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Charge transport limitations in perovskite solar cells: The effect of charge extraction layers

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Abstract

Understanding the charge transport characteristics and their limiting factors in organo-lead halide perovskites is of great importance for the development of competitive and economically advantageous photovoltaic systems derived from these materials. In the present work we examine the charge carrier mobilities in $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPI) thin films obtained from a one-step synthesis procedure and in planar n-i-p devices based on these films. By performing Time-of-Flight measurements, we find mobilities around $6 \text{ cm}^2/\text{Vs}$ for electrons and holes in MAPI thin films, while in working solar cells

the effective device mobility values are reduced by three orders of magnitude. From complementary experiments on devices with varying thicknesses of electron and hole transport layers, respectively, we identify the charge extraction layers and the associated interfaces rather than the perovskite material itself as the major limiting factors of the charge carrier transport time in working devices.

Keywords

Hybrid Perovskites, Thin Films, Solar Cells, Charge Carrier Mobility, Photocurrent, Charge Extraction Layer

1 Introduction

Hybrid organometal halide perovskites, a materials class revealing outstanding optoelectronic properties including large absorption coefficients^{1,2} and easily tunable bandgaps,^{3,4} have undergone a rapid development^{1,5-7} towards particularly promising candidates for integration into photovoltaic devices.⁸⁻¹¹ Facile solution processing at low temperature and the use of cheap and abundant precursor compounds¹²⁻¹⁴ combined with power conversion efficiencies surpassing 21%¹⁵ render organic-inorganic perovskites competitive with modern technologies, for example CIGS or silicon.¹⁶ Among a variety of possible material combinations and device architectures,¹⁷⁻¹⁹ the state-of-the-art layout for planar n-i-p perovskite solar cells comprises the small organic molecule spiro-OMeTAD as the hole transporter and compact TiO_x as the hole blocking layer.²⁰ However, these charge extraction materials can introduce some challenging issues to the stacked system. Spiro-OMeTAD for instance is known to be unstable and suffers from degradation processes²¹⁻²³ whereas TiO_x has been suggested to contribute to the hysteretic J - V behavior.^{24,25} Thus, the examination of the physical processes determining and limiting the charge transport properties is essential to balance material suitability (in terms of stability or production costs) and optoelectronic per-

formance, both being key aspects on the way towards further development of high-efficiency solar cells.

In this work we present a detailed study of the charge carrier mobilities, playing an important role on charge carrier transport properties in devices in general, in both perovskite thin films and stacked solar cells based on methylammonium lead triiodide (MAPI). From Time-of-Flight (ToF) photocurrent measurements we determine mobilities of approximately $6 \text{ cm}^2/\text{Vs}$ for electrons and holes in MAPI films derived from a one-step deposition approach, while we extract device mobilities being decreased by three orders of magnitude. By tuning the thickness of the hole as well as of the electron transporting material, we find that the transport time of photoinduced charge carriers under a constant external bias does not reflect the transport characteristics of the MAPI film but is mainly determined by the charge selective layers.

2 Results and discussion

Pristine methylammonium lead triiodide (MAPI) films as well as thin MAPI absorber layers incorporated in photovoltaic devices were derived from a previously published synthesis protocol describing a fast deposition-crystallization procedure (FDC)²⁶ (see Supporting Information and Figure S1 for further details). Scanning electron micrographs of FDC-derived MAPI (Figure 1a) grown on FTO-coated glass substrates confirm a high surface coverage of large crystals with few grain boundaries and without pinholes, resulting in visually smooth films.

To identify absorber material-related properties affecting the charge transport in perovskite based solar cell devices we first focused on charge carrier mobilities in the pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. For this purpose, the MAPI thin film was deposited on top of laterally arranged metallic contacts with electrode spacings d in the range of several micrometers as shown in Figure 1b. To protect the moisture-sensitive perovskite from degradation in air, the samples were

top-coated with a thin layer of poly(methyl methacrylate) (PMMA), thus permitting experiments under ambient conditions. This architecture allows for photocurrent measurements at different charge carrier travel distances through the film via the Time-of-Flight (ToF) measurement technique.

Figure 1: Schematic illustration of the employed sample layout and the experimental setup. (a) SEM micrograph showing a top view of the investigated MAPI thin film. The image shows a high substrate coverage of the perovskite containing large crystals without the presence of pinholes. (b) Schematic of the laterally contacted perovskite thin film with varying spacings d between the electrodes. To prevent the film from degradation caused by moisture the MAPI layer is capped with PMMA. Upon pulsed laser light, charge carriers are induced in the absorber material and generate a photocurrent which allows for the observation of the charge carrier transit time used to derive the charge carrier mobility.

In brief, charge carriers are generated in the perovskite layer upon photoexcitation provided by a pulsed laser. The created charge carriers are separated by an applied DC voltage and start moving towards the corresponding electrode, thus creating a current that is recorded with an oscilloscope. Because the charge carriers are locally created near one electrode, the polarity of the applied voltage determines whether the contribution of electrons or holes to the photocurrent extracted at the opposite electrode is observed. Further experimental details can be found in Figure S2 of the Supporting Information. Figure 2a depicts the obtained time-resolved photocurrent traces for different electrode distances after pulsed excitation at 540 nm and a pulse duration of 7 ns. Because ionic migration within the perovskite film is anticipated and can affect the current flow, the DC field at 5 kV/cm

was applied only during the short measurement period of single seconds to mitigate this influence. Since the observable influence of ion migration in electrical measurements, i.e. photocurrent transients, is known to occur in the timeframe of several minutes,^{27–29,32} we do not expect this to affect the investigated system significantly.

Figure 2: Extraction of the charge carrier mobility in the perovskite layer from photocurrent experiments in lateral configuration. (a) Time-resolved photocurrent transients for three different electrode spacings obtained upon focused illumination close to one contact under DC biasing at 5 kV/cm. The broadening of the ToF traces for increasing gap sizes reflects larger transit times t_{tr} of the charge carriers through the film. (b) Extracted transit times for holes and electrons as a function of electrode spacing. t_{tr} scales linearly with the corresponding electrode distance, allowing for the determination of the μ and resulting in a value of $5.78 \pm 0.34 \text{ cm}^2/\text{Vs}$ for holes and $6.26 \pm 0.22 \text{ cm}^2/\text{Vs}$ for electrons.

The linear dependence of the transit time t_{tr} on the electrode spacing d is visible in Figure 2a and 2b screening the respective distance carriers need to travel before contributing to the generated photocurrent. The identification of t_{tr} from the presented ToF transients is based on a procedure adapted from literature³³ and was performed via linear fit functions (illustrated in Figure S3, Supporting Information). To enhance the reproducibility of the determination of t_{tr} , a fit routine was programmed based on iterative modeling of the linear functions' slopes close to the point of interest in the transient. The algorithm determines two linear fit functions for the plateau and the decay of the double logarithmic j - t profile whereas the transit time is defined by the point where they intersect. According to

$$\mu = \frac{d}{E \cdot t_{tr}} \quad (1)$$

with d being the inter-electrode distance and E the applied electric field, the average charge carrier mobility is obtained by linearly fitting the curve relating the transit time with the electrode spacing (see Figure 2b). As described by the model in Equation 1 the slope of the linear regression allows for the determination of the charge carrier mobility in the MAPI film and results in $\mu_{MAPI,h+} = 5.78 \pm 0.34 \text{ cm}^2/\text{Vs}$ and $\mu_{MAPI,e-} = 6.26 \pm 0.22 \text{ cm}^2/\text{Vs}$.

In the literature different charge carrier mobilities have been reported for MAPI ranging from $3 \text{ cm}^2/\text{Vs}$ to several tens of cm^2/Vs ^{34–38} using contactless measurement techniques including time-resolved microwave conductivity (TRMC) and THz spectroscopy. For contacted MAPI films on the other hand, FET and Hall mobility measurements provide lower values between 0.5 and $8 \text{ cm}^2/\text{Vs}$.^{39–41} The charge carrier mobilities obtained here for contacted films are well within the range of these values. In contrast to the contactless techniques mentioned above, which probe a rather local mobility, we determine the mobilities in lateral direction over several micrometers, where the influence of grain boundaries and defects, i.e. potential trapping sites, becomes significant. To our knowledge, none of the optimized solution processing techniques available at present (see for example refs.^{14,26,29}) permit film thicknesses exceeding $300\text{--}500 \text{ nm}$, thus the thickness dependence of the material cannot be studied in the vertical direction in a significant range.

To gain further insights into the transport processes of photoinduced charge carriers in working solar cell devices, we complemented our studies by investigating thin film stacks incorporating the previously analyzed organolead halide perovskite material. With the MAPI film being sandwiched between spiro-OMeTAD and TiO_x as hole and electron transport layers, respectively, and contact layers (gold and FTO), the illumination of the perovskite occurs from the transparent FTO side. A detailed description of the complete sample preparation procedure can be found in the Supporting Information.

In the following experiments we focused on the effects of the charge extraction layers on the

(a)

(b)

(c)

Figure 3: Characterization of the MAPI-based photovoltaic devices. (a) Cross-sectional views of the stacks with varying layer thicknesses of the hole transporter spiro-OMeTAD. The MAPI and TiO_x thicknesses were kept constant at 360 nm and 70 nm, respectively. MAPI residues visible on the spiro-OMeTAD layer are a result of cutting the sample prior to the SEM measurement and are not induced by film growth. (b) $J-V$ performance of working devices with different thicknesses of the hole transport layer (HTL) under simulated AM 1.5G illumination. (c) Statistical analysis of corresponding power conversion efficiencies from more than 120 individual photovoltaic devices. Best average performance was observed for a spiro-OMeTAD layer thickness of 370 nm.

transit time of charge carriers for constant thickness of the absorber material while varying the thickness of the charge extraction layer. Cross-sectional SEM images of photovoltaic devices confirm the successful tuning of the thickness of the hole transport layer (HTL) spiro-OMeTAD (see Figure 3a) ranging from 170 to 740 nm at constant TiO_x and MAPI thickness (70 and 360 nm, respectively). We note that the MAPI residues visible on the HTM layer (see for example second cross-section in Figure 3a) result from cutting the solar cell shortly before performing the SEM measurement. These residues attach to the cross-section and are not induced by a non-uniform deposition of the organic spiro-OMeTAD layer on the absorber material which could occur if the MAPI surface would be rough. Moreover, the MAPI film thickness seen in the SEM cross-sections corresponds to the typical values deduced using AFM or profilometers.^{30,31}

J - V analysis (Figure 3b) of this type of cells under simulated AM 1.5G illumination confirms proper operation characteristics with typical deviations of $\pm 2\%$. Furthermore, PCE statistics from more than a total of 120 solar cells indicate that the conversion of incident light to current reaches the best average performance value of $12.8 \pm 1.14\%$ for a HTL thickness of 370 nm (see Figure 3c). Equivalent measurements on photovoltaic devices with varying thickness of the electron transport layer (ETL) TiO_x as well as the corresponding cross-sections of the samples can be found in Figure S4 of the Supporting Information.

Subsequently, we conducted ToF measurements on the stacked devices with varying thickness of hole or electron transport layer. For this purpose, the samples were illuminated from the transparent FTO side using an aperture mask with an active area of approximately $3 \times 3 \text{ mm}^2$, identical with the illuminated area in the cell performance experiments. Figure 4a illustrates the j - t profiles for stacked devices with different spiro-OMeTAD layer thicknesses. The transit time was extracted by employing the same fitting routine which was used for the transients in the lateral configuration. To verify the applicability of Equation 1 to the obtained data, the transit times at different applied bias voltages were plotted as shown in Figure 4b where t_{tr} follows a linear dependence on U_{bias} . From this follows that the device

Figure 4: Photocurrent transients obtained for complete perovskite-based solar cell devices using the described experimental setup. (a) Representative transients of photovoltaic devices (as shown in Figure 3a) with varying thicknesses of the hole transporting material spiro-OMeTAD on top of the photoactive perovskite layer. (b) Extracted transit times as a function of reciprocal applied bias voltage for a defined thickness of the spiro compound. The transit time follows a linear dependence on the inverse voltage (see mobility equation 1). (c) Transit times determined from the transients shown in (a) versus corresponding spiro-OMeTAD thickness. When increasing the layer thickness of the hole transporter the transit time is extended. (d) Effect of electron transport layer (TiO_x thickness) on the transit of charge carriers across the stack. Similar to the results shown in (c), the electron extraction layer affects the transport speed of charge carriers. The MAPI layer thicknesses in (c) and (d) were kept constant at 350 nm.

mobility derived from the slope of the linear regression relating t_{tr} and U_{bias} results in a value of $\mu_{device} = (6.05 \pm 0.19) \cdot 10^{-3} \text{ cm}^2/\text{Vs}$ (assuming $d = d_{\text{TiOx}} + d_{\text{MAPI}} + d_{\text{spiro}}$) which is in agreement with reported device mobilities.⁴³ As seen in Figure 4 the transport of charge carriers is substantially influenced by the thickness of the HTL, which is reflected in larger t_{tr} values starting from 0.82 up to 1.51 μs for increased travel distances, ranging from 170 to 740 nm (Figure 4c). A similar effect is observed for increasing ETL thickness (Figure 4d), where the transit time increases from 0.87 to 1.05 μs with thicknesses ranging from 70 to 150 nm. We note that the growth of the ETL on the rather rough FTO surface consequently leads to some variations in the thickness (see also Supporting Information, Figure S4a), resulting in large error bars in the chart. Furthermore, the chemical fabrication process employed for the samples in these specific experiments does not allow to create uniform films below a certain thickness of approximately 60-70 nm, thus our measurements include samples with ETL thickness exclusively above the minimal obtainable thickness. On the other hand, the minimum thickness of the spiro-OMeTAD layer is limited by the formation of pinholes to about 170 nm at which a reduction of the PCE starts being observed.

We find similar slopes for the HTL and ETL of 1.22 ± 0.07 and $2.43 \pm 0.36 \text{ nm/ns}$. Based on the charge carrier mobility values obtained from the experiments on laterally contacted MAPI, the average drift velocity v_d of holes through the absorber layer is calculated according to

$$v_d = \mu_{MAPI,h^+} \cdot E \quad (2)$$

and results in 290 nm/ns. With the thickness of MAPI (approximately 360 nm) in the full solar cell device, the contribution of the perovskite absorber layer to the overall transit time of the device can be estimated to $\sim 1 \text{ ns}$. This number represents an upper limit because it can be expected that in the vertical solar cell architecture the charges will have to pass a smaller number of grain boundaries than in the lateral measurements presented in Figure 2. Clearly, the estimated transit time is much smaller than the effective transit times observed

for the HTL and the ETL. From our observations in the ToF experiments performed on the devices, we suggest that the effective charge carrier transit times in perovskite solar cells are mainly affected by the thickness of spiro-OMeTAD and to a lesser extent by the thinner TiO_x layer. This also leads to a reduction of the PCE for thicker and to pinholes and shunting for thinner spiro-OMeTAD layers, resulting in an optimum thickness of around 370 nm.

Consequently, the measurements on the contacted film establish that the absorber layer and its properties could be excluded from affecting the transport of photogenerated charges in working devices. This highlights that rather the thickness of the extraction layers, in particular of the HTL, is a major limiting factor for charge transport. Recently published investigations already demonstrate different approaches to replace the commonly employed material spiro-OMeTAD by other organic or inorganic hole transporters such as EDOT-OMeTPA⁴⁴ or graphene,⁴⁵ respectively, and TiO_x by tin dioxide.^{46,47}

3 Conclusion

In this study we investigated mobilities of light-induced charge carriers in both individually contacted MAPI thin films and photovoltaic stacks based on this type of hybrid perovskite. Employing the Time-of-Flight photocurrent technique, we observe charge carrier mobilities of $5.78 \pm 0.34 \text{ cm}^2/\text{Vs}$ for holes and $6.26 \pm 0.22 \text{ cm}^2/\text{Vs}$ for electrons in individual perovskite films in lateral dimensions. Compared to the device mobilities determined for the n-i-p architecture consisting of FTO/ TiO_x /MAPI/spiro-OMeTAD/Au and resulting in values decreased by three orders of magnitude, the photoactive perovskite layer can clearly be excluded of being a charge transport limiting factor in the device. Complementary ToF experiments on solar cells with varying spiro-OMeTAD thickness demonstrate a significant increase of the charge carriers' transit time through the device stack with increasing extraction layer thickness. By tuning the TiO_x thickness, we observe a similar effect on the transit times. From this we conclude that mainly the thickness of spiro-OMeTAD contributes

substantially to the transit time and to the effective device mobility. Hence, the hole transport layer represents a major transport limiting factor in the working device that should be considered in efforts aimed at of further device and interface engineering.

4 Experimental

4.1 Perovskite thin film synthesis

Perovskite thin film deposition was done following a previously published synthesis route.²⁶ A detailed description of the slightly modified synthesis procedure can be found in the Supporting Information.

4.2 Laterally arranged gold contacts on glass

In-plane gold electrodes were fabricated using microstencil lithography techniques. Supplementary details on the fabrication of the structures on the glass substrate are described in the Supporting Information.

4.3 Solar cell fabrication

Photovoltaic device preparation was carried out by successive deposition of electron transport layer (TiO_x), perovskite, hole transport layer (spiro-OMeTAD) and gold front contact on top of FTO (fluorine doped tin oxide) coated glass substrates. Further details are specified in the Supporting Information.

4.4 Time-of-Flight measurements

Charge carrier mobilities in laterally contacted thin films were determined via Time-of-Flight (ToF) measurements (see Supporting Information, Figure S2). The films were illuminated from the semi-transparent glass/gold bottom side by employing pulsed laser excitation at

540 nm and a pulse width of 7 ns. To extract the photogenerated charges, a constant DC field is applied at the electrodes solely for the measurement period of approximately 1 s to prevent ionic migration within the perovskite.^{27,28,32} The created current is recorded as a function of time resulting in ToF transients shown in Figure 2a. Charge carrier mobilities in stacked solar cell devices were extracted from photocurrent measurements employing the same experimental setup by illuminating the samples from the transparent glass side. For all solar cells, a full data set comprising photocurrent transients at bias voltages between 1.2 and 3.0 V was recorded in steps of 200 mV to confirm the applicability of Equation 1 to the determined transit times (Figures 4b and S5b).

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Supporting Information Available

The following files are available free of charge.

Characterization details of the MAPI film, schematic of the employed experimental setup, evaluation of photocurrent transients.

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Graphical TOC Entry