Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber

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Organic-inorganic perovskites have shown promise as high-performance absorbers in solar cells, first as a coating on a mesoporous metal oxide scaffold and more recently as a solid layer in planar heterojunction architectures. Here, we report transient absorption and photoluminescence-quenching measurements to determine the electron-hole diffusion lengths, diffusion constants, and lifetimes in mixed halide (CH$_3$NH$_3$PbI$_3$Cl$_x$) and triiodide (CH$_3$NH$_3$PbI$_3$I$_x$) perovskite absorbers. We found that the diffusion lengths are greater than 1 micrometer in the mixed halide perovskite, which is an order of magnitude greater than the absorption depth. In contrast, the triiodide absorber has electron-hole diffusion lengths of ~100 nanometers. These results justify the high efficiency of planar heterojunction perovskite solar cells and identify a critical parameter to optimize for future perovskite absorber development.

Photovoltaic (PV) solar energy conversion has the potential to play a major role in future electricity generation. Most currently installed PV arrays consist of crystalline or polycrystalline silicon; in second generation thin-film architectures, light is absorbed and charge generated in a solid layer of this semiconductor (7). Beyond these existing technologies are a myriad of other emerging device concepts based on a broad range of materials, all varying to become the cheapest yet suitably efficient technology to enable widespread uptake of solar energy (2–6). Some of the most promising technologies for ultimate low-cost manufacture are solution-processed, such as organic photovoltaics (OPV), dye-sensitized solar cells (DSSCs), and semiconductor-sensitized or extremely thin absorber solar cells (7, 8). However, these designs typically require a complex distributed donor-acceptor heterojunction to ionize charge because the exciton and charge carrier diffusion lengths in these materials are much shorter than the absorption depth (7, 9–11). Emerging from the field of DSSCs, the inorganic-organic perovskite family of materials taking the form ABX$_3$ (A = CH$_3$NH$_3$; B = Pb$^2+$; and X = Cl$^-$, Br$^-$, or I$^-$) has within the past 12 months been used to fabricate high-performance hybrid solar cells, with reported power conversion efficiencies (η) of between 7 and 15% (12–20). These perovskite absorbers can be solution-processed in air and absorb light broadly across the solar spectrum. In the first experiments, the perovskite absorber was used as a sensitizer on mesoporous titania electrodes, along with a solid-state organic hole transporter (HTM) such as 2,7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD), with the perovskite effectively replacing the dye conventionally used in a DSSC (12, 13, 21). Subsequently, the mixed halide CH$_3$NH$_3$PbI$_3$Cl$_x$ perovskite devices have been reported to yield η >12% when the titania is replaced with an insulating mesoporous alumina scaffold in meso-superstructured solar cells (MSSCs), demonstrating that the perovskite itself can at least sustain sufficient electron transport to enable highly efficient charge collection (12, 16). Entirely removing the mesoporous alumina to create a thin-film planar heterojunction has resulted in solution-processed devices with close to 100% internal quantum efficiency for charge collection, but with lower η of 5% (16). Very recently, we have demonstrated that if an extremely uniform solid perovskite absorber film can be prepared—for example, through vapor deposition—then the highest efficiencies can be achieved in solid thin-film planar heterojunction architectures (19).

Despite the rapid increase in efficiency associated with the evolution of this technology, most of the fundamental questions concerning the photophysics and device operation remain unanswered. Arguably, the most critical question concerning whether mesostructured or planar heterojunction perovskite solar cells will eventually dominate is what the exciton or the electron and hole diffusion lengths are in these materials. We performed photoluminescence (PL)–quenching measurements in order to extract the electron-hole diffusion lengths in triiodide (CH$_3$NH$_3$PbI$_3$I$_x$) and mixed halide (CH$_3$NH$_3$PbI$_3$Cl$_x$) perovskite thin films. We show that both electron and hole diffusion lengths are >1 μm for the mixed halide perovskite—a factor of ~5 to 10 greater than the absorption depth. In contrast, the diffusion lengths in the triiodide perovskite are only on the order of or slightly shorter than the absorption depth (~100 nm). The larger diffusion length in the mixed halide perovskite results from a much longer recombination lifetime and is consistent with far superior performance in MSSCs and planar heterojunction solar cells, as we demonstrate here.

PL quenching has been previously used successfully with organic semiconductors in order to extract the diffusion lengths of charge carriers in solar cells (22–25). The magnitude of the PL quenching is directly related to the diffusion length of the charge carriers, as shown in Fig. 1. In these materials, the charge carriers are electrons and holes, which are the excitons that form the photoexcitation. This means that knowledge of the diffusion lengths allows the calculation of the exciton lifetime, which is the migration time between the formation of the exciton and its subsequent dissociation into an electron-hole pair. Exciton lifetimes in perovskites are typically between 10 and 100 ns (26–28). However, in previous studies, investigations were limited to cases where the excitons were predominantly bound in either a donor or acceptor material, and the diffusion lengths were determined from the PL decay curves. Our study allows determination of the diffusion lengths under more realistic conditions, where excitons are formed throughout the perovskite layer.

**Fig. 1.** Optical characterization of the mixed halide perovskite CH$_3$NH$_3$PbI$_3$Cl$_x$. (A) Absorption (red squares) and PL (black circles) spectra of a 270-nm-thick layer of CH$_3$NH$_3$PbI$_3$Cl$_x$ coated with PMMA. (B) Transient absorption spectra of CH$_3$NH$_3$PbI$_3$Cl$_x$ upon excitation at 500 nm (40 μJ/cm$^2$ pulses). Each gated spectrum has been integrated for 200 ns, and the PL was removed. (C) Normalized photobleaching (PB) (red squares, left axis) and PL dynamics (black circles, right axis) probed at 750 and 770 nm, respectively. Biexponential fitting of the PB data (dark red line) leads to a dominant time constant of τ$_1$ = 283 ± 6 ns, matching the dynamics of the PL (τ$_2$ = 273 ± 7 ns), followed by a long-lived tail. (Inset) The photoinduced absorption (PA) dynamics at 550 nm (blue squares) with a biexponential fit (dark blue line; dominant time constant of τ$_1$ = 288 ± 12 ns), also matching the dynamics of the PL and the dominant component of the PB.
to determine the diffusion length of the photoexcited bound electron-hole pair, the exciton (22). By simply fabricating solid thin films in the presence or absence of an excitation-quenching layer, and modeling the PL decay to a diffusion equation, it is possible to accurately determine the exciton lifetime, diffusion rate, and diffusion length (22). However, for the organolead trihalide perovskites studied here, there is relatively little literature on probing the fundamental photophysics, and even the most basic question of whether PL occurs via free carrier recombination from the conduction and valence band electrons, or is preceded by exciton formation, remains unknown. Exciton binding energies for CH$_3$NH$_3$PbI$_3$ have been reported in the range of 37 to 50 meV in the orthorhombic phase (23–25). In principle, at ambient temperature these values are comparable to thermal energies ($k_BT$ ~ 26 meV, where $k_B$ is the Boltzmann constant and $T$ is the temperature); thus, both free carriers and weakly bound excitons should coexist with interchange being possible between the two populations. However, provided all species (bound or free charges) decay with the same rate or through the same channel, the PL decay should still be representative of recombination rate or through the same channel, the PL decay represents a photoinduced absorption (PA). From biexponential data fitting, we retrieved the dominant time constant of both the PB and PA to be ~280 ns, followed by a long-lived tail (>1 µs). As we show in Fig. 1C, the PA band decay (288 ± 12 ns) mirrors the PB recovery dynamics (283 ± 6 ns), suggesting that the spectra arise from the same population. If we compare the transient absorption decays with the transient PL decay ($\tau_e = 273 ± 7$ ns, where $\tau_e$ is the time taken for the PL to fall to 1/e of its initial intensity), there is a strikingly close match. This indicates that the decay of the radiative species we are monitoring with the PL represents the decay of all absorbing species (free carriers or weakly bound excitons) in the perovskite film. We can therefore use PL-quenching measurements to determine a relevant diffusion constant and length in the perovskite films. We cannot, however, categorically determine whether this corresponds to the diffusion of free charge or excitons, but in either case, it will represent the relevant diffusion length for charge extraction in the solar cell. Additionally, we can safely exclude any contribution to the PL from trap states, which would be at lower energy and whose presence would otherwise complicate the subsequent PL-quenching analysis.

![Fig. 2. PL measurements and fits to the diffusion model for the mixed halide and triiodide perovskites in the presence of quenchers. (A) Cross-sectional SEM image of a 270-nm-thick mixed halide absorber layer with a top hole-quenching layer of Spiro-OMeTAD. (B) and (C) Time-resolved PL measurements taken at the peak emission wavelength of the (B) mixed halide perovskite and (C) triiodide perovskite with an electron (PCBM; blue triangles) or hole (Spiro-OMeTAD; red circles) quencher layer, along with stretched exponential fits to the PMMA data (black squares) and fits to the quenching samples by using the diffusion model described in the text (details are available in the supplementary materials). A pulsed (0.3 to 10 MHz) excitation source at 507 nm with a fluence of 30 nJ/cm$^2$ impinged on the glass substrate side. (Inset) Comparison of the PL decay of the two perovskites (with PMMA) on a longer time scale, with lifetimes $\tau_e$ quoted as the time taken to reach 1/e of the initial intensity.](Image 341x487 to 554x573)

Table 1. Values for diffusion constants ($D$) and diffusion lengths ($L_D$) from fits to PL decays using the diffusion model described in the text. The errors quoted predominantly arise from perovskite film thickness variations, which are ± 35 nm for the triiodide perovskite films and ± 40 nm for the mixed halide perovskite films.

<table>
<thead>
<tr>
<th>Perovskite</th>
<th>Species</th>
<th>$D$ ($cm^2 s^{-1}$)</th>
<th>$L_D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NH$_3$PbI$_3$,Cl$_x$</td>
<td>Electrons</td>
<td>0.042 ± 0.016</td>
<td>1069 ± 204</td>
</tr>
<tr>
<td></td>
<td>Holes</td>
<td>0.054 ± 0.022</td>
<td>1213 ± 243</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>Electrons</td>
<td>0.017 ± 0.011</td>
<td>129 ± 41</td>
</tr>
<tr>
<td></td>
<td>Holes</td>
<td>0.011 ± 0.007</td>
<td>105 ± 32</td>
</tr>
</tbody>
</table>
The quenching samples were prepared by means of spin-coating layers of either a hole-acceptor (Spiro-OMeTAD) or an electron-accepting fullerene [phenyl-C_{61}-butyric acid methyl ester (PCBM)] on top of the perovskite films. In Fig. 2A, we show a scanning electron microscopy (SEM) image of a ~270-nm-thick CH$_3$NH$_3$PbI$_3$-Cl$_x$ absorber layer with a ~100-nm-thick Spiro-OMeTAD hole-quenching layer. We show SEM images of all sample configurations in figs. S1 and S2 and absorption spectra in fig. S3, which indicate that the mixed halide and triiodide perovskites have very similar bandgaps.

We present the time-resolved PL decays, measuring the peak emission at ~770 nm, for the mixed halide and triiodide perovskite absorbers in Fig. 2, B and C, respectively. The excitation fluence was kept to 0.03 μJ cm$^{-2}$/pulse so as to ensure that nonlinear effects, such as excitation-charge annihilation, are unlikely to occur. The thickness of the CH$_3$NH$_3$PbI$_3$-Cl$_x$ films was 270 ± 40 nm, and the thickness of the CH$_3$NH$_3$PbI$_3$ films was 180 ± 35 nm, which is comparable with optimum device thicknesses. The corresponding steady-state spectra are shown in fig. S4. The PL decay of the neat CH$_3$NH$_3$PbI$_3$-Cl$_x$ film exhibits a time-constant of $\tau_e = 273 ± 7$ ns. The addition of the PCBM and Spiro-OMeTAD electron and hole-quenching layers accelerates the PL decay, with observed time constants $\tau_e$ of 6.1 ± 0.1 ns and 5.1 ± 0.1 ns, respectively. In contrast, the lifetime for the neat CH$_3$NH$_3$PbI$_3$ film is only $\tau_e = 9.6 ± 0.3$ ns, and this is quenched further, but not by such a large fraction, to 3.17 ± 0.03 ns for electrons and 4.2 ± 0.1 ns for holes.

The PL decay dynamics were modeled by calculating the number and distribution of excitations in the film $n(x,t)$ according to the one-dimensional diffusion equation

$$\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} - k(t)n(x,t) \quad (1)$$

where $D$ is the diffusion coefficient and $k(t)$ is the PL decay rate in the absence of any quencher.

To confirm the importance of the determined diffusion length in full solar cells, and to test whether the measurement correlates well with device results, we fabricated solution-processed thin-film planar heterojunction solar cells with both the mixed halide and triiodide perovskites. We formed solid perovskite films on fluoroine-doped tin oxide (FTO)–coated glass substrates, coated with an n-type TiO$_2$ compact layer so as to ensure selective collection of electrons at the FTO substrate. Subsequently, p-type Spiro-OMeTAD was deposited as a hole-transporting layer so as to form a planar p-i-n heterojunction architecture. Current-voltage characteristics for the best devices fabricated are shown in Fig. 3. The CH$_3$NH$_3$PbI$_3$-Cl$_x$ planar heterojunction solar cells reach power conversion efficiencies in excess of 12%, which is the highest solution-processed planar heterojunction perovskite efficiency reported to date. In contrast, we were only able to attain $\eta$ of ~4% with the CH$_3$NH$_3$PbI$_3$. Upon optimization of devices to obtain the highest efficiencies, we found that a thick layer of CH$_3$NH$_3$PbI$_3$-Cl$_x$ was preferable (~500 nm). However, the best CH$_3$NH$_3$PbI$_3$ cells had a perovskite layer thickness of only 140 nm. This observation is consistent with the diffusion-length calculations, in which the triiodide films are limited by the ~100-nm diffusion length, so that photogenerated charge in thicker films cannot be efficiently extracted before recombining. A full set of device results and average performances is given in table S1.

This work indicates that with correct tuning of the perovskite absorber, nano- or mesostructures are not necessary in order to achieve highly efficient charge generation and collection. Our results hence pave the way for further advances in planar heterojunction perovskite solar cells. Fundamentally, there still remain many open questions for the community concerning the nature of the excited state, the relative fraction of free and bound charge pairs at room temperature, and the interplay between the two species. Furthermore, this work introduces a new question as to why the small addition of chloride ions to the organolead triiodide perovskite results in such a striking increase in the electron-hole diffusion length, predominantly arising from a substantial inhibition of nonradiative electron-hole recombination. Understanding these subtleties will enable further improvement of the current family of materials.

References and Notes
3. Z. He et al., Nat. Photonics 6, 593 (2012).
Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH$_3$NH$_3$PbI$_3$

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Low-temperature solution-processed photovoltaics suffer from low efficiencies because of poor exciton or electron-hole diffusion lengths (typically about 10 nanometers). Recent reports of highly efficient CH$_3$NH$_3$PbI$_3$-based solar cells in a broad range of configurations raise a compelling case for understanding the fundamental photophysical mechanisms in these materials. By applying femtosecond transient optical spectroscopy to bilayers that interface this perovskite with either selective-electron or selective-hole extraction materials, we have uncovered concrete evidence of balanced long-range electron-hole diffusion lengths of at least 100 nanometers in solution-processed CH$_3$NH$_3$PbI$_3$. The high photoconversion efficiencies of these systems stem from the comparable optical absorption and charge-carrier diffusion lengths, transcending the traditional constraints of solution-processed semiconductors.

An ideal solar cell material should combine good optical absorption characteristics with efficient charge-transport properties. Low-temperature solution-processed light-harvesting films prepared by techniques such as spin-coating and chemical bath deposition are typically amorphous or poorly crystalline (1–3), consecutively suffering from poor charge-carrier transport (4). This limitation necessitates device designs that decouple light absorption and charge-carrier transport lengths, including light-trapping strategies such as plasmonics (5, 6) as well as the sensitized solar cell architecture (7, 8). The recent development of organic-inorganic halide perovskite materials such as CH$_3$NH$_3$PbI$_3$ as light harvesters in solid-state sensitized solar cells has led to reports of impressive efficiency values of up to 15% (9). This remarkable material has been used in a variety of photovoltaic architectures. A configuration used by Kim et al. (10) and Heto et al. (11) sandwiches the thin perovskite layer between a rough mesoporous TiO$_2$ photoanode and a hole-transporting layer such as 2,2′,7,7′-tetakis(N,N-di-p-methoxyphenylamino)-9,9′-spirobifluorene (Spiro-OMeTAD). Lee et al. (12) have shown that efficient solar cells can be fabricated by replacing the TiO$_2$ photoanode with an insulating Al$_2$O$_3$ scaffold, implying good electron-transport properties. Unexpectedly, Etgar et al. (13) reported an efficiency of 5.5% in a configuration without the hole-transporting layer, indicating good hole-transport properties. These indications of ambipolar charge-transport capabilities are supported by a recent report by Ball et al. (14) that demonstrated that ~350-nm-thick planar films sandwiched between a TiO$_2$ compact layer and a hole-transporting layer can generate short-circuit current densities of 15 mA/cm$^2$. These reports together imply that the electron- and hole-transport lengths within these organic-inorganic hybrid materials are high. Nonetheless, the innate dynamics of the photoexcited electrons and holes in CH$_3$NH$_3$PbI$_3$ driving the high efficiencies in these solar cells are unknown. Herein, through femtosecond transient optical spectroscopy of CH$_3$NH$_3$PbI$_3$ heterojunctions with selective electron and hole extraction, we successfully decoupled electron and hole dynamics and show evidence of long electron- and hole-transport lengths (both over 100 nm). Our findings indicate that this class of materials does not suffer from the bottleneck of low collection lengths that handicaps typical low-temperature solution-processed photovoltaic materials.

In this study, electron-extraction layers (such as [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM), C$_{60}$) with conduction band levels below that of CH$_3$NH$_3$PbI$_3$ and hole-extraction layers (such as Spiro-OMeTAD, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)) with valence band levels above CH$_3$NH$_3$PbI$_3$ were interfaced to CH$_3$NH$_3$PbI$_3$ to permit decoupling of the electron and hole dynamics (fig. S1). Comparing measurements on pure CH$_3$NH$_3$PbI$_3$ against CH$_3$NH$_3$PbI$_3$/hole acceptor bilayers and CH$_3$NH$_3$PbI$_3$/electron acceptor bilayers enables identification of electron and hole signatures in the organic-inorganic halide. Under identical experimental conditions, the photoluminescence (PL) quantum yield of the 65-nm-thick CH$_3$NH$_3$PbI$_3$ is greatly reduced when the perovskite is interfaced with an electron-extracting PCBM layer or a hole-extracting Spiro-OMeTAD layer (Fig. 1A). The PL intensity is quenched by a factor of 12.5 in the bilayer with Spiro-OMeTAD and by a factor of 50 in the bilayer with PCBM (table S1). Given that the current configurations are ideal layered systems (figs. S2 and S3), these high degrees of PL quenching, comparable to closely blended donor-acceptor systems, are particularly revealing (15–19). With a linear absorption coefficient of 5.7 × 10$^4$ cm$^{-1}$ at 600 nm (Fig. 2A and fig. S4), near-homogeneous generation of the charge carriers in these 65-nm CH$_3$NH$_3$PbI$_3$ layers can be ensured (20). The PL quenching is expected to originate from the charge-carrier extraction across the interface (21–27). Efficient PL quenching suggests that the charge-carrier diffusion length inside the CH$_3$NH$_3$PbI$_3$