c^2)).*(exp(-(E_pr-del_u)./(k*T))).*(1-exp(-(J_em./((k0)^2./exp(((k2.*E_pr)./(k*T))-1))).*(d*10^(-9))))));
E = vpasolve(rand == Q1*(((2*pi)*x^2)/(h^3*c^2))*(exp(-(x-del_u)/(k*T)))*(1-exp(-(J_em/((k0)^2/exp(((k2*x)/(k*T))-1)))*(d*10^(-9)))));
% The corresponding random photon energy E is generated from


% the random PL Intensity according to the PL spectrum.
sz = size(E);
if (isempty(E) | (sz > 1))
    % E is unsolved or non-single element array
    continue
else
    lambda0 = (1.24/E_g)*10^3;
    % Cut-off wavelength of FAPbI3 material (815.7895 nm)
    lambda = (h*c)/E;
    % Photoluminescence photon wavelength (m)
    Lam3 = double(lambda*10^9);
    if ((Lam3 > lambda0) | (Lam3 < 400))
        % The photon will not be absorbed by the FAPbI3 material

        % and will eventually refract from the material, and the
```

photon regeneration process will end.

```
                Tau(i, 1) = sig_tau;
                Ione_s(i, 1) = t;
                break
            else
                data = xlsread('A2.xlsx');
                % Read in the data of FAPbI3 absorption spectrum
obtained from Getdata software analysis
                [m1, ~] = find(data(:, 1) <= Lam3);
                M1 = min(m1);
                if (isempty(M1))
                    continue
                else
                    alpha3 = 10^(-2) * data(M1, 2);
                    alpha1 = alpha3;
                    z = z3;
                    theta3 = rand*pi;
                    theta1 = theta3;
                end
            end
            % Since the materials used in the simulation are assumed to
be analytically pure,
```

```
                                % the effect of impurities can be disregarded in the calculation
of the absorption coefficient.
                                    end
                                else
                                    % Annihilation by non-radiative recombination of carriers
                                    Tau(i, 1) = sig_tau;
                                    Ione_s(i, 1) = t;
                                    break
                                end
                            else
                                % The carrier does not undergo a recombination process,
                                % and the photon regeneration cycle is not yet over until recombination
occurs.
                                continue
                            end
                        end
                    end
                end
            end
        end
    end
end
ratio = Tau./tau0;
mean_ratio = mean(ratio);
% The value of (tau/tau0)_{avg} (i.e., A_{CL}) for a specific d (or QYi) is calculated by
```

mean_ratio.

end

References

[1] J. K. Katahara and H. W. Hillhouse. Journal of Applied Physics, 2014, **116**, 173504.

[2] H. Z. Lu, Y. H. Liu, et al. Science, 2020, **370**, 6512.

[3] X. Lu, Z. Zhao, K. Li, S. Wei, et al. Acta Physico-Chimica Sinica, 2016, **32**, 1439-1445.

[4] L. Q. Xie, L. Chen, Z. A. Nan, et al. Journal of the American Chemical Society, 2017, **139**, 3320-3323.

[5] B. Wu, L. Li, Y. Wang, et al. Opt. Lett., 2021, **46**, 2988-2991.

[6] G. L. Li, J. M. Zhong, et al. Laser & Optoelectronics Progress, 2016, **53**, 043101.

[7] J. H. Heo, H. J. Han, D. Kim, et al. Energy Environ. Sci., 2015, **8**, 1602.

[8] L.J. Phillips, A. M. Rashed, et al. Solar Energy Materials and Solar Cells, 2015, **147**, 327-333.

[9] C. H. Teh, R. Daik, E. L. Lim, et al. J. Mater. Chem. A, 2016, **4**, 15788.

[10] R. Brenes, M. Laitz, J. Jean, et al. Phys. Rev. Applied, 2019, **12**, 014017.

[11] S. Lee, K. Choi, C. H. Min, et al. MRS Bulletin, 2020, **45**, 439–448.

[12] I. L. Braly, D. W. deQuilettes, L. M. Pazos-Outón, et al. Nature Photon, 2018, **12**, 355–361.