Impact of Residual Lead Iodide on Photophysical Properties of Lead Triiodide Perovskite Solar Cells

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Abstract

The role of residual lead iodide on the photophysical properties of methylammonium lead iodide is still unclear and contradictory views exist about its impact. Herein, we report that there is a critical amount of residual lead iodide, which is beneficial for the solar cell performance. We employed transient absorption spectroscopy to investigate the charge carrier recombination dynamics in perovskite solar cells and to address the role of different amounts of residual lead iodide. The amount of lead iodide is varied through the perovskite thin film preparation protocol upon a modified two-step fabrication process. We observe slower carrier dynamics at the perovskite/titanium dioxide interface in the presence of residual lead iodide when exciting the perovskite at the perovskite/titanium interface, which correlates with improved solar cell device performance. Excitation from the perovskite side indicates that the effect of residual lead iodide is primarily at the titanium dioxide interface. Increasing the lead iodide content further did not alter the carrier recombination; on the contrary, it resulted in lower device performance. Our study confirms that the presence of lead iodide can have a beneficial effect, as it reduces charge carrier recombination at the perovskite/titanium dioxide interface.

Keywords: Perovskite, lead iodide, spectroscopy, charge carrier recombination, interfacial recombination.

1. Introduction

Metal halide perovskite semiconductors have rapidly evolved as solution-processed photovoltaic materials in thin film devices,^[1] and power conversion efficiencies (PCEs) recently exceeded 25%.^[1c, 2] Methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$, *a.k.a.* MAPbI₃) is the archetypal lead halide perovskite light absorber in photovoltaics.^[1b, 3] In this respect, one of the most fascinating and surprising observations is the role of remnant (unreacted) precursors, such as lead iodide (PbI_2), present within the perovskite layer and its impact on the photophysics of the perovskite semiconductor and ultimately the photovoltaic performance.

Initial studies demonstrated a clear correlation between residual PbI_2 and solar cell performance.^[2a, 4] Studies have since focused on the importance of residual PbI_2 on solar cell performance and have hypothesized several effects such as energy level alignment between the perovskite, PbI_2 , and the titanium dioxide (TiO_2) electron transporting layer (ETL), grain boundary effects, and changes to the crystallinity of the perovskite.^[5] However, these studies have made conflicting statements about the role of PbI_2 , some finding it beneficial, while others claiming the opposite. One of the most comprehensive studies to date presented by Jacobsson et al. has utilized complementary characterization techniques on single step-processed perovskite films to show conclusively that slightly PbI_2 -enriched samples indeed exhibit an improved device performance.^[6] The explanation presented is that PbI_2 acts as a barrier for recombination at the perovskite/ TiO_2 interface,^[7] and also plays a role in grain boundary passivation, in turn reducing carrier recombination.^[8] In addition, investigation of residual PbI_2 in perovskites and its role at both the grain boundaries and the interfaces has been addressed through advanced spectroscopic and imaging techniques, for instance, scanning electron microscopy complemented by cathodoluminescence and photoluminescence imaging has been used as well as Kelvin probe force microscopy and electron beam-induced current techniques.^[9]

Despite extensive studies on the effects of PbI_2 , the vast majority of them address the device performance, while a clear picture of the photophysical processes and role of PbI_2 on

the charge carrier dynamics, specifically the recombination, in the perovskite semiconductors is still missing. Transient absorption (TA) spectroscopy is a powerful tool to unveil the charge carrier dynamics and the associated photophysical processes, as proven for many other material systems.^[10]

Herein, we investigate the charge carrier generation and recombination dynamics in perovskite photoactive layers prepared by a two-step deposition protocol, which allows us to vary the residual PbI_2 content. Specifically, the PbI_2 solution preparation was varied: the PbI_2 was first dissolved in N,N-dimethylformamide (DMF), or in dimethylsulfoxide (DMSO), or PbI_2 -DMSO complex precursor was dissolved in DMF (designated here as complex c-DMSO).^[11] In all cases, the second step was the conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ using identical MAI solution dipping processes. The resulting $\text{CH}_3\text{NH}_3\text{PbI}_3$ films possess different PbI_2 content upon conversion, as indicated by X-ray diffraction (XRD) analysis, with DMF and DMSO-processed PbI_2 samples exhibiting high and intermediate residual PbI_2 content, respectively, while c-DMSO samples exhibited the lowest PbI_2 content. Transient absorption spectroscopy analysis was performed by exciting the quartz substrate/ TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film stack from both sides using a 532 nm pump laser,^[12] namely, from the perovskite film's top surface or through the TiO_2 -coated quartz substrate. This allows us to distinguish photophysical phenomena at the TiO_2 /perovskite interface and establish a correlation between the charge carrier dynamics and the performance of devices using TiO_2 as ETL. Exciting the perovskite absorber layer from the TiO_2 side leads to significantly prolonged charge carrier dynamics in PbI_2 -deficient cases, while samples with medium PbI_2 contents exhibit the fastest recombination. However, when exciting from the perovskite side, a different behavior is observed: medium PbI_2 contents retard the charge carrier recombination and PbI_2 deficiency leads to fast recombination. We note that the highest PCEs correspond to the planar heterojunction $n-i-p$ devices, exhibiting the lowest PbI_2 content, in line with the observation of slow charge carrier recombination dynamics.

2. Experimental Methods

2.1 Metal halide perovskite solar cell fabrication

Pre-patterned fluorine-doped tin oxide (FTO)-coated glass (Pilkington, TEC-8) was used as substrate for solar cell fabrication. Substrates were cleaned successively in detergent, deionized water, acetone and isopropanol in an ultrasonic bath for 15 minutes each. All substrates were treated with UV-ozone for 10 minutes, and treated with oxygen plasma for 3 minutes prior to the sample preparation. The same cleaning protocol was applied to quartz glass substrates used for transient absorption spectroscopy measurements. A compact layer of TiO_2 was deposited by spin-coating a solution containing 350 μL of titanium isopropoxide and 35 μL of hydrochloric acid (HCl) in 5 mL ethanol at 2000 rpm for 60 seconds, followed by annealing at 490 $^\circ\text{C}$ for 60 minutes. The ~ 300 nm thick mesoporous TiO_2 layer was deposited by spin-coating (2000 rpm for 60 s) solutions of commercial Greatcell Solar (18 NR-T) paste diluted in ethanol (1:5 weight ratio). After initial drying at 150 $^\circ\text{C}$ for 20 minutes, the TiO_2 film was further sintered at 490 $^\circ\text{C}$ for 60 minutes. After the film had cooled down to room temperature, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film deposition was completed using a two-step protocol in a nitrogen (N_2) filled glove box, as described below. All the synthesis and deposition steps described below were carried out in a N_2 filled glove box with oxygen and humidity levels below 0.1 ppm.

PbI_2 solutions were prepared with different precursors and solvents. To prepare the PbI_2 solutions in DMF and DMSO, 461 mg lead (II) iodide powder (PbI_2 , Alfa Aesar) was mixed with 1 mL of anhydrous DMF (Sigma Aldrich) and anhydrous DMSO (Sigma Aldrich), respectively. The PbI_2 -DMSO complex solution was prepared according to a procedure reported earlier.^[11a] In short, PbI_2 was dissolved in 15 mL of DMSO at 60 $^\circ\text{C}$ overnight. 35 mL of toluene was slowly added to the PbI_2 solution to induce precipitation of a white powder from the yellow transparent solution. The precipitate was filtered and washed once with toluene and

then dried at room temperature. The white powder of the PbI_2 -DMSO complex was obtained after annealing overnight in a vacuum oven at 60 °C. The 1.3 M PbI_2 -DMSO complex solvent was dissolved in DMF solution at 70 °C. All solutions were used directly without additional purification. All three PbI_2 precursor solutions were spin-coated on a TiO_2 -coated FTO/glass substrate at 2000 rpm for 60 seconds. Afterwards, the substrate was transferred to a hotplate preheated to 70 °C, and thermal treatment was done for 2 minutes in order to remove any residual solvents.^[13] After cooling down to room temperature, the films were dipped into a MAI-isopropanol solution (10 mg/mL) for 10 minutes, followed by washing in anhydrous isopropanol to remove excess MAI. Finally, the films were annealed at 90 °C on a hot plate for 15 seconds to complete the conversion process and to evaporate the residual solvent.

A Spiro-OMeTAD hole-transporting layer was deposited in air by spin-coating. A 0.79 M solution in 1 mL chlorobenzene was prepared, along with 17.5 μL Li-TFSI and 28.5 μL tBP additives. The coating process was carried out at 2000 rpm for 30 seconds in air (with a relative humidity of $20 \pm 5\%$ at 21°C). Immediately after spin coating the Spiro-OMeTAD layer, the devices were stored in the dark in dry air overnight. Finally, 20 nm gold and 80 nm silver electrodes were thermally evaporated in a vacuum chamber.

2.3 Thin film and device characterization

The XRD measurements were performed using a Bruker D8 Advance, (AXS System, Germany) X-ray diffractometer in θ -2 θ configuration using a $\text{Cu-K}_{\alpha 1}$ radiation source with a wavelength of 1.5406 Å. Scanning electron microscopy (SEM) was performed using a field emission SEM (FESEM, FEI Nano Nova). Steady state absorption measurements were performed using a UV-visible spectrometer (Varian Cary 6000i UV-visible spectrometer, Agilent Technologies) over the spectral range from 200-800 nm with 1 nm steps. Steady-state photoluminescence (PL) spectra were acquired using a Fluoromax-4 spectrofluorometer (Horiba Scientific) using a 633 nm laser excitation source.

The photovoltaic device performance was evaluated by collecting current density – voltage (J – V) characteristics under sun illumination (99 mW/cm², AM 1.5G, Newport, Oriel Class A, 91195A) calibrated using a Si-reference cell certificated by NREL. The solar cells were masked during the J – V measurements to define an active area of 0.1 cm². A sweep rate of 10 mV/sec was used for all J – V measurements without applying any preconditioning.

2.4 Time-resolved measurements

Transient absorption (TA) spectroscopy measurements were performed using a classical optical pump-probe scheme. All measurements were conducted in the time range from 1 nanosecond (ns) to 100 microseconds (μ s). Initially, the fundamental of a titanium:sapphire amplifier (Coherent Legend DUO), operating at 800 nm with a repetition rate of 3 kHz and a pulse energy of 4.5 mJ is split into 3 lines (2 mJ, 1 mJ and 1.5 mJ) to pump two optical parametric amplifiers (Light conversion TOPAS Prime). One of the TOPAS is used to generate tunable pump pulses, while the second one generates signal (1300 nm) and idler (2000 nm) only. A fraction of the signal beam of the second TOPAS was focused into a c-cut 3 mm thick CaF₂ window, thereby generating a white-light supercontinuum from 350 to 1000 nm. This white-light supercontinuum probe was used for long delay TA measurements. The excitation (pump pulse) was provided by an actively Q-switched Nd:YVO₄ laser (INNOLAS piccolo AOT) frequency-doubled to provide pulses at 532 nm. The excitation was triggered by an electronic delay generator (Stanford Research Systems DG535), itself triggered by the TTL sync from the Legend DUO, allowing precise control of the delay between pump and probe with a jitter of roughly 100 ps.

Pump and probe beams were focused on the sample to overlap spatially. The transmitted fraction of the white light was guided to a custom-made prism spectrograph (Entwicklungsbüro Stresing) where it was dispersed by a prism onto a 512 pixel NMOS linear image sensor (HAMAMATSU S8381-512). The probe pulse repetition rate was 3 kHz but the excitation was

directly generated at 1.5 kHz frequency covering a temporal range from 1 ns to 100 μ s delays, while the detector array was read out at 3 kHz. Adjacent diode readings corresponding to the transmission (T) of the sample after excitation and in the absence of an excitation pulse were used to calculate $\Delta T/T$. Moreover, the measurements were averaged over several thousand shots to obtain a better signal-to-noise ratio. Finally, the chirp induced by the transmissive optics was corrected with a home-built Matlab code by reevaluating for each wavelength the delay at which pump and probe are simultaneously arriving on the sample as the time of the signal amplitude. All measurements were performed at room temperature under a dynamic vacuum of $<10^{-5}$ mbar to minimize degradation effects.

3. Results and discussion

Structural and morphological characterization of the thin films were performed by XRD and SEM as shown in Figures 1a and 1b, respectively. The XRD patterns (Figure 1a) are presented for all three perovskite thin films. The sample exhibiting the most prominent (100) PbI_2 diffraction peak ($2\theta = 12.5^\circ$, indicated as “*”) is the one prepared using DMF as solvent. The sample prepared with DMSO has a lower (100) peak intensity, while the c-DMSO sample has the lowest peak intensity of all samples. The changes in integrated intensities reflect approximately the relative amount of residual crystalline PbI_2 remaining in the samples after the two-step deposition and conversion.^[14] This is further ensured by using identical coating conditions to achieve nominally identical thicknesses of the perovskite films in the 350-400 nm range. Changing the concentration of the PbI_2 or modifying the crystallization process controls the amount of excess PbI_2 in the perovskite. The crystallization varies for different precursor solvate phases and thus directly controls the residual PbI_2 . This implies, that different precursor solvate phases result in distinct amounts of residual crystalline PbI_2 .^[15] The most intense diffraction feature from the films is the (110) perovskite peak ($2\theta = 14.7^\circ$). Its integrated

intensity remains nearly constant for all three films. Additional perovskite peaks are also present and assigned to the tetragonal crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$.^[16]

Figure 1: (a) XRD patterns of perovskite thin films prepared by a two-step process using different precursor solutions, namely PbI_2 in DMF, PbI_2 in DMSO and $\text{PbI}_2 \bullet \text{DMSO}$ (c-DMSO) in DMF in the first step. The characteristic (100) PbI_2 peak (*) and several perovskite peaks (110), (112), (220), and (222) are apparent. (b) Plan-view SEM images of PbI_2 thin films (top

row) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films (bottom row) prepared on glass. (c) UV-Vis absorbance and (d) PL spectra of perovskite thin films.

SEM was conducted on dried PbI_2 films and converted $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, respectively, to compare their surface morphologies (Figure 1b), and the films were prepared according to the three recipes. PbI_2 films prepared using DMF exhibit higher surface roughness and apparently more porosity, as evidenced by significant surface corrugations and valleys. In contrast, the film prepared from DMSO is significantly more compact and smooth. The c-DMSO based preparation method yields films with many morphological similarities to the DMF-based one in that the film appears rougher and exhibits more valleys. However, the main difference is that the features are more angular and distinct crystallites appear on the surface, when c-DMSO is used in contrast to the more round-shape features observed when DMF is used. Some of the morphological characteristics observed in the PbI_2 films prevail after conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, as seen in the lower panel of Figure 1b. In fact, films converted from PbI_2 /DMF are more compact, but still exhibit round-shape features. Films prepared from PbI_2 /DMSO are again more compact and appear to be smoother, while PbI_2 (c-DMSO)/DMF yields a film resembling the PbI_2 /DMF case with additional isolated crystallites covering the surface, which resemble perovskite cuboids. The actual perovskite formation in the case of PbI_2 /DMF was previously investigated,^[17] it is slower compared to the conversion of PbI_2 formed from DMSO and c-DMSO, where the solvent-lead coordination is stronger. Furthermore, in case of PbI_2 /DMSO a previous study confirmed that structural conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ begins prior to annealing.^[18]

Steady-state UV-vis absorbance spectra of the three $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film samples on mesoporous TiO_2 -coated glass substrates prepared with similar thicknesses using the different PbI_2 precursor routes are compared in Figure 1c. The perovskite film obtained by conversion from PbI_2 cast from c-DMSO exhibits a sharp absorption edge around 750-770 nm and

additionally higher absorbance compared to the other two samples. The absorption shoulder is least pronounced in case of films converted from PbI_2 cast from DMF, while films converted from PbI_2 cast from DMSO exhibit a moderately defined shoulder. PL measurements conducted on glass/ETL/perovskite samples following excitation at 633 nm used similar experimental conditions (geometry etc.). With the above three preparation methods, a strong emission peak is detected at 775 nm (Figure 1d). The observed PL peak at 775 nm is the same for all $\text{CH}_3\text{NH}_3\text{PbI}_3$ and it is assigned to the perovskite phase. The intensity of the peak varies significantly and is related to the presence of unreacted PbI_2 , as also discussed in literature.^[19] In fact, the PL intensity is remarkably reduced when going from DMF (highest residual PbI_2 content) to DMSO and to c-DMSO (lowest residual PbI_2 content). Hence, the results demonstrate that radiative recombination is sensitive to the presence of unreacted PbI_2 .

We fabricated also mesoporous *n-i-p* photovoltaic devices using TiO_2 as the mesoporous ETL. The $J-V$ characteristics of typical solar cells are displayed in Figure 2. As summarized in Table 1, the devices based on PbI_2 cast from DMF and DMSO, yielded low and intermediate average PCEs of 9.7% and 11.0%, respectively. Devices based on PbI_2 prepared from c-DMSO were the most efficient, yielding an average PCE of 13.2%. These differences can be explained in part by systematic changes of the short-circuit current density (J_{SC}), open circuit voltage (V_{OC}), and fill factor (FF), all of which increase with decreasing residual PbI_2 content in the perovskite film. In addition, hysteresis is observed in all three cases, but it is comparatively pronounced in the case of c-DMSO/DMSO relative to PbI_2 /DMSO and PbI_2 /DMF.

The higher V_{OC} might be due to enhanced band alignment and suppressed interfacial recombination since V_{OC} depends strongly on non-radiative recombination pathways.^[20] The increment in J_{SC} is caused by changes of several key parameters that determine the photocurrent such as absorbance, free-carrier generation, and charge recombination. As observed from the

UV-vis spectra the absorbance is highest for the c-DMSO sample, which translates into a higher absorption coefficient. In general, light-harvesting properties are also correlated with the relative increment in J_{SC} , in our case absorbance is higher for the same sample and lead to efficient charge generation. Thus, more photo-generated carriers, enhanced morphology and reduced recombination implies that the J_{SC} is higher for this sample. Additionally, higher J_{SC} is associated with relatively effective charge transport for the case of the c-DMSO sample, as it exhibits the longest recombination compared to DMF and DMSO ones. Conversely, the prolonged charge carrier lifetime is consistent with the increment of V_{OC} and FF . Hysteresis is associated with few issues and Ravishankar et al. proposed a dynamic hysteresis model, which quantitatively explains the different hysteretic features.^[21] According to this model, hysteresis behavior could be due to ionic movement and electrode polarization without including the effect of trap-assisted recombination.^[21a] Moreover, presence of defect and trap states at the perovskite/ETL and perovskite/HTL interfaces respectively cause interfacial recombination which also has an impact on the device performance as well as the hysteresis behavior as discussed in literature where a proposed interfacial passivation lead to significant improvement of the performance.^[20c, 22] From our findings, we can also correlate that a compact structure of c-DMSO confirmed by SEM is correlated to a higher FF due to higher contact quality with both TiO_2 and spiro-OMeTAD.

Figure 2: The J – V characteristic of the respective devices with the reverse bias (RB) and forward bias (FB) in a) and the statistics of 10 devices presented in b). All devices were tested at 10 mV/s scan rate without any preconditioning.

Table 1: Figures of merit of champion perovskite solar cells prepared with the respective precursor solvents.

PbI ₂ precursor route	Scan	J_{SC}	V_{OC}	FF	PCE
	direction	(mA/cm^2)	(V)	(%)	(%)
PbI ₂ /DMF	V_{OC} to J_{SC}	17.96	0.86	61.1	9.7
	J_{SC} to V_{OC}	18.56	0.88	57.6	9.2
PbI ₂ /DMSO	V_{OC} to J_{SC}	19.90	0.90	62.6	11.0
	J_{SC} to V_{OC}	19.40	0.89	60.8	10.1

PbI₂(c-DMSO)/DMF	V_{OC} to J_{SC}	20.30	0.95	68.5	13.2
	J_{SC} to V_{OC}	20.10	0.93	64.2	12.0

We investigated the photophysical processes, specifically the dynamics of photo-generated charge carriers in the different types of CH₃NH₃PbI₃ absorber layers, containing different amounts of residual PbI₂ to understand the relation between carrier dynamics and solar cell device performance. When interpreting the results of these experiments, it is important to recall that residual PbI₂ in CH₃NH₃PbI₃ films prepared using the two-step method is typically present near the TiO₂ contact.^[5a, 19a, 23] The same holds for the one-step synthesis method of CH₃NH₃PbI₃ on TiO₂.^[24] We conducted transient absorption (TA) spectroscopy measurements on glass/TiO₂/CH₃NH₃PbI₃:(residual)PbI₂ stacks by optical excitation at 532 nm from either the top (perovskite) or bottom (titania) side of the samples. The photons are absorbed in the first ca. 100 nm of CH₃NH₃PbI₃ due to the large absorbance and thus limited light penetration depth at that wavelength. Hence, excitation from either side of the film should allow a direct comparison of the dynamics of photo-generated charge carriers in the bulk of CH₃NH₃PbI₃ (top illumination) and near the TiO₂/CH₃NH₃PbI₃ interface (bottom illumination), as depicted in Figure 3. Furthermore, analysis of the excited state dynamics allows to correlate the device characteristics to the sample's residual amount of PbI₂.^[12] Photo excitation from the perovskite side generates free carriers in the top part of the perovskite layer. Recombination predominantly takes place at the surface and at the grain boundaries hence, only a fraction of the charge carriers generated near the top are able to reach the TiO₂ interface. However, when the same sample is excited from the TiO₂/CH₃NH₃PbI₃ (bottom) side, the dynamics are expected to be different due to the presence of the TiO₂ interface and the larger local abundance of residual PbI₂.

The acquired TA spectra for the respective excitation directions are presented in Figures 3a, 3b and 3c (perovskite side) and 3e, 3f, and 3g (TiO₂ side) for the three different samples, namely DMF, DMSO, and c-DMSO, containing different residual PbI₂ contents, respectively.

In all cases, a positive and narrow peak appears at 1.60 eV in the TA spectra, assigned to a combination of ground state bleach (GSB) and stimulated emission (SE),^[3d] while a broad photo-induced absorption (PIA) band is apparent from 1.70-2.25 eV. For all samples, the decay of the GSB is concluded in 45 ns for the respective illumination directions. To obtain further insight into the associated charge carrier dynamics, the decay was tracked at the maximum of the GSB, as plotted in Figures 3d and 3h for top and bottom excitation, respectively. Insets covering a shorter time window of 15 ns are depicted in the respective figures to highlight the ground state recovery.

Following optical excitation from the top (perovskite), the DMSO sample exhibits a slower GSB recovery compared to the c-DMSO and DMF samples, with the latter being the fastest. In contrast, when exciting from the bottom (titania/perovskite interface), the GSB recovery is fastest for DMSO followed by DMF and c-DMSO. More precisely, it appears that the ground state recovery in DMF-based samples is rather similar irrespective of the excitation direction. However, we observe strikingly different charge carrier dynamics from perovskite films prepared using DMSO and c-DMSO, depending on the excitation direction. We note that this observation is in line with a previous study addressing the difference in charge carrier dynamics at the interface with respect to the excitation direction.^[12]

Figure 3: TA spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films prepared from: a) DMF, b) DMSO and c) c-DMSO presented for various ns- μ s delay, when excitation is performed from the perovskite side. The characteristic perovskite ground state bleach appears at 1.60 eV. d) Charge carrier dynamics extracted at the GSB across a time window of 45 ns (inset shows the charge carrier dynamics within the first 15 ns). TA spectra at selected time delays for three representative perovskite samples as the illumination is performed from the TiO_2 side are shown in e), f) and

g). In h) the charge carrier dynamics at the ground state bleach are shown across a time window of 45 ns, while the inset shows the corresponding recovery in the first 15 ns. The bump in the traces present at 12-14 ns is due to an experimental artefact.

For top-illuminated samples, the kinetic traces point to a slower recovery of the ground state in the DMSO sample, while a faster decay of the GSB signal is observed in the c-DMSO and DMF samples (Figure 3d). In the case of DMSO, which has a medium PbI_2 content and yielded the most compact films, the slower recombination can be explained by the beneficial effect of excess PbI_2 , acting as a trap state passivation agent, thereby reducing the carrier recombination compared to films prepared with DMF or c-DMSO.^[24] The latter two films exhibit significant surface roughness, including valleys, exposed grain boundaries, and crystallites (Figure 1b). This implies more defects acting as recombination sites near the surface of the DMF-based film, possibly reducing the apparent passivation effect of excess PbI_2 present in the film.^[2a] Films prepared from c-DMSO exhibit a more crystalline texture near the surface and contain the lowest PbI_2 content. Hence, we expect a faster ground state recovery compared to DMSO owing to fewer defects and a reduced effect of passivation by residual PbI_2 .

When exciting from the TiO_2 side, distinct differences of the recombination at the interface between the perovskite and TiO_2 are observed. The corresponding TA spectra are shown in Figure 3e, 3f and 3g with the associated charge carrier dynamics plotted in Figure 3h. The charge carrier dynamics is significantly retarded for the case of c-DMSO, while DMSO is exhibiting the fastest ground state recovery. Furthermore, the DMF sample exhibits slower charge carrier dynamics than the DMSO sample, but faster compared to the c-DMSO sample. We can directly relate this to the amount of residual PbI_2 incorporated in the different samples. Initially, the content is reduced when changing from DMF to DMSO as solvent, resulting in faster charge carrier recombination (Figure 3h inset), while further reduction of the PbI_2 content results in slower carrier recombination as seen for the case of c-DMSO. We propose the

following explanation for this observation: the initial electron transfer from perovskite to TiO_2 occurs via tunneling, as the PbI_2 layer is relatively thin in the case of c-DMSO. After charge transfer the PbI_2 layer reduces the carrier recombination at the perovskite/ TiO_2 interface, as also reported in previous studies.^[8b, 25] Furthermore, band edge matching between perovskite, PbI_2 and TiO_2 , as schematically displayed in Figure 4, can play a role and is used to explain different charge recombination dynamics in the presence of residual PbI_2 .^[5a, 8b] After electron transfer from the perovskite layer to TiO_2 , the possibility of recombination with holes in the perovskite layer exists, as Ti^{3+} defect sites in TiO_2 might be energetically matched with the perovskite.^[8b] If unreacted PbI_2 exists, which has a higher conduction band energy than the perovskite, it will act as a barrier which can be overcome by tunneling only, in turn reducing recombination at the interface as shown in Figure 4b. Such formation of energy barriers hinders the recombination at surface defects and trapped states. On the other hand, the DMSO sample has a comparably thicker PbI_2 layer (Figure 4c), as its content is enriched, which hinders electron transfer from the perovskite to TiO_2 . Therefore, recombination in the case of DMSO occurs within the perovskite rendering the charge carrier extraction less effective. Consequently, we ascribe the better device performance in case of c-DMSO to PbI_2 acting as an effective passivation layer at the interface reducing carrier recombination and thereby enhancing the device performance.^[8b, 26] Analogously, the enriched PbI_2 content in the DMF sample prevents electron transfer to TiO_2 as in the case of DMSO, however, the relative difference in the dynamics observed between the two samples can be explained by charge carrier trapping at perovskite grain boundaries, which is dominant in the case of the DMSO sample. Furthermore, in both scenarios, the fastest ground state recovery is observed for the DMF sample, regardless of the direction of the excitation. In addition, it has more trap states and surface defects as implied by its morphology and concluded from steady-state PL measurements. We note that the observation of effective electron injection as a consequence of an excess of PbI_2 in the case of c-DMSO is in line with previous studies reported by Nazeeruddin and Boschloo.^[4b, 19a]

Kamat and co-workers have previously suggested various recombination schemes.^[27] In our case, two different decay components (fast and slow) are clearly apparent, and we attribute this multi-component decay to the convolution of Shockley-Read-Hall (trap-assisted non-radiative recombination) and band-to-band radiative recombination, since Auger recombination becomes dominant only at higher carrier concentrations ($>10^{18} \text{ cm}^{-3}$) for perovskite thin films.^[20a, 28] We note that here we abstain from fitting the dynamics with two or more exponentials, as such parametrization does not accurately reflect the physical processes and thus does not provide any meaningful insight. Instead, we compare the recombination dynamics qualitatively. Carrier recombination in perovskites occurs through various pathways, at grain boundaries, across grain boundaries, at defect states, surface defects, and at interfaces.^[20a, 29] Analogously, the obtained dynamics for DMSO can be understood as follows: the fast decay component can be ascribed to recombination of trapped electrons and the slower decay component can be associated with electron-hole recombination occurring across grain boundaries.^[29-30] Furthermore, for c-DMSO the fast component can be ascribed to trapping of electrons, while the slower decay component is associated with electron-hole recombination. Notably, for all three samples the rapid decay component appears to be similar, indicating a similar physical process is associated with it.

Similarly, as the excitation is performed from the TiO_2 side (Figure 3h), the decay components in the case of the DMF sample can be assigned to trap-assisted and electron-hole recombination, respectively, as they are equivalent to excitation performed from the perovskite side. In the case of the DMSO sample, we attribute the components to electrons trapped in defect states close to the conduction band, as this component is faster than observed for the other samples. Similarly, the slower component can be attributed to recombination occurring within the grains, which is relatively prolonged. Finally, the decay components for the c-DMSO sample are ascribed to a physical process, taking place within the bandgap of TiO_2 as electron transfer has already taken place. Accordingly, we propose that the fast decay component is

linked with electrons trapped close to the conduction band and the longer decay component is ascribed to a defect state lying deeper in the conduction band, as has been reported for TiO_2 .^[26] Thus, charge extraction from TiO_2 is suitable as the carrier recombination is substantially reduced. In contrast, charge carriers trapped on the surface or at perovskite grain boundaries, as observed for the DMF and DMSO samples, are detrimental for the device performance, which is in line with the literature.^[31] Recently, great deal of work has been reporting the effect of the additives into the perovskite absorber layer improving the grain size, reducing the defect trap density, prolonged carrier lifetime and crystallinity.^[32] In our case, we affirm that the c-DMSO sample matches some of the properties reported by these studies, however the residual lead iodide should not be considered as an additive. Finally, one of the great challenges toward commercialization of perovskite solar cells is stability. Jiang and co-workers proposed that long term stability of perovskite solar cells can be improved by a moderate amount of lead iodide.^[33] However, high contents of residual lead iodide cause further degradation and are detrimental for the solar cell.

Figure 4: Relative band position diagram and proposed recombination pathways, indicated by numbers in brackets, present at the perovskite/ TiO_2 interface as the excitation is executed from the TiO_2 side. In a) carrier recombination routes in the absence of PbI_2 , and the associated

pathways are: (1) excitation upon photo absorption, (2) band-to-band radiative recombination, and (3) charge recombination at the interface. In b) excess PbI_2 and c) further enriched PbI_2 , here (3) represents the electron transfer to TiO_2 .

4. Conclusion

In summary, the impact of different residual PbI_2 amounts in metal halide perovskite films on the carrier extraction and recombination and device performance was examined. Confirmation of the presence of different residual PbI_2 amounts incorporated in the samples was obtained through XRD measurements. SEM imaging demonstrated that c-DMSO samples possess more angular and distinct crystallites on the surface compared to DMF and DMSO samples. The c-DMSO sample showed the highest PCE and exhibited the slowest ground state recovery compared to the other two samples when excitation was performed from the TiO_2 side. More specifically, our results demonstrate reduced carrier recombination at the perovskite/ TiO_2 interface for the most efficient sample, as PbI_2 serves as a passivation layer. Further experiments confirmed increased light absorption and PL quenching for the c-DMSO sample. The SEM, the device performance, and the transient spectroscopy measurements confirm that a moderate content of PbI_2 as in the case of c-DMSO sample is beneficial for the device performance. We observed a clear correlation between the device performance and charge carrier recombination dynamics at the interface investigated by transient absorption spectroscopy. However, a threshold for the residual PbI_2 content exists, beyond which residual PbI_2 becomes detrimental for the photovoltaic device performance.

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Moderate content of residual lead iodide is beneficiary for perovskite solar cells revealed by transient absorption spectroscopy. More specifically, photoexcitation from the perovskite/TiO₂ side displays retarded charge carrier recombination at the interface.

Keyword

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Impact of Residual Lead Iodide on Photophysical Properties of Lead Triiodide Perovskite Solar Cells