
Carlito S. Ponseca, Jr.,*† Tom J. Savenije,‡ Mohamed Abdellah,‡‡ Kaibo Zheng,‡ Arkady Yartsev,‡ Tobjörn Pascher,‡ Tobias Harlang,‡ Pavel Chabera,‡ Tonu Pullerits,‡ Andrey Stepanov,§ Jean-Pierre Wolf,§ and Villy Sundström,*†

‡Division of Chemical Physics, Lund University, Box 124, 221 00 Lund, Sweden
§Department of Chemical Engineering, Delft University of Technology, 2628 BL Delft, The Netherlands
¶GAP-Biophotonics, University of Geneva, 1211 Geneva 4, Switzerland
†Department of Chemistry, Qena Faculty of Science, South Valley University, Qena 83523, Egypt

Supporting Information

ABSTRACT: Organometal halide perovskite-based solar cells have recently been reported to be highly efficient, giving an overall power conversion efficiency of up to 15%. However, much of the fundamental photophysical properties underlying this performance has remained unknown. Here, we apply photoluminescence, transient absorption, time-resolved terahertz and microwave conductivity measurements to determine the time scales of generation and recombination of charge carriers as well as their transport properties in solution-processed CH$_3$NH$_3$PbI$_3$ perovskite materials. We found that electron–hole pairs are generated almost instantaneously after photoexcitation and dissociate in 2 ps forming highly mobile charges (25 cm$^2$ V$^{-1}$ s$^{-1}$) in the neat perovskite and in perovskite/alumina blends; almost balanced electron and hole mobilities remain very high up to the microsecond time scale. When the perovskite is introduced into a TiO$_2$ mesoporous structure, electron injection from perovskite to the metal oxide is efficient in less than a picosecond, but the lower intrinsic electron mobility of TiO$_2$ leads to unbalanced charge transport. Microwave conductivity measurements showed that the decay of mobile charges is very slow in CH$_3$NH$_3$PbI$_3$, lasting up to tens of microseconds. These results unravel the remarkable intrinsic properties of CH$_3$NH$_3$PbI$_3$ perovskite material if used as light absorber and charge transport layer. Moreover, finding a metal oxide with higher electron mobility may further increase the performance of this class of solar cells.

A highly efficient solar cell material should absorb light over a wide spectral range, generate charges with high efficiency, and transport these photogenerated charges to the electrodes with minimum losses. Several groups have reported power conversion efficiencies (PCEs) from 10% to 15% for solution processed organometal halide perovskite (OMHP)-based solar cells in the past two years. More recently, it was shown that these classes of materials have electron–hole diffusion lengths of at least 100 nm for triiodide absorber and longer than 1 μm for trihalide OMHP. However, the fundamental photophysical processes underlying solar cell function need to be understood in order to fully utilize the properties of these materials. For instance, it is not known whether the exceptionally long diffusion lengths are related to molecular excitons, i.e., tightly bound electron–hole pairs, or to highly mobile charge carriers. Hence, the nature of the initial photophysical product is not known. The exact role of the metal oxide TiO$_2$ as electron acceptor and charge transport layer in an OMHP-based photovoltaic cell is also not understood. Moreover, the influence of introducing OMHP in the open voids of sintered isolating nanoparticles (NPs), e.g., Al$_2$O$_3$, on the optoelectronic properties, has not yet been addressed. Therefore, a study on the charge carrier dynamics, including photogeneration and recombination is very much warranted but still lacking in the current literature.

In this work, a combination of spectroscopic techniques, namely photoluminescence (PL), transient absorption (TA), time-resolved terahertz spectroscopy (TRTS), and time-resolved microwave conductivity (TRMC) were used to monitor the light-induced processes from the subpicosecond to a hundred of microseconds time scale. We should stress that both TRTS and TRMC have been demonstrated as powerful techniques for studying charge carrier dynamics and the mobility in different organic and inorganic systems. Neat methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) was prepared to elucidate the intrinsic transport properties of the OMHP, while CH$_3$NH$_3$PbI$_3$ on Al$_2$O$_3$ was studied to resolve the influence of the nanostructure on the charge carrier dynamics. To clarify the role of an electron-accepting metal oxide on the dynamics of excited states in the perovskite, samples with CH$_3$NH$_3$PbI$_3$ introduced in TiO$_2$ NPs were also prepared. The importance and complexity of different material contacts, their heterogeneity, and differences in the morphology for the charge carrier dynamics were pointed out in ref 13. Here we focus on the carrier dynamics in neat CH$_3$NH$_3$PbI$_3$ and when a layer of mesoporous NPs TiO$_2$ and Al$_2$O$_3$ is filled with OMHP.

Received: December 11, 2013
Published: March 21, 2014

dx.doi.org/10.1021/ja412583t/J. Am. Chem. Soc. 2014, 136, 5189–5192
The early time THz kinetics of neat CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$, and CH$_3$NH$_3$PbI$_3$/TiO$_2$ are shown in Figure 1a. For neat CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$ an instrument limited rise ($A = 70\%$) assigned to generation of electron–hole pairs is followed by a second ($\sim 2$ ps, $A = 30\%$) rise before reaching its maximum. Upon photoexcitation, electron–hole pairs are initially Coulombically bound and require an activation energy on the order of the thermal energy, $kT$, to dissociate into mobile charges. This dissociation could take a few ps and in this case manifested as the dissociation into mobile charges. This dissociation could take a few ps and in this case manifested as the dissociation into mobile charges.

Within the experimental error, we found that they are identical, implying that carrier mobility has to remain constant for at least 1 ns, otherwise a faster decay of the THz kinetics would be observed. Consequently, this means that the decay of the THz conductivity is a result of a decreasing carrier concentration (nongeminate recombination, see below). The dependence of the THz decay on the excitation density is also illustrated in Figure S2, wherein at the lowest excitation density ($2.0 \times 10^{12}$ ph/cm$^2$ per pulse) there is no decay observed for the first 200 ps where the charge carrier mobility is found to be highest, i.e., $25$ cm$^2$/V·s. We note that this remarkably high THz mobility in solution processed OMHP is similar with the mobility recently obtained by Werheffbennig et al.$^{15}$

THz photoconductivity spectra were also measured 10 ps after photoexcitation (Figure 3). Within experimental error, both the amplitude and shape of the spectra of neat CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$$_3$PbI$_3$/Al$_2$O$_3$ are the identical. However, for charges are not instantaneously created. Furthermore, the negative signal, in a wavelength region lacking ground-state absorption, is a characteristic of stimulated emission, which agrees with the steady-state PL spectra (Figure 1b inset) showing radiative recombination. In contrast, a single component ultrafast rise with positive sign manifests in the kinetics of CH$_3$NH$_3$PbI$_3$/TiO$_2$. This is consistent with the time scale of the appearance of electrons in TiO$_2$.$^{1,14}$ and identical to the rise time of the THz kinetics (Figure 1a). Although not complete, strong quenching of the PL in CH$_3$NH$_3$PbI$_3$/TiO$_2$ is additional evidence for electron injection. A scanning electron microscope image (Figure S1C) of CH$_3$NH$_3$PbI$_3$/TiO$_2$ shows no evidence of domains of CH$_3$NH$_3$PbI$_3$ larger than 500 nm, which means that the mesoporous network of CH$_3$NH$_3$PbI$_3$ is formed within TiO$_2$ NPs similar to that presented in ref 1. However, smaller domains of CH$_3$NH$_3$PbI$_3$ may also be present due to voids that may have been created by the TiO$_2$ NPs, but their contribution is relatively small, as evidenced by the strong PL quenching and the ultrafast rise in THz kinetics indicating that electron injection is still very efficient.

THz photoconductivity kinetics on tens of ps time scale, for all three studied materials, exhibit a slow decay as shown in the inset of Figure 1a. Since the THz response is a product of carrier concentration and mobility, it is not possible to conclude, based on the THz kinetics alone, if this decay is due to decrease of charge concentration (i.e., charge recombination) or to relaxation of carrier mobility with time. Optical TA on the other hand is a direct measure of the carrier concentration. In Figure 2 kinetics of neat CH$_3$NH$_3$PbI$_3$ was measured with TA and TRTS at similar intensities ($\sim 10^{13}$ ph/cm$^2$ per pulse). Within the experimental error, we found that they are identical, implying that carrier mobility has to remain constant for at least 1 ns, otherwise a faster decay of the THz kinetics would be observed. Consequently, this means that the decay of the THz conductivity is a result of a decreasing carrier concentration (nongeminate recombination, see below). The dependence of the THz decay on the excitation density is also illustrated in Figure S2, wherein at the lowest excitation intensity ($2.0 \times 10^{12}$ ph/cm$^2$ per pulse) there is no decay observed for the first 200 ps where the charge carrier mobility is found to be highest, i.e., $25$ cm$^2$/V·s. We note that this remarkably high THz mobility in solution processed OMHP is similar with the mobility recently obtained by Werheffbennig et al.$^{15}$
From the THz measurements of porous TiO$_2$ we know electron or hole mobilities this quantity can be derived. However, due to the low intrinsic mobility of TiO$_2$, injection is limited to a few ps due to favorable band energy alignment of TiO$_2$ and the OMHP. Consequently, from the measured THz mobility of CH$_3$NH$_3$PbI$_3$/TiO$_2$ at different pump probe delays (100 ps, cyan 200 ps, magenta 600 ps, gray 950 ps), space charge-limited photocurrents lowering the PCE. There-fore, it is important to assess the mobilities of both electrons and holes. A THz measurement on only one material does not provide this information, but by comparing several materials with the same, i.e., the THz response is mainly due to holes in the OMHP phase allows rapid di ffusion away from their locus of fusion away from their locus of recombination.19,20 The high mobility of electrons and holes in the OMHP phase rapidly to recombine with the OMHP phase allows rapid diffusion away from their locus of recombination, effectively retarding geminate recombination. The consequence of this is intensity-dependent TRMC kinetics dominated by nongeminate electron–hole recombination. The TRMC kinetics measured down to the lowest intensity shows that geminate recombination must be very slow, at least tens of microseconds (Figure 4a,b). However, since the TRMC response is a product of carrier concentration and mobility, just as in TRTS, it is not possible to extract from a single transient the precise contribution of charge carrier recombination and carrier relaxation to the observed TRMC decay. Nevertheless, at the lowest excitation intensity (5.9 × 10$^9$–6 × 10$^{11}$ ph/cm$^2$ per pulse) and up to 100 μs, all transients exhibit a nonexponential decay with a characteristic behavior for nongeminate charge recombination. The high mobility of electrons and holes in the OMHP phase rapidly to recombine with the OMHP phase allows rapid diffusion away from their locus of recombination, effectively retarding geminate recombination. However, due to the low intrinsic mobility of TiO$_2$, injection is limited to a few ps due to favorable band energy alignment of TiO$_2$ and the OMHP. Consequently, from the measured THz mobility of CH$_3$NH$_3$PbI$_3$/TiO$_2$ at different pump probe delays (100 ps, cyan 200 ps, magenta 600 ps, gray 950 ps), space charge-limited photocurrents lowering the PCE. Therefore, it is important to assess the mobilities of both electrons and holes. A THz measurement on only one material does not provide this information, but by comparing several materials with the same, i.e., the THz response is mainly due to holes in the OMHP phase allows rapid diffusion away from their locus of recombination.

Unbalanced electron and hole mobilities, which are orders of magnitude different in bulk heterojunction solar cells, result in space charge-limited photocurrents lowering the PCE. Therefore, it is important to assess the mobilities of both electrons and holes. A THz measurement on only one material does not provide this information, but by comparing several materials with the same, i.e., the THz response is mainly due to holes in the OMHP phase allows rapid diffusion away from their locus of recombination.

CH$_3$NH$_3$PbI$_3$/TiO$_2$, the spectral shape is qualitatively different, and the signal size is approximately four times lower than for CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$ (as also shown in the THz kinetics of Figure 1a, inset). From the above observations we can draw a number of conclusions: First, the identical THz spectra and photoconductivity kinetics of neat CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$ show that the presence of Al$_2$O$_3$ does not alter the dynamics and mobility of the charges in the OMHP, on the distance scale probed by the THz measurements (<100 nm). Second, the presence of TiO$_2$ NPs accelerates formation of charge carriers, which leads to efficient electron injection in <1 ps due to favorable band energy alignment of TiO$_2$ and the OMHP. However, due to the low intrinsic mobility of TiO$_2$, injection leads to unbalanced transport of charges (see below), lowering the overall mobility. We also show in Figure 3 that the THz photoconductivity spectra (normalized with excitation and decay due to nongeminate recombination) at different pump probe delay times (100–950 ps) are identical, supporting our assertion that mobility remains high up to at least 1 ns.

Unbalanced electron and hole mobilities, which are orders of magnitude different in bulk heterojunction solar cells, result in space charge-limited photocurrents lowering the PCE. Therefore, it is important to assess the mobilities of both electrons and holes. A THz measurement on only one material does not provide this information, but by comparing several materials with the same, i.e., the THz response is mainly due to holes in the OMHP phase allows rapid diffusion away from their locus of recombination.

Figure 3. THz photoconductivity spectra measured 10 ps (trace with symbols) after photoexcitation and normalized with $n_{exc}$. Solid traces are THz photoconductivity spectra of CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$ at different pump probe delays (blue 100 ps, cyan 200 ps, magenta 600 ps, gray 950 ps).

Figure 4. TRMC kinetics of (a) CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$ and (b) CH$_3$NH$_3$PbI$_3$/TiO$_2$ at different excitation densities measured up to 100 μs.
By combining the results of TRTS, TRMC, and TA, we can now paint a picture of the carrier dynamics in all three studied samples, covering the time scale from less than a picosecond to hundreds of microseconds and over a very wide range of carrier densities. At high carrier density ($10^{13} - 10^{14}$ ph/cm$^2$ per pulse) achieved in the TRTS and TA measurements (Figures 1, 2, S2) extensive electron--hole nongeminate recombination leads to charge quenching and decay of photoc conductivity signal and absorption on the picosecond to several hundred picosecond time scale. From the measurement of TRTS kinetics at low intensity ($\sim 10^{12}$ ph/cm$^2$ per pulse; Figure S2) and comparison with TA kinetics (Figure 2), a maximum mobility of $\sim$25 cm$^2$ V$^{-1}$ s$^{-1}$ was concluded to last for at least 1 ns, for neat CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/Al$_2$O. With the TRMC measurements we can reach much lower excitation intensities and carrier densities, such that the rate and impact of nongeminate recombination on the dynamics becomes progressively slower and less pronounced (Figure 4). At the lowest carrier density achieved ($5.9 \times 10^{9}$ ph/cm$^2$ per pulse, Figures 4, S3), there is almost no decay of the microwave conductivity over 1 $\mu$s, showing that decay of carrier mobility as well as carrier population occurs on a $>1$ $\mu$s time scale, and microwave mobility exceeding 3 cm$^2$ V$^{-1}$ s$^{-1}$ may extend to the microsecond time scale in neat CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/Al$_2$O. The fact that nongeminate recombination persists down to very low carrier densities is another signature of charge motion over long distances. In CH$_3$NH$_3$PbI$_3$/TiO$_2$ the peak mobility is lower by approximately a factor of 4 as a result of electron injection to TiO$_2$.

Our findings show that neat perovskite and perovskite/Al$_2$O$_3$ have several nearly ideal solar cell properties: highly mobile electron and holes are formed within a few picoseconds, and mobilities of both are almost balanced and remain high to microsecond time scale. Very slow microsecond time scale recombination at ambient solar intensities in combination with high and almost equal electron and hole mobilities guarantees very efficient charge collection and thus high solar cell efficiency. The results also show that, as a consequence of electron injection from the perovskite to the TiO$_2$ with very low electron mobility, overall mobility is lowered. We note also that the lower Fermi level of TiO$_2$ decreases the open circuit voltage leading to lower overall efficiency. A possible improvement of solar cell performance would be to engineer the active materials such that both electron and hole mobilities are on the level of the electron mobility in the perovskite.

**REFERENCES**