High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites

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A new generation of thin-film photovoltaic cells based on organo-metal halide perovskite absorbers has recently emerged with extraordinary power conversion efficiencies (PCE).[1] Initial PCEs reported around 10 % were soon superseded by values ranging from 12% to over 15% as materials control and device protocol improved.[2] Methylammonium lead trihalide perovskite materials allow low-cost solution processing and absorb broadly across the solar spectrum, making them an exciting new component for clean energy generation. Interestingly, two different device concepts have appeared: in one, the lead halide compound CH$_3$NH$_3$PbI$_3$ is deposited on the surface of mesoporous TiO$_2$, which is then infiltrated with the solid-state hole transporter spiro-OMeTAD.[1a] The resulting cell has an analogous structure to a conventional solid-state dye-sensitized solar cell, in which upon photoexcitation electrons transfer from an excited dye to the TiO$_2$ conduction band and subsequently diffuse to the contact.[3] The first reported power conversion efficiencies of up to 9.7% for cells based on CH$_3$NH$_3$PbI$_3$ by far exceeded previous records achieved with cells employing dyes as absorbers (≤6%).[4] In another approach, Lee et al. obtained efficiencies of up to 10.9% using the mixed halide perovskite material CH$_3$NH$_3$PbI$_{1-x}$Cl$_x$ as both absorber and electron transporter, thus eliminating the need for a bulk heterojunction with a separate electron-transporting material. In this concept, the mesoporous TiO$_2$ is replaced by Al$_2$O$_3$, which does not allow electron injection due to its high-lying conduction band, acting simply as an inert scaffold for the perovskite. Most recently, vapour deposition of highly uniform solid organolead trihalide perovskite films has been shown to allow PCEs as high as 15.4% in planar-heterojunction device structures.[2d]

Given the rapid rise in performance of organolead trihalide perovskite photovoltaic devices, little is known about what makes these materials so successful at generating and transporting photocurrents. Some work on transport properties has been published on the related tin halides[5] and recently Hall-effect conductivity measurements have been performed on CH$_3$NH$_3$PbI$_3$.[6] Other studies on lead halides mostly focused on optical and excitonic properties[7] or theoretical band structure calculations.[8] It has recently been shown that charge carriers are capable of travelling over distances of up to a micron in some perovskite absorbers, which exceeds their typical absorption depth.[9] However, the mechanism causing such an extended diffusion range remains mysterious, given that long charge-carrier diffusion distances require both low recombination rates and/or high charge mobility. Satisfying both requirements simultaneously is generally difficult given the fundamental Langevin limit for kinetic recombination, which typically holds for conductors with charge mobilities below the order of 1–10 cm$^2$V$^{-1}$s$^{-1}$.[10]

In this work, we show that both CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_{1-x}$Cl$_x$ exhibit unexpectedly long charge carrier diffusion lengths because of non-Langevin charge carrier recombination. Using transient THz spectroscopy, we determine that bi-molecular recombination rates are abnormally low in these materials, defying the Langevin limit by at least four orders of magnitude. We also establish lower bounds for the high-frequency charge mobility of 11.6 cm$^2$V$^{-1}$s$^{-1}$ for CH$_3$NH$_3$PbI$_{1-x}$Cl$_x$ and 8 cm$^2$V$^{-1}$s$^{-1}$ for CH$_3$NH$_3$PbI$_3$, which are remarkably high for solution-processed materials. The combination of high charge mobility and low bi-molecular recombination leads to carrier diffusion lengths that exceed one micron and are significantly longer for the mixed halide system. We propose that such reduced bi-molecular charge recombination arises from spatial separation of electrons and holes in the system, which may be tuned through substitutions affecting the electronic structure of the metal-halide system.

In order to highlight the relevance of our spectroscopic study to solar cell operation we correlated our findings with the performance of matching devices. Figure 1a shows a schematic of the device structure employed: the metal-halide perovskite acts as both light absorber and charge transporter while spiro-OMeTAD functions as the hole transporter. The organolead trihalide perovskite is infiltrated into a 400 nm-thick scaffold layer of Al$_2$O$_3$ nanoparticles whose main function is to improve uniformity of coating, inhibiting pin-hole formation and the associated dark current leakage.[2,11] We term this device a meso-superstructured solar cell (MSSC); however, it is important to note that electrons and holes have to travel through the perovskite layer to reach the respective extraction layers, compact TiO$_2$ and spiro-OMeTAD, in analogy to a planar-heterojunction device structure. For spectroscopic measurements, metal-halide perovskite films were deposited under identical conditions on z-cut quartz, but with the electrodes and spiro-OMeTAD layers omitted.

The mixed halide perovskite CH$_3$NH$_3$PbI$_{1-x}$Cl$_x$ was synthesized as described in[10] and[12] with excess methylammonium which may compensate losses of the organic material during the annealing process. The triiodide perovskite CH$_3$NH$_3$PbI$_3$
reported in [1a] and [2a] on the other hand was synthesized at a 1:1 molar ratio of CH\textsubscript{3}NH\textsubscript{3}I to PbI\textsubscript{2}. For best comparability we therefore prepared two kinds of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} materials – the non-stoichiometric type with excess methylammonium (3:1) and the stoichiometric type (1:1). Spectroscopy samples and devices were made using the same stock of perovskite precursor – full details can be found in Supporting Information.

Figure 1b presents typical current-density-voltage-characteristics of solar cells incorporating the three different organolead trihalide perovskites. Maximum power conversion efficiencies (PCE) recorded under simulated sunlight (AM1.5) were 12.7% for the mixed halide, 8.5 % for the non-stoichiometric (3:1) triiodide, and below 1% for the stoichiometric (1:1) triiodide perovskite. Detailed statistics of photovoltaic performance data for all fabricated devices can be found in SI. The low performance of devices incorporating CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} (1:1) may in part be attributed to poor film formation as evidenced by the large amount of scattering seen in the corresponding UV/vis absorption spectrum (Figure 1c).

We proceed to unravel the charge dynamics in the perovskite materials following pulsed photoexcitation. It is still unclear to what extent primary photoexcited species in organolead trihalide perovskites at room temperature divide into free charges or exciton populations. Exciton binding energies of between 37 meV [12] and 50 meV [7d] have been proposed for (orthorhombic) CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} at low temperature (5 K). In both studies the diamagnetic shift of the magnetooabsorption spectrum was measured to magnetic fields in excess of 40 T and the exciton binding energy was derived making assumptions about the value of the high frequency dielectric function. [12] We find that emission spectra and absorption onsets (Figure 1c) for all three investigated metal-halide perovskites are very similar, therefore any variation in exciton binding energy is likely to be relatively small. The proposed exciton binding energies of 37–50 meV are comparable to thermal energies at room temperature

\[ k_B T \approx 26 \text{ meV}. \]

Following photoexcitation, both free charge carriers and excitons may therefore be present, with their populations interchanging dynamically over the course of their lifetime.

Figure 2 displays the transient THz transmission dynamics following photoexcitation of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3−x}Cl\textsubscript{x} and CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} (3:1) for a range of different excitation fluences (data for CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} (1:1) in SI). In these experiments, the...
sample is excited by an optical light pulse at a wavelength of 550 nm and subsequently probed by a terahertz-frequency pulse after a well defined delay (see[13] and SI for details of apparatus). In the presence of free charges, the measured relative change in THz electric field transmission is proportional to the photoinduced conductivity in the material.[14] By scanning the full waveform of a THz pulse transmitted through the sample the complex dielectric function in the THz range is also directly reconstructed (THz spectra given in SI). In principle, any photoexcited species coupling to electro-magnetic THz radiation may be responsible for the observed THz transmission transients. We argue here that the observed dynamics arise solely from the photoconductivity of free charges. First, for an assumed exciton binding energy of ~40 meV, the energy of probe photons employed here (1 THz corresponds to 4 meV) is too low to couple to significant intra-excitonic resonances. Second, the shape of the transient THz spectra is incompatible with an excitonic absorption and more akin to those reported to describe charge motion in polycrystalline materials (see SI).[14]

Table 1. Charge-carrier decay constants, Langevin ratio, charge mobility and device efficiencies for organolead trihalide perovskite materials listed in Column 1. Columns 2 and 3 show the third ($\phi k_3$) and second ($\phi k_2$) order charge-carrier decay constants as determined from fits to the excitation-fluence dependence of the THz transient photoconductivity data (Figure 2). Column 4 gives mono-molecular recombination rates $k_1$ derived from mon-exponential fits to the tails of photoluminescence decay transients taken under low-fluence excitation (see SI). Column 5 lists the effective charge carrier mobilities $\mu$ derived from the initial THz photoconductivity. Column 6 compares the bimolecular-recombination-rate-to-mobility ratio $(k_2/\mu)^{\ast}$ (from Columns 3 and 5) to that expected from Langevin theory $(k_2/\mu)_L = e (\varepsilon_\infty \varepsilon_0)^{\ast}$, multiplied by $\varepsilon_0^{\ast}$. Column 7 lists maximum power conversion efficiencies achieved with the material incorporated into full photovoltaic device structures.

| Material                  | Charge Carrier Decay Constants | Mobility $\mu$ | Langevin $k_2/\mu_L$ | Device $PCE_{max}$ |
|---------------------------|--------------------------------|----------------|----------------------|-------------------|
| CH$_3$NH$_3$PbI$_3−x$Cl$_x$ | 9.9 x 10$^{−9}$ cm$^3$s$^{−1}$ | 11.6           | $2.4 \times 10^{−6}$ | 12.7              |
| CH$_3$NH$_3$PbI$_3$ (3:1) | 3.7 x 10$^{−9}$ cm$^3$s$^{−1}$ | 8.1            | $6.4 \times 10^{−5}$ | 8.5               |
| CH$_3$NH$_3$PbI$_3$ (1:1) | 1.3 x 10$^{−8}$ cm$^3$s$^{−1}$ | 8.2            | $6.2 \times 10^{−5}$ | 0.9               |

$\phi$ is the branching ratio of generated free charge-carrier density per absorbed photon density, which is unknown, but falls in the range 0 $\leq \phi \leq 1$. Hence values listed in Columns 2, 3, 4 represent lower limits of $k_3$ and $k_2$ and $\mu$.

To unravel the charge recombination rates associated with both mono-molecular (arising e.g. from trap-assisted recombination) and higher-order processes, we fit solutions to the differential equation

$$\frac{dn(t)}{dt} = -k_1n^3 - k_2n^2 - k_3n$$

to the THz photoconductivity transients, where $n$ is the photoinduced charge carrier density. Here we assume that the photoconductivity decay is solely influenced by a change in charge carrier density, rather than mobility, which is reasonable given the absence of visible photoconductivity decay in the low fluence regime over the observation window (Figure 2a). Global fits were used for each set of fluence-dependent transients and the spatial variation of the charge density profile was taken into account (see SI for full details of fitting procedure). We make two striking observations from our analysis. First, we find that the monomolecular charge carrier recombination rate is exceptionally low in these materials. Data shown in Figure 2 allow for high-quality fits (solid lines) incorporating just second- and third-order decay components, which sets an upper limit of $k_1$ from (25 ns$^{-1}$) $\leq$ (CH$_3$NH$_3$PbI$_3−x$Cl$_x$) and $k_1 \leq$ (6 ns$^{-1}$) (CH$_3$NH$_3$PbI$_3$) for the monomolecular recombination rate. Such absence of trap- or impurity-assisted recombination over the timescale of nanoseconds is excellent news for use of organolead trihalide perovskites in photovoltaic cells and is in contrast with other materials commonly used, such as GaAs[16] and mesoporous TiO$_2$.[13] Second, we find that the bi-molecular charge recombination rate is an order of magnitude lower than for triiodide materials. As we show below, this leads to markedly larger diffusion lengths even at elevated charge carrier densities for the mixed halide perovskite making this material more more suitable for planar-heterojunction devices.

Performance differences between the three organolead trihalide perovskites could also potentially arise from discrepancies in the charge carrier mobility $\mu$. We elucidate such effects, by determining the effective charge carrier mobility for the three organolead trihalide perovskites in the low-fluence
regime. Such values can be directly derived from the photoinduced change of THz electric field transmission $\Delta T/T$ (as shown in Figure 2) which is proportional to the photocconductivity. We extract the effective charge carrier mobility $\phi\mu$ from the photocconductivity onset value (prior to charge recombination) with knowledge of the absorbed photon density and optical parameters, as described in SI. Here, $\phi$ is the ratio of free-charge-carrier density generated per photon density absorbed, which is unknown and may depend on factors such as the exciton binding energy. We determine effective mobilities of 11.6 cm$^2$ V$^{-1}$ s$^{-1}$ for CH$_3$NH$_3$PbI$_3$Cl$_x$ and ~8 cm$^2$ V$^{-1}$ s$^{-1}$ for both CH$_3$NH$_3$PbI$_3$ variants. These values are exceptionally high for solution-processed materials, surpassing charge mobilities reported for mesoporous TiO$_2$ used in dye-sensitized solar cells by at least a factor of $20^{15,18,19}$ and those of typical $\pi$-conjugated molecular semiconductors by several orders of magnitude.$^{19}$ We note that effective charge carrier mobility values represent lower bounds for the actual mobilities since the photon-to-charge branching ratio $\phi$ must fall between 0 and 1. Interestingly, Stoumpos et al. recently reported a DC dark electron mobility of ~66 cm$^2$ V$^{-1}$ s$^{-1}$ for unintentionally doped single crystalline bulk CH$_3$NH$_3$PbI$_3$ obtained from 4-probe resistivity and Hall-effect measurements.$^{20}$ Comparison with our values suggests that, within the nano-second diffusion range, the solution-processed materials investigated here do not incur substantial charge carrier mobility losses at grain boundaries. We stress that effective charge carrier mobilities are relatively similar for the mixed halide and trihalide perovskite materials. Given that the emission spectra for the two types are relatively similar for the mixed halide and mixed-halide perovskite under typical device operating conditions.

We extract a diffusion length $L$ from these trends using $L(n) = (D/R_{\text{total}}(n))^1/2$, where $D = \mu_k T e^{-1}$ is the diffusion constant. Figure 3(c) displays the dependence of the diffusion length on charge carrier density derived for the cases of a photon to charge branching ratio of 1, corresponding to THz mobilities of 11.6 cm$^2$ V$^{-1}$ s$^{-1}$ and 8.1 cm$^2$ V$^{-1}$ s$^{-1}$ for CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$ (3:1), respectively. We note that for $\phi < 1$ diffusion lengths would be even larger.
mobility is crucial to the development of planar heterojunction photovoltaic devices incorporating organolead trihalide perovskites.

To propose an explanation for these effects, we note that there are interesting parallels with early low-temperature measurements on lead-halide ionic crystals, which showed that while conduction band maxima consist of 6s- and 5p orbitals of lead and iodine, respectively, while conduction band minima mostly incorporate 6p-orbitals of lead.[24] This scenario is reminiscent of the case of metal alkali halides for which long life times had been reported earlier.[25] Such spatial charge separation may explain the stark deviation from Langevin theory we observe for charge recombination in the organolead trihalide perovskites. Understanding and predictive modelling of such effects will therefore allow for directed photovoltaic material and device development.

In conclusion, we find that methylammonium lead trihalide perovskites are particularly well-suited as light absorbers and charge transporters in photovoltaic cells because they allow for an unexpected combination of both low charge recombination rates and high charge-carrier mobilities. We establish lower bounds of \(~10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) for the high-frequency charge mobility, which is remarkably high for a solution-processed material. We reveal that planar heterojunction photovoltaic cells may only be achieved because the ratio of bi-molecular charge recombination rate to charge mobility is over four orders of magnitude lower than that predicted from Langevin theory. Such effects are likely to arise from spatial separation of opposite charge carriers within the metal-halide structure or across a crystalline domain. Modelling and tuning recombination channels, e.g. through halide and metal substitutions, or crystallite size, will hold the clue to raising material performance.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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[1] a) H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel, Nat. Photon. 2013, 486; b) M. M. Lee, J. Teuscher, N.-G. Park, Sci. Rep. 2012, 2, 591; c) M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, 2012, 338, 643.

[2] a) J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, J.-h. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel, S. I. Seok, Nat. Photon. 2013, 7, 486; b) J. M. Ball,
M. M. Lee, A. Hey, H. J. Snaith, *Energy Environ. Sci.* 2013, 6, 1739;
c) J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature* 2013, 499, 316;
d) M. Liu, M. B. Johnston, H. J. Snaith, *Nature* 2013, 501, 395.
[3] U. Bach, D. Lupo, P. Comte, J.-E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature* 1998, 395, 583.
[4] a) N. Cai, S.-J. Moon, L. Cevey-Ha, T. Moehl, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, *Nano Lett.* 2011, 11, 1452;
b) J. Bouclé, J. Ackermann, *Polym. Int.* 2012, 61, 355.
[5] a) D. Mitzi, C. Feild, Z. Schlesinger, R. Laibowitz, *J. Solid State Chem.* 1995, 114, 159;
b) Y. Takahashi, R. Obara, K. Nakagawa, *J. Phys. Chem. Solids* 1988, 57, 3714.
[6] C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, *Inorg. Chem.* 2013, 52, 9019.
[7] a) D. B. Mitzi, K. Chondroudis, C. R. Kagan, *IBM J. Res. Dev.* , IBM Corp. 2001, 45, 29;
b) M. Hirasawa, T. Ishihara, T. Goto, *J. Phys. Soc. Jpn.* 1994, 63, 3870;
c) T. Ishihara, *J. Lumin.* 1994, 60, 269;
d) K. Tanaka, T. Takahashi, T. Ban, T. Kondo, K. Uchida, N. Miura, *Solid State Commun.* 2003, 127, 619.
[8] a) I. B. Koutselas, L. Ducasse, G. C. Papavassiliou, *J. Phys.: Condens. Matter* 1996, 8, 1217;
b) T. Urmenbayashi, K. Asai, T. Kondo, A. Nakao, *Phys. Rev. B* 2003, 67, 155405;
c) E. Mosconi, A. Amat, M. K. Nazeeruddin, M. Grätzel, F. De Angelis, *J. Phys. Chem. C* 2013, 117, 13902;
d) J. Even, L. Pedesseau, J.-M. Jancu, C. Katan, *J. Phys. Chem. Lett.* 2013, 4, 2999.
[9] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelauou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, *Science* 2013, 342, 341.
[10] a) P. Langevin, *Ann. Chim. Phys.* 1903, 28, 433;
b) M. Pope, C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* Oxford Science, New York, NY, USA 1999.

[11] G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely, H. J. Snaith, *Adv. Funct. Mater.* DOI: 10.1002/adfm.201302090.
[12] M. Hirasawa, T. Ishihara, T. Goto, K. Uchida, N. Miura, *Physica B* 1994, 201, 427.
[13] P. Tiwana, P. Parkinson, M. B. Johnston, H. J. Snaith, L. M. Herz, *J. Phys. Chem. C* 2010, 114, 1363.
[14] a) C. A. Schmuttenmaer, *Chem. Rev.* 2004, 104, 1759;
b) H. Némec, P. Kuzel, V. Sundström, *J. Photochem. Photobiol. A-Chem.* 2010, 215, 123;
c) R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz, M. Bonn, *Rev. Mod. Phys.* 2011, 83, 543;
d) J. Lloyd-Hughes, T.-I. Jeon, *J. Infrared, Millimeter, Terahertz Waves* 2012, 33, 871.
[15] a) A. R. Beattie, P. T. Landsberg, *P. Roy. Soc. Lond. A Mat.* 1959, 249, 16;
b) A. Haug, *J. Phys. Chem. Solids* 1988, 49, 599.
[16] J. Lloyd-Hughes, S. K. E. Merchant, L. Fu, H. H. Tan, C. Jagadish, E. Castro-Camus, M. B. Johnston, *Appl. Phys. Lett.* 2006, 89, 232102.
[17] A. C. Defranzo, B. G. Pazol, *Appl. Optics* 1993, 32, 2224.
[18] E. Hendry, F. Wang, J. Shan, T. F. Heinz, M. Bonn, *Phys. Rev. B* 2004, 69, 081101.
[19] a) P. Parkinson, J. Lloyd-Hughes, M. B. Johnston, L. M. Herz, *Phys. Rev. B* 2008, 78, 115321;
b) M. P. de Haas, J. M. Warman, T. D. Anthopoulos, *Adv. Funct. Mater.* 2006, 16, 2274.
[20] A. Pivikas, G. Juška, A. J. Mozer, M. Scharber, K. Arlauskas, N. S. Sariciftci, H. Stubb, R. Osterbacka, *Phys. Rev. Lett.* 2005, 94, 176806.
[21] G. J. Adriaenssens, V. I. Arkhipov, *Phys. Rev. Lett.* 2005, 94, 176806.
[22] P. Tiwana, P. Docampo, M. B. Johnston, H. J. Snaith, L. M. Herz, *ACS Nano* 2011, 5, 5158.
[23] T. Makino, M. Watanabe, T. Hayashi, M. Ashida, *Phys. Rev. B* 1998, 57, 3714.
[24] M. Iwanaga, M. Watanabe, T. Hayashi, *Phys. Rev. B* 1998, 57, 3714.
[25] R. T. Williams, K. S. Song, *J. Phys. Chem. Solids* 1990, 51, 679.