ARTICLE
Carrier Recombination of Organic-Inorganic 3D Halide Perovskite Single Crystals†

Chao Hea,b, Xia Li b, Yu-hao Wub, Hai-Lung Dain, Dong-feng Zhao a, Yang Chen a

a. Hefei National Laboratory For Physical Sciences at the Microscale and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China
b. Department of Chemistry, Temple University, Philadelphia 19122, Pennsylvania, United States of America

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Organic-inorganic 3D halide perovskite materials recently have become one of the major players of hybrid semiconductors for photovoltaic and optoelectronic applications. The diffusion length of charge carriers is one of the critical parameters for justifying photovoltaic applications of materials. In this work, we propose a realistic kinetic model in order to fully understand carrier relaxation rate of photoexcited organic perovskites with a negligible exciton formation in photoluminescence lifetime measurements. We find that the extraction of carrier relaxation rate has to be made from multiplefluence-dependent photoluminescence lifetime measurements with global fittings, instead of a traditional single-fluence lifetime measurement. To demonstrate the validity of the model, two kinds of p-doped CH₃NH₃PbI₃ single crystals were grown up by intentionally increasing defects. Global fittings of the kinetic model to the two kinds of single crystals yield doping density, trap density, and recombination constants. Our methodology provides a self-contained approach to determine diffusion lengths of organic 3D halide perovskite materials.

Key words: Perovskite, CH₃NH₃PbI₃ single crystal, Photoluminescence lifetime, Diffusion length

I. INTRODUCTION

In the last several years, organic-inorganic metal-halide perovskites AMX₃ (A=organic ion; M=Ge²⁺, Sn²⁺, Pb²⁺; X=Cl, Br, I) have attracted tremendous attention due to its photovoltaic (PV) applications [1−16]. The power conversion efficiency (PCE) of the perovskite-based solar cells has reached up to 20% [17, 18]. The halide perovskite materials feature a number of optical, electronic, and engineering properties including high absorption coefficients, long carrier diffusion lengths, solution-processed, etc. [19, 20]. Of all the optical properties, the diffusion length (DL) of carriers is one of the most critical parameters for justifying photovoltaic applications of the materials [2, 10, 14, 20]. For these reasons, it is desirable to explore carrier recombination mechanisms behind its high PCE. Despite tremendous efforts, the understandings of carrier recombination of the hybrid halide perovskites are still lacking.

Carrier recombination of hybrid halide perovskites is intrinsically similar to that of inorganic semiconductor [21]. Like in inorganic semiconductors, photoexcited electrons and holes in halide perovskite materials behave as free carriers due to their weak binding energy [19, 21, 22]. As a result, the rate of carrier recombination determines the diffusion length of carriers in the materials [20, 23]. The determination of the charge recombination rate for the perovskite materials is based primarily on four experimental techniques, including time-resolved photoluminescence measurements (TRPL) [19, 20], time-resolved microwave conductance (TRMC) [22], transient photovoltage measurements [24−26], and time-resolved THz measurements (TR-THz) [27]. Time-dependent signals from the above-mentioned measurements are often employed to extract the lifetime for charge recombination in organic perovskites [1]. Although time-dependent traces appear to exhibit more than one relaxation manner, a single recombination process is often assumed to describe the carrier dynamics in most cases [11]. As a matter of fact, the carrier recombination after photoexcitation is manifested in dynamical behaviors of electrons, holes, and traps, leading to rich kinetic information in the perovskite materials [19, 22].

Previous theoretical treatments for charge recombin-
ation in halide perovskite materials consists primarily of the following models [19, 22, 27]. In an early work, an explanation fluorescence decay in low- and high-fluence regimes quantifies fluorescence yield [19]. In this model, the formation and dissociation processes of exciton in photoexcitation of halide perovskite were fully considered. However, it is not feasible to truly extract the rate of carrier recombination due to too many parameters in the kinetic model. Based on time-resolved optical pump-Terahertz (TR-THz) probe measurements, a simplified minority-carrier recombination model was proposed to explain time-dependent THz responses of halide perovskites [27]. In fact, the minority-carrier recombination model holds well in case when materials are heavily-doped semiconductors and when high-level injections occur. As such, many processes are not included. Another generic kinetic model was proposed to describe both TRMC and TR-PL measurements [22]. It seems that the model could describe TRMC measurements well but fail to fit time-resolved photoluminescence data. Of them, TR-PL is the most used technique for obtaining diffusion length [19, 20].

Here we shall present a full description of carrier lifetimes for organic 3D halide perovskites in a free carrier picture. In this work, we proposed a realistic kinetic model for photoluminescence lifetime measurements for both low-trap and high-trap organic perovskites with a negligible exciton formation in the case of intrinsic organic semiconductor. To demonstrate the validity of the model, we grew CH$_3$NH$_3$PbI$_3$ single crystals with two different methods. We measured photoluminescence lifetimes at different fluences before the annihilation process takes place. Global fittings of the kinetic model to the two kinds of single crystals yield doping density, trap density, and recombination rate constants. Our methodology provides a self-contained approach to determine diffusion length of organic 3D halide perovskite materials.

II. EXPERIMENTS

A. Preparations of single crystals

CH$_3$NH$_3$X was prepared by reacting CH$_3$NH$_2$ and HX with the molar ratio of 1:2:1. The HX (HCl 11 mL, 38% in water, EMD; HBr 15.18 mL, 48% in water, Aldrich; HI 17.7 mL, 57% in water, Alfa Aesar) was added dropwise into the CH$_3$NH$_2$ (33% in ethanol, Aldrich) in a flask with stirring in an ice bath for 2 h, the mixture solution was evaporated at about 65 °C to remove the solvent. The resulting snow-white product CH$_3$NH$_3$X (X=Cl, Br, I) was recrystallized from ethanol and dried in a vacuum oven at 60 °C overnight.

1. Fast crystallization of CH$_3$NH$_3$PbI$_3$ crystal

Preparation of optimal precursor solution: CH$_3$NH$_3$I and PbI$_2$ (1:1 by molar, PbI$_2$, 2 mol/L) was dissolved in gamma-butyrolactone (GBA). The solution of CH$_3$NH$_3$PbI$_3$ was heated and kept at about 100 °C for overnight, then large number of small crystals can be obtained. To get larger crystals, just one crystal was used as a seed placed into the fresh precursor solution, heated and kept at 100 °C for a desired size crystal growing, and larger crystals needed longer time.

2. Slow crystallization of CH$_3$NH$_3$PbI$_3$ crystal

5.86 g lead (II) acetate trihydrate (99%, Sigma Aldrich) was dissolved in 20 mL of HI (57wt.% aq. solution, Alfa Aesar) in a 100 mL flask heated at 100 °C with constantly stirring. 1.33 mL CH$_3$NH$_2$ (40 wt.% aq. solution, Sigma Aldrich) was added into the solution, and numerous small crystals were precipitated, which were kept for 30 min stirring. Raw crystals and mother solution were transferred into a 20 mL vial, in which a piece of glass inserted with 3/4 in and 1/4 out of the sealed vial. The bottom of the vial was kept at 65 °C for 4 days for crystals growing. A small temperature gradient between bottom and top of the solution induced sufficient convection to homogeneous crystal growth. At the end, dense and tiny (∼μm of size) crystals on the glass were harvested.

B. Photoluminescence and lifetime measurements

The optical absorption measurements of CH$_3$NH$_3$PbI$_3$ single crystals were performed on a home-built microscope as described elsewhere [28–30]. Briefly, it was equipped with an intensity-tunable halogen-lamp (Lumina-I) as an unpolarized broadband radiation source. A polarizer was used to select polarizations from the unpolarized UV-Vis lamp. An objective with ×10 magnification subsequently focused the selected polarized light onto a CH$_3$NH$_3$PbI$_3$ single crystal at normal incident angle. Transmitted light was then collected by a condenser and focused into a grating spectrometer (Andor Shamrock 500 with grating blazed at 500 nm, 150 groove/mm), followed by a thermo-cooled CCD (Newton, Andor). Prior to linear absorption measurements, the CH$_3$NH$_3$PbI$_3$ single crystal needs to be located. To accomplish this, we used illumination from a LED pen. Two beam splitters were placed in between the polarizer and the objective. One of them (BS$_2$) functioned to combine the UV-Vis light from the lamp and the illumination light into a collinear light path. The light reflected back from the sample is captured by a camera (Thorlabs, Compact USB 2.0 CMOS Camera) after being reflected by the other beam splitter (BS$_1$). Since the illumination light is collinear with UV-Vis light, we could precisely position the sample under the objective.

III. CHARGE CARRIER RECOMBINATION MECHANISMS

Generally, carrier recombination includes nonradiative trapped-assisted recombination ($k_{nr}$), radiative bi-

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molecular recombination \((k_r)\). In addition, nonradiative carrier-carrier annihilation recombination could occur at high fluence. Electrons and holes could recombine in both nonradiative and radiative manners. In addition to nonradiative surface recombination, there are two other kinds of nonradiative recombination processes, including SRH trap-assisted nonradiative recombination at low fluence and carrier-carrier Auger recombination at high photoexcitation fluorescence. In order to clarify the physical picture for the photoexcited carrier dynamics, we consider the two commonly encountered situations, including “Monomolecular” and “Bimolecular” regimes. The former depends on the trap cross-section, energetic depth, trap density, and energy distribution, and the latter is involved in three body interactions. A realistic kinetic model for relaxation processes of n-type hybrid perovskites is sketched in FIG. 1. Upon photoexcitation, the electrons in the conduction band (CB) relax by trap-assisted monomolecular recombination \(k_T\), electron-hole bimolecular recombination \(k_b\), and annihilation recombination \(k_A\). Meanwhile, the holes in the valence band (VB) relax by escaped electron-hole recombination \(k_R\), electron-hole bimolecular recombination \(k_b\), and annihilation recombination \(k_A\). The trapped-assisted recombination is related to trap densities and trapping rate constant. Bimolecular recombination depends on trap, carrier densities, and doping level of materials. Here we write three differential equations to describe dynamics of free electrons, free holes, and trap electrons for organic-inorganic hybrid semiconductors with negligible photogenerated excitons upon photoexcitation.

\[
\frac{dn_e(t)}{dt} = G(t) - k_T n_e(t)(N_T - n_e(t)) - k_b n_h(t). \tag{1}
\]

\[
\frac{dn_h(t)}{dt} = G(t) - k_b n_h(t)(n_e(t) + n_0) - k_R n_e(t), \tag{2}
\]

\[
\frac{dn_t(t)}{dt} = k_R n_t(t)(N_T - n_t(t)) - k_R n_t(t)(n_e(t) + n_0). \tag{3}
\]

where \(G(t)\) represents the photoexcited formation of electron and hole carriers, \(n_e(t)\), \(n_h(t)\), \(n_t(t)\) describe the time-dependent concentrations of the free electrons, free holes, and trapped electrons, \(N_T\) is the maximum accessible concentration of trap states, \(n_0\) corresponds to n-doping electron concentrations, \(k_b\), \(k_T\), \(k_R\), and \(k_A\) represent the rate constants for radiative bimolecular recombination (band-to-band), electron trap filling, and trap escaping, and three-body Auger recombination, respectively. Our crystal is n-doping. Here we just show the situation of p-doping. For n-type doping, all the terms related to \(n_h(t)\) are changed to \(n_e(t)+h_0\) (n-doping electron concentration) and those related to \(n_e(t)+n_0\) to \(n_e(t)\). It is noted that the time dependent photoluminescence intensity \(I(t)\) is proportional to \(n_e(t)(n_e(t)+n_0)\). As such, one has to know \(n_e(t)\) and \(n_h(t)\) in order to obtain \(n_h(t)\) and \(n_h(t)\) in order to obtain \(k_b\), \(k_T\), \(k_R\), \(k_A\), \(N_T\), and \(h_0\).

A. In a linear regime (low fluence)

At low fluence, the fluorescence intensity is proportional to applied light intensity. Therefore, Eqs.(1–3) could be simplified to exclude annihilation. The time-dependent concentrations of free electrons, free holes, and trapped electrons are, therefore, given by,

\[
\frac{dn_e(t)}{dt} = G(t) - k_T n_e(t)(N_T - n_e(t)) - k_b n_h(t)(n_e(t) + h_0) \tag{4}
\]

\[
\frac{dn_h(t)}{dt} = G(t) - k_b n_h(t)(n_e(t) + h_0) - k_R n_e(t) \tag{5}
\]

\[
\frac{dn_t(t)}{dt} = k_T n_t(t)(N_T - n_t(t)) - k_R n_t(t)(n_e(t) + h_0) \tag{6}
\]

There is no analytical solution to Eqs.(4–6) for \(n_e(t)\), \(n_h(t)\), and \(n_t(t)\). In order to extract \(k_b\), \(k_T\), \(k_R\), \(N_T\), and \(h_0\), one has to make a numerical evaluation of Eqs.(4–6) with time-dependent photoluminescence data. From Eqs.(4–6), photoluminescence kinetic trace follows a single exponential in the case of heavily doped and trap-assisted dominant materials \((k_T N_T \gg k_b n_0)\) and \(N_T - n_e(t) \approx N_T\).

B. In a nonlinear regime (high fluence with trap-filled and annihilation)

In this case, the annihilation rate is much larger than the first order trap-filling rate in the linear regime. In the later time, all trap sites are occupied and the num-

FIG. 1 Kinetic model for relaxation processes of n-type hybrid perovskites. Upon photoexcitation, the electrons in CB relax by trap-assisted recombination \(k_T\), electron-hole bimolecular recombination \(k_b\), and annihilation recombination \(k_A\). Meanwhile, the holes in VB relax by electron-hole bimolecular recombination \(k_b\), and annihilation recombination \(k_A\).
FIG. 2 Photoluminescence spectra for the slow-growth (A), and fast-growth (B) CH$_3$NH$_3$PbI$_3$ single crystals, both of which exhibit a maximum peak located at 775 nm. (C) Photoluminescence kinetic traces at low fluence of 0.05 μJ/cm$^2$ for the slow-growth (red), and fast-growth (blue) CH$_3$NH$_3$PbI$_3$ single crystals. Above 0.5 μJ/cm$^2$, the photoluminescence signals show a nonlinear behavior with illuminated fluence.

From Eq.(7) and Eq.(8), we are only able to obtain three parameters ($k_1$, $k_b$, $k_A$) at high fluence since $k_T$ and $N_T$ is bound together.

IV. RESULTS AND DISCUSSION

Photoluminescence spectra are shown in FIG. 2(A) for the slow-growth single crystals, and (B) fast-growth CH$_3$NH$_3$PbI$_3$ single crystals. Both the materials exhibit photoluminescence peak centered at around 775 nm. FIG. 2(C) presents photoluminescence kinetic traces at low fluence of 0.05 μJ/cm$^2$ for the two kinds of single crystals. We see that the two materials exhibit different kinetic behaviors. Although one could numerically fit any of kinetic traces with Eqs.(1–3), there are many satisfying groups of solutions due to multiple parameters in the nonlinear fitting function.

To correctly extract the materials parameters, we performed fluence-dependent photoluminescence kinetic experiments on the slow-growth and fast-growth single crystals. FIG. 3 displays time-resolved fluorescence lifetime traces of the two kinds of single crystals, at two different photoexcited fluences of 0.052 μJ/cm$^2$ and 0.405 μJ/cm$^2$, respectively, for the slow-growth and fast-growth single crystals. A global fitting is necessary to extract the parameters. To check the saturation, we plotted photoluminescence intensity at $t=0$ as a function of laser fluence as shown in FIG. 4 from 0.019 μJ/cm$^2$ to 4.268 μJ/cm$^2$. Additional fast process takes place as excitation intensity increases. This fast decay corresponds to three-body annihilation recombination.

Thus, we suggest the following procedure for analyzing fluorescence lifetime data: (i) determine linear regime for fluence-dependent fluorescence measurements, (ii) measure time trace of fluorescence for difference fluences in a linear regime, (iii) global fitting the fluence-dependent time traces to obtain parameters using Eqs.(1–3), (iv) never go to a nonlinear regime to obtain annihilation rate.

Table I lists time-resolved fluorescence lifetime traces of two crystals, slow-growth and fast-growth CH$_3$NH$_3$PbI$_3$ single crystals, at high fluence 4.268 μJ/cm$^2$. Obviously, this fluence was high enough that the trap states of two crystals were all occupied in the excitation process. Fast-growth CH$_3$NH$_3$PbI$_3$ crystal had much higher trap state concentration than slow-growth CH$_3$NH$_3$PbI$_3$ single crystal.

Knowing both charge carrier mobility $\mu$ and effective carrier-density dependent recombination rate $R_{\text{eff}}$, the charge carrier diffusion length could be obtained. For a given material, effective carrier-density dependent re-
TABLE I The fitting parameters from Eqs.(1−3).

<table>
<thead>
<tr>
<th></th>
<th>$k_b/(10^{-10} \text{ cm}^3/\text{s})$</th>
<th>$k_T/(10^{-10} \text{ cm}^3/\text{s})$</th>
<th>$k_R/(10^{-10} \text{ cm}^3/\text{s})$</th>
<th>$N_T/(10^{15} \text{ cm}^3)$</th>
<th>$N_0/(10^{15} \text{ cm}^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow-growth crystal</td>
<td>6.84</td>
<td>11.4</td>
<td>&lt;10$^{-6}$</td>
<td>3.41</td>
<td>4.33</td>
</tr>
<tr>
<td>Fast-growth crystal</td>
<td>17.05</td>
<td>217.05</td>
<td>&lt;10$^{-6}$</td>
<td>3.54</td>
<td>3.69</td>
</tr>
</tbody>
</table>

Combination rates $R_{\text{eff}}$ is the sum of the first-order ($k_T$), second order ($k_b$) and third order recombination rates ($k_A$). Using our data to predict diffusion length for the two single crystals. The minority-carrier diffusion length $L_D$ is given by

\[ L_D(n) = \frac{\mu k_b T^{1/2}}{e k(n)} \]

\[ k(n) = k_2(n_0 + n) + k_T N_T + k_A n^2 \]

where $T$ is temperature, $k_B$ is the Boltzmann constant, and $e$ is the elementary charge. In order to compare carrier diffusion length for the two kinds of single crystals, we estimated the diffusion length as a function of charge-carrier density $n$ for two different trap-assisted carrier recombination rates. From Table I, we adopt the following values: $\mu=30 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, $k_b=10^{-10} \text{ cm}^3/\text{s}$, $k_T=10^{-10} \text{ cm}^3/\text{s}$, $k_A=10^{-28} \text{ cm}^6/\text{s}$, $h_0=10^{15} \text{ cm}^{-3}$.

We found that the fast-growth and slow-growth single crystals exhibit carrier diffusion lengths about of 1 and 3 $\mu$m, respectively (FIG. 5). As compared to the values reported in the literature [2, 22], the intrinsic diffusion length for CH$_3$NH$_3$PbI$_3$ is on the order of 10$^{-6}$ m. Carrier-diffusion lengths need to exceed the typical absorption depths of up to a few hundred nanometers in order for charges to be collected efficiently in heterojunction devices.

Previous studies used $-dn/dt=A_n + B_n$ by considering a nonradiative monomolecular trapping rate plus a bimolecular radiative recombination rate [11]. From this model, the trap-assisted rate at low excitation den-

FIG. 3 Fluorescence lifetime traces of CH$_3$NH$_3$PbI$_3$ single crystal under low fluence (0.052 $\mu$J/cm$^2$) and moderate fluence (0.405 $\mu$J/cm$^2$) of slow-growth (A) and fast-growth (B) crystals, respectively. The solid lines represent fitted kinetics traces.

FIG. 4 Experimental time-resolved fluorescence lifetime traces of slow-growth and fast-growth crystals under different excitation intensities, ranging from 0.019 $\mu$J/cm$^2$ to 4.268 $\mu$J/cm$^2$, which were photoexcited by a 400-nm 2.5-MHz laser.

FIG. 5 The calculated diffusion length as a function of carrier density, based on the fitting results from Table I and Eqs. (9) and (10).
sities and the traps are completely filled, then the intrinsic bimolecular rate can be extracted. It should be noted that it was not our intention to propose a new kinetic model for describing carrier dynamics for hybrid perovskites. However, a majority of the reports related to carrier dynamics are very confusing, or even totally wrong.

V. CONCLUSION

we have presented a full description of carrier lifetimes, which is suitable for where exciton generation can be ignored by examining the commonly-used two models. In this work, we suggest a realistic approach to use a generic model for fluorescence lifetime measurements for low-trap and high-trap organic perovskites with a negligible exciton formation. To fully understand our model, we synthesized CH$_3$NH$_3$PbI$_3$ single crystals with two different methods. Physically, photoexcitation is followed by two main relaxation channels including trap-assisted non-radiative recombination and band-to-band radiative recombination. Although this technique holds great potential in research themes involving the determination of diffusion length, the data analysis of luminescence lifetimes can get quite complex. It requires a comprehensive understanding of the underlying relaxation processes. We introduce experimental and theoretical aspects of photo-induced carrier lifetimes with a strong focus on data analysis.

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