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Published in:
Advanced Functional Materials

DOI:
[10.1002/adfm.201602519](https://doi.org/10.1002/adfm.201602519)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2016

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Shao, S., Abdu-Aguye, M., Sherkar, T. S., Fang, H-H., Adjokatse, S., ten Brink, G., Kooi, B. J., Koster, L. J. A., & Loi, M. A. (2016). The Effect of the Microstructure on Trap-Assisted Recombination and Light Soaking Phenomenon in Hybrid Perovskite Solar Cells. *Advanced Functional Materials*, 26(44), 8094-8102. <https://doi.org/10.1002/adfm.201602519>

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The Effect of the Microstructure on Trap-Assisted Recombination and Light Soaking Phenomenon in Hybrid Perovskite Solar Cells

Shuyan Shao, Mustapha Abdu-Aguye, Tejas S. Sherkar, Hong-Hua Fang, Sampson Adjokatse, Gert ten Brink, Bart J. Kooi, L. Jan Anton Koster, and Maria Antonietta Loi*

Despite the rich experience gained in controlling the microstructure of perovskite films over the past several years, little is known about how the microstructure affects the device properties of perovskite solar cells (HPSCs). In this work, the effects of the perovskite film microstructure on the charge recombination and light-soaking phenomenon in mixed halide HPSCs are investigated. Devices with noncompact perovskite morphology show a severe light soaking effect, with the power conversion efficiency (PCE) improved from 3.7% to 11.6% after light soaking. Devices with compact perovskite morphology show a negligible light soaking effect, with PCE slightly increased from 11.4% to 11.9% after light soaking. From device investigations, photoluminescence, and impedance spectroscopy measurements, it is demonstrated that interface electron traps at the grain boundaries as well as at the crystal surface dominate the light soaking effect. Severe trap-assisted recombination takes place in HPSCs using noncompact films, while it is effectively eliminated in devices with compact films. Moreover, how the grain size of the perovskite film affects the light soaking phenomenon is investigated. In the case of compact perovskite films, the size of the grains has a limited effect on the light soaking. In these compact films, grains are fused and trap states are effectively reduced.

as unstable output characteristics (light soaking phenomena) as well as the role of the traps and mobile ions, are poorly understood.

The light soaking phenomenon has been observed in perovskite solar cells with various device structures, which causes concern about the instability in power output of this kind of solar cell. However, the severeness of the light soaking effect is reported to vary from laboratory to laboratory and has been the subject of intense debate regarding the underlying mechanism. One of the proposed scenarios is the trap-filling/detrapping mechanism,^[16,17] in which traps are filled under illumination. However, the long time scale observed in this process causes controversial arguments about the location, properties of the trap states, and the role of photo-generated carriers and mobile ions in the trap-filling process. The second scenario considers a sort of doping mechanism in which the mobile ions are proposed to drift toward the opposite electrode under a photo-generated electric field, causing p and n doping at anode and cathode, respectively.^[18] This last mechanism does not take into account the role of traps in the light soaking phenomenon. Moreover, the mobile species and their drift directions are under debate. The third scenario proposed to explain the light soaking effect considers variations in the crystal structure of the perovskite due to the alignment of methylammonium cations under light and bias.^[19] However, due to different device structures adopted and perovskite morphology obtained in different research laboratories, it is difficult to draw conclusions from these studies.

The planar device structure has attracted intensive interest due to the simple low-temperature processing. The photovoltaic performance of these devices is greatly dependent on the perovskite film processing.^[20–22] Poor coverage and the microcrystallinity of the perovskite films have been shown to produce low device performance. However, various strategies to improve the perovskite film morphology, such as optimizing the annealing temperature, new deposition methods, use of additives, new precursors, and solvent engineering have been developed.^[21–27] Despite the rich knowledge gained in controlling the

1. Introduction

Hybrid perovskite (HP) materials have appealing properties such as high absorption coefficient, balanced charge transport, and long carrier diffusion length, which make them ideal as photo-absorbing layers in photovoltaic devices.^[1–4] Over the past five years, perovskite solar cells (HPSCs) have witnessed an unprecedented increase in power conversion efficiency (PCE), which currently exceeds 20% due to intensive research on optimizing the device structure, the interfacial layers, and the deposition strategies.^[5–15] Despite this, several questions related to the operational mechanism of these solar cells, such

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DOI: 10.1002/adfm.201602519

morphology, little is known about how the morphology influences the final properties of HP solar cells. Recently, Ginger and co-workers demonstrated that the microstructure of perovskite films affects the local carrier lifetime and emission intensity.^[28] They found that the lifetime is much shorter and emission is much weaker at grain boundaries than within grains. The large fluctuation in emission intensity from grain to grain implies variation in the population of the trap states. This study indicates that the morphology influences the fundamental properties of perovskite films, which in turn affect the properties of the solar cells.

Here, we investigate how the perovskite film microstructure, such as grain boundaries and grain size, affects the light soaking phenomenon in mixed-halide perovskite solar cells. To the best of our knowledge, it has not yet been explored how the perovskite film microstructure affects the light soaking phenomenon in planar perovskite solar cells. We demonstrate that devices using noncompact perovskite films (open grain boundaries) show severe light soaking effect, with the open circuit voltage (V_{OC}) improving from 0.42 to 0.87 V, fill factor (FF) improving from 0.46 to 0.7, and PCE improving from 3.7% to 11.6% after light soaking (illumination for more than 1 h). Instead, devices with compact (fused grain boundaries) perovskite film morphology show a very weak light soaking effect with the V_{OC} improved from 0.86 to 0.88 V, FF improved 0.72 to 0.74, and PCE improved from 11.4% to 11.9%. Light intensity-dependent V_{OC} and photoluminescence (PL) combined with impedance spectroscopy (IS) measurements indicate that severe trap-assisted recombination of the charge carriers takes place in devices using noncompact perovskite films, and it is effectively suppressed in devices using compact films. The fact that the devices using compact films with smaller grain sizes show a negligible light soaking effect indicates that the trap density is reduced when grain boundaries are fused. Our experimental results demonstrate that interface electron traps are the source for the light soaking effect in HPSCs.

2. Results and Discussion

2.1. Morphology of Perovskite Film With and Without PC₆₀BM Layer

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements were performed to examine the morphology of the perovskite film spin-cast at different speeds with and without a 50 nm thick PC₆₀BM layer (Figure 1). In general, the morphology of the perovskite film is determined by the nucleation and growth of the grains. The fast evaporation of the solvent at high rotational speed enables formation of a higher density of nuclei, which leads to small grain domains and denser perovskite polycrystalline films. On the contrary, the relatively slower evaporation of the solvent produces a lower number of nuclei, which grow into larger grains and result in a less compact film. To obtain perovskite films of different morphologies, films were spin-cast at 1000 and 3000 rpm. Detailed information for the film deposition can be found in the experimental section. As can be seen from Figure 1a,b, the perovskite films cast at low spin speed display large grains

of dimensions up to 2 μm , but it also displays pin holes of several hundreds of nanometers in size, which results in isolated grains with open grain boundaries (see the dashed line circle in Figure 1a). More compact Perovskite films with smoother morphology could be obtained by spin-coating the solution at high spin speed (Figure 1c,d). Though the grain size is smaller, the grains in the compact film are intimately connected with each other, which produces fused grain boundaries (see the solid line circle in Figure 1c). After PC₆₀BM deposition, in both types of perovskite morphologies, considerably reduced surface roughness with root-mean-square values of 9 and 4 nm are obtained. This is also assumed to be determined by the PC₆₀BM penetration into the pin holes (see Figure 1e,f; Figure S1, Supporting Information), as was suggested by other authors.^[29,30]

2.2. Device Structure and Photovoltaic Performance

In this work, we fabricated p-i-n planar device structures that consist of an indium tin oxide (ITO)/hole extraction layer (HEL)/CH₃NH₃PbI_{3-x}Cl_x/50 nm and electron extraction layer (EEL)/Al, where poly (3,4-ethylenedioxythiophene)/poly (styrene-sulfonate) (PEDOT:PSS) and PC₆₀BM are HEL and EEL, respectively. Before measuring their current–voltage characteristics, the devices were stored in the dark without applying external bias.

We therefore examined the effect of light soaking on the performance of the devices with different perovskite film morphologies. The J – V scans were performed between -0.4 and 1.4 V. In between J – V scans, the devices were illuminated at open circuit condition. Figure 2a,b shows the J – V curves of the two types of devices (one with noncompact film and the other with compact film fabricated at 1000 and 3000 rpm, respectively) before and after light soaking. The device performance parameters are listed in Table 1. In Figure 2a, it is evident that before light soaking, the device having the noncompact perovskite film as the active layer shows very poor initial performance: it has a V_{OC} of 0.42 V, a J_{SC} of 19.40 mA cm^{-2} , an FF of 0.46, and a PCE of 3.7%. After 1.5 h light soaking, the device shows a V_{OC} of 0.87 V, a J_{SC} of 19.0 mA cm^{-2} , an FF of 0.70, and a PCE of 11.6%. It is noted that the PCE is more than two times higher than its initial value and important to observe that the light soaking phenomenon is reversible. After 1.5 h storage in the dark (without bias), the soaked noncompact film device shows a performance similar to its original value before light soaking. After another 1.5 h light soaking, the device shows

Table 1. Summary of the effect of the light soaking on the performance parameters of the noncompact and compact (large grains) film devices using a 50 nm thick PC₆₀BM layer as EEL.

Device	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	PCE [%]
Noncompact perovskite ^{b)}	0.42	19.4	0.46	3.7
Noncompact perovskite ^{a)}	0.87	19.0	0.7	11.6
Compact perovskite ^{b)}	0.86	18.4	0.72	11.4
Compact perovskite ^{a)}	0.88	18.3	0.74	11.9

^{a,b)} Device performance before and after light soaking.

Figure 1. SEM and AFM topographic images for a,b) noncompact perovskite film, c,d) compact perovskite film, e,f) noncompact perovskite film with PC₆₀BM on top, and g,h) compact perovskite film with PC₆₀BM on top.

similar device performance to that after the first round of light soaking. Figure S2 (Supporting Information) shows that the hysteresis of J - V curves is not affected by the light soaking, indicating a different mechanism underlying the hysteresis and the light soaking phenomena. It is also important to underline that the morphology of the perovskite film is not changed by the light soaking (see Figure S3 in the Supporting Information). Moreover, from Figure S1 (Supporting Information), we observe that the thickness of the perovskite film exceeds

the depth of the pin holes. Therefore, the direct contact of the PEDOT:PSS and PC₆₀BM should be from very small to non-existent. To elucidate the eventual role of the PEDOT:PSS/PC₆₀BM junction in the light soaking phenomenon, we fabricated devices with structure ITO/PEDOT:PSS/PC₆₀BM/Al and investigate how the device performance changes with light soaking time (see Figure S4 in the Supporting Information). Clearly, a Schottky junction forms between PEDOT:PSS and PC₆₀BM; also, the device performance does not show variations

Figure 2. J - V curves of HPSCs using a) noncompact and b) compact perovskite film, measured before (solid squares) and after (solid circles) light soaking under one sun illumination (the open squares are measured for the light-soaked device after storing them in the dark for 1.5 h. Open circles are measured after light soaking them again for another 1.5 h).

with prolonged light soaking, which excludes any variation in the PEDOT:PSS/PC₆₀BM junction as a possible mechanism for the light soaking in hybrid perovskites.

Devices using compact perovskite films as active layer show very weak dependence on the light soaking, as shown in Figure 2b. Before light soaking, a V_{OC} of 0.86 V, J_{SC} of 18.4 mA cm⁻², FF of 0.72, and a PCE of 11.4% are shown. After light soaking, only minor variation (i.e., a V_{OC} of 0.88 V, J_{SC} of 18.3 mA cm⁻², FF of 0.74, and PCE of 11.9%) is recorded. When comparing these two devices, it is interesting to observe that the two devices have similar V_{OC} and FF values after light soaking, despite the significant difference in their initial performances. The slightly higher J_{SC} value of the device using the noncompact perovskite film is due to the small difference in absorption of the two films (see Figure S5 in the Supporting Information). These results demonstrate that the light soaking phenomenon strongly depends on the microstructure of the perovskite active layer. To further understand the effects of the grain size on the light soaking phenomenon, devices having a compact perovskite film and even smaller grain sizes than the other compact device were fabricated (see Figure S6 in the Supporting Information). This device also shows negligible light soaking effect.

These results indicate that the open grain boundaries in the perovskite film are detrimental for the device performance. We further investigated the light soaking effects in devices with n-i-p structure (fluorine-doped tin oxide (FTO)/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/Spiro-OMeTAD/Au). In this case, we also observe a severe light soaking effect in devices with noncompact perovskite film; these results exclude the effect of device structure on the light soaking phenomenon (see Figure S7 in the Supporting Information).

Figure S8 (Supporting Information) summarizes how the device parameters for the noncompact and the compact device vary under continuous illumination. The device using the noncompact perovskite layer displays a fast increase in V_{OC} from 0.42 to around 0.8 V within the first 30 min and then shows saturation after 1.5 h light soaking. The J_{SC} does not show significant variation within the light soaking time, while the FF and PCE follow a similar trend as the V_{OC} . For the device using the compact perovskite film, all the device parameters stay almost constant over the same light soaking time.

2.3. The Dark J - V Curves and Capacitance Under Illumination

Figure 3a,c shows the effect of the light soaking on the J - V curves measured under dark conditions for the noncompact and compact layer devices. In HPSCs with a noncompact perovskite film, the built-in voltage before light soaking is 0.4 V, while it increases to around 0.8 V after light soaking. Instead, for devices using compact perovskite films, no observable changes in the built-in voltages (about 0.9 V) with light soaking are observed.

Figure 3. The dark J - V curves measured before and after light soaking, and capacitance measured under one sun condition for HPSCs using a,b) noncompact perovskite films and c,d) compact perovskite films.

Figure 3b,d shows the variation of the capacitance with applied bias at a frequency of 4000 Hz under one sun illumination for the two device types. In between scans, the devices were stored under illumination at open circuit condition. Since the peak capacitance occurs at the maximum charge carrier density when the external bias compensates the built-in potential, the shift in the peak capacitance demonstrates variation in the built-in voltage of the solar cell.^[31] Similar to what has been observed from dark J - V curves, the peak shifts toward higher voltage in devices using noncompact perovskite films, while the peak does not shift in devices using compact perovskite layers. These observations are in agreement with the variation of V_{OC} under illumination.

2.4. Light Intensity Dependent J_{SC} and V_{OC}

The light intensity dependence of the device performance was studied in noncompact and compact layer devices before and after light soaking. To detect the effect of the light intensity on the initial device performance, the experiments were carefully designed to minimize the effect of light soaking and the J - V curves were recorded every 1.5 h between each point measured at different light intensity. During these 1.5 h intervals, the devices were stored under dark conditions to recover to their initial state. To detect the effect of light intensity on soaked device performance, the J - V curves were measured on a soaked device sequentially under varied light intensity without any extra storage in the dark.

Figure S9 (Supporting Information) shows a logarithmic plot of the J_{SC} as a function of the light intensity of the two devices. The slopes of the J_{SC} versus the logarithm of the light intensity are 1 for both devices regardless of light soaking, indicating the absence of bimolecular recombination and allowing us to exclude its involvement in the light soaking phenomenon.^[10,30] These results are in agreement with the relatively stable J_{SC} observed under illumination.

Figure 4a,b shows semi-logarithmic plots of the V_{OC} versus light intensity for the two types of devices. Previous studies indicate that the *ideal factor* n is equal to 1 in the absence of the trap-assisted recombination, while in the case of the trap-assisted recombination, n deviates from unity and varies up to a value of 2.^[10] Before light soaking, the device using a noncompact perovskite film as active layer shows a slope of 1.70 kT q^{-1} ($n = 1.7$), indicating significant trap-assisted recombination due to the high trap density at the open grain boundaries. After light soaking, the slope is reduced to 1.38 kT q^{-1} ($n = 1.38$), indicating suppressed charge recombination.

For devices using compact perovskite films, there is no obvious variation in the magnitude of n (Figure 4b), which is 1.34 and 1.22 before and after light soaking, respectively. The lower slope values indicate that the trap-assisted recombination is reduced effectively in the devices having compact morphology. These results are in good agreement with the weak light soaking effect observed in the device performance under illumination. Therefore, the compact perovskite films are characterized by a lower trap density due to the fused grain boundaries and consequently by strongly reduced recombination of the charge carriers.

Figure 4. Light intensity-dependent V_{OC} after (circles) and before (squares) light soaking for devices with a) noncompact and b) compact perovskite films.

2.5. Spectroscopic Study

It has been shown that the hybrid perovskite films may contain under-coordinated metal ions at crystal surfaces and also at the grain boundaries between individual crystals, which lead to halide vacancy defects that act as electron traps.^[32] Recent theoretical studies also indicate that the halide vacancies are the dominant defects due to their small formation energy.^[33,34]

Figure 5a shows the confocal fluorescence images for the noncompact and compact perovskite films recorded in ambient conditions, keeping excitation and acquisition parameters constant. Previous studies suggested that shallow traps contribute to radiative recombination, while deep traps produce nonradiative recombination.^[27] Here, the noncompact perovskite film shows inhomogeneous emission, implying nonuniform distribution of deep trap states,^[27] while regions in proximity of the open grain boundaries emit weakly. This can be due to the accumulation of deep traps, probably caused by iodide vacancies at the interface. The PL intensity not only varies from grain to grain but also within the grains due to variation in the quality of the individual crystals. Instead, the compact perovskite film shows brighter and more homogeneous emission. This further indicates that in the fused grain boundaries of the compact perovskite film, the deep trap density is dramatically reduced. Therefore, we speculate that the open grain boundaries are characterized by a high density of deep trap states and that the fused grain boundaries help to eliminate those deep trap states in the perovskite film. This is further confirmed by photoluminescence measurements, showing that the compact perovskite film has much higher PL intensity and its peak emission shifts

Figure 5. a) Confocal microscopy images ($20 \times 20 \mu\text{m}$) for noncompact and compact perovskite film. b) Steady-state PL spectra for pristine non-compact and compact perovskite films. c) The variation in the PL intensity of the perovskite film (noncompact and compact)/PC₆₀BM samples with light soaking time.

toward shorter wavelengths in comparison to the noncompact perovskite film (see Figure 5b). These results also explain the weak dependence of the device performance of the compact layer (small grains) device on light soaking.

Figure 5c shows the variation in PL intensity of the perovskite/PC₆₀BM samples with light soaking. The noncompact perovskite film shows fast increase in PL intensity within the first 30 min and then slowly saturates in about 1.5 h light soaking. The rise in PL intensity is attributed to the trap-filling process occurring with light soaking. In contrast, the compact perovskite film shows minor improvement in the PL intensity over the same period of illumination. The enhanced PL intensity with light soaking of the noncompact perovskite/PC₆₀BM

sample suggests high trap density in the perovskite film even after PC₆₀BM deposition; therefore, the PL results highlight that the light soaking phenomenon is dominated by trap-assisted recombination. The similar trend for the PL intensity in the perovskite films and the device performance suggest the same underlying mechanism. When the traps are filled under continuous light soaking, the larger splitting in the quasi-Fermi energy levels leads to an enhanced V_{OC} . In the meantime, free charge carriers are extracted more easily to the EEL, leading to enhanced FF and PCE.

2.6. Impedance Spectroscopy Under Illumination

Impedance spectroscopy was performed on the noncompact and compact layer devices at open circuit voltage under 100 mW cm^{-2} illumination. Figure 6a,b shows the recorded Nyquist plots. For devices fabricated with the noncompact

Figure 6. Impedance spectra of devices before and after light soaking with a) noncompact perovskite film and b) compact perovskite film. Measurements are performed under 1 sun illumination at open circuit conditions.

perovskite film, the IS spectra show asymmetric semi-arcs, likely due to the chemical capacitance (C_μ), which could be fitted with the equivalent circuit, as shown in Figure 6a. The fitting results are listed in Table S1 (Supporting Information). R_s is the series resistance; R_1 and C_1 are the resistance and capacitance of the bulk HP layer, respectively. While the R_1 and C_1 parameters are not dependent on the light soaking time, C_μ depends strongly on it. Recent studies attribute C_μ to the trap states at the HP/PC₆₀BM or PC₆₀BM/electrode interface.^[35] Since the same PC₆₀BM/Al interface is used in both devices, we speculate that C_μ is related to the trap states at the HP/PC₆₀BM interface and is not determined by Al evaporation. Here, the noncompact perovskite film gives rise to a much higher trap density due to the larger number of grain boundaries and much larger PC₆₀BM/HP interface. As shown in Figure 6a, with prolonged light soaking, the C_μ and chemical resistance R_μ are significantly reduced and the semi-arcs become symmetric, indicating reduced traps at the HP/PC₆₀BM interface. Devices fabricated with the compact perovskite layer show distinctive features in the Nyquist plots (see Figure 6b). First, there are no significant variations in the shape of the semi-arcs with light soaking. Second, the symmetric semi-arcs could be fitted well with a simple ideal semiconductor equivalent circuit model. The absence of the chemical capacitance confirms the much lower trap density at the HP/PC₆₀BM interface. Similar to the device using the noncompact perovskite film, the R_s , C_1 , and R_1 for the device using the compact perovskite are not dependent on the light soaking time (Table S2, Supporting Information). The impedance spectroscopy results demonstrate that the interface traps rather than bulk traps dominate the light soaking effect.

2.7. Simulation of the J - V Curves

To investigate the effect of interface traps on device performance, we simulated the working mechanism of the solar cell by means of a 1D drift-diffusion model.^[36] The model takes into account the generation, transport, and trap-assisted recombination of charge carriers. The details of the model can be found in the Supporting Information.

The simulated J - V curves for a device with interface traps are compared to that without traps in Figure 7. The device has a high V_{OC} of 1.05 V in the absence of interface traps in the perovskite film, while the V_{OC} is reduced to about 0.68 V in the presence of interface traps. A higher density of interface traps causes further loss in V_{OC} and FF. These results demonstrate the detrimental impact of the interface traps on the device performance and indicate that the device performance could be further improved by reducing the trap density in the perovskite film.

2.8. Temperature-Dependent Light Soaking

Finally, we discuss the trap-filling process beyond the time scale for the trap filling by photo-generated electrons. Temperature-dependent light soaking experiments were performed for the devices with noncompact and compact perovskite films. The

Figure 7. The simulated J - V curves under light illumination with and without interface traps. Square symbols represent the situation without interface traps; circle symbols represent the situation with an interface trap density of $2 \times 10^{23} \text{ m}^{-3}$; and triangles represent an interface trap density of $4 \times 10^{23} \text{ m}^{-3}$.

devices were stored in the dark for 12 h after each measurement at a given temperature. The full symbols in Figure 8a show the variation in V_{OC} of the device using the noncompact perovskite film under continuous illumination at different temperatures. The open symbols represent the values of the V_{OC} at different temperatures measured in the devices, which have been previously brought to saturation. The V_{OC} saturates much slower at low temperature (lower than 295 K), while the V_{OC} does not saturate even with four hours of light soaking. The number of traps filled decreases as the temperature falls.^[37] The slower trap-filling process at lower temperature indicates that mobile ions also contribute to the trap-filling process. Recently, other experimental evidence for the iodine anions drifting to the PC₆₀BM EEL has been reported.^[38] Our results could be explained by iodide anions drifting to the perovskite surface (especially at open grain boundaries) and coordinating with the positively charged iodine vacancies due to electrostatic interactions (see Figure 8c).

Devices fabricated with compact perovskite films show negligible change in light soaking with temperature, which is in agreement with the fact that the compact packing of perovskite crystallites can effectively reduce iodine vacancies due to the fused grain boundaries (see Figure 8b,d).

3. Conclusion

In conclusion, we have investigated how the grain boundaries and grain size in perovskite films affect the charge recombination and light soaking effect in HPSCs. We find that interface trap-assisted recombination dominates the light soaking effect. The devices made with a compact perovskite film show very weak light soaking effect due to lower trap-assisted recombination, while those with a noncompact perovskite film show a strong light soaking effect due to significant trap-assisted recombination. Our results demonstrate that improving the morphology of the perovskite film to eliminate the grain boundaries is an effective way to eliminate the light soaking effect.

Figure 8. Time and temperature dependence of the V_{OC} with light soaking using a) noncompact perovskite films and b) compact perovskite films. Schematic illustration of the trap distribution in c) noncompact perovskite film and d) compact perovskite film.

4. Experimental Section

Materials: $\text{CH}_3\text{NH}_3\text{I}$ was purchased from Luminescence Technology Corporation. PEDOT:PSS water dispersion (Clevios VP AI 4083) was acquired from Heraeus. PbCl_2 (99.99%), N,N-dimethylformamide (DMF) (99.8%), and chloroform (99.8%) were acquired from Sigma-Aldrich.

Fabrication of the Devices: The devices were fabricated as previously reported.^[10] ITO-coated glass substrates were sonicated sequentially in detergent, deionized water, acetone, and isopropanol for 20 min, respectively. After spin-drying, the cleaned ITO substrates were further dried at 140 °C for 10 min. Then, the ITO substrates were subjected to a UV ozone cleaning treatment for 20 min. A 45 nm-thick PEDOT:PSS layer was spin-coated onto the ITO substrates and dried at 140 °C for 10 min. A precursor solution (40% wt) of $\text{CH}_3\text{NH}_3\text{I}$ and PbCl_2 in a 3:1 molar ratio was spin-coated on top of PEDOT:PSS and the substrates were stored under high vacuum ($<10^{-6}$ mbar) for 12 h. An annealing step was performed on the aforementioned substrates at 100 °C for 1 h in a nitrogen-filled glovebox. Films of 210 and 280 nm-thick $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ were obtained. Then, a 50 nm-thick PC_{60}BM layer was deposited on top of the perovskite layer. The device structure was completed by evaporating 100 nm-thick Al under high vacuum $<1 \times 10^{-6}$ mbar.

Characterization of the Perovskite Solar Cells: The current density–voltage characteristics of the perovskite solar cells were measured under simulated AM 1.5 G solar illumination using a Steuernagel Solar constant 1200 metal halide lamp in a nitrogen-filled glovebox. The light intensity was calibrated to be 100 mW cm^{-2} by using a calibrated Si cell.

Impedance Spectroscopy: Impedance spectroscopy was performed with a SP-200 Bio-Logic potentiostat equipped with an electrochemical impedance spectroscopy analyzer by applying a 15 mV ac signal at a frequency of 4000 Hz at open circuit voltage, illuminating the sample with 1 sun at AM 1.5.

Steady-State PL Measurement: The samples were excited at 400 nm by the second harmonic of a mode-locked Ti:sapphire (Mira 900) laser delivering pulses of 150 fs with a repetition rate of 3.45 MHz and power of 50 μW in a nitrogen atmosphere.

Morphology Characterization: AFM topographical images were recorded in tapping mode using a Bruker MultiMode 8 microscope

with TESP probes. SEM topographical images were recorded on a XL 30 ESEM microscope.

Supporting Information

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

Acknowledgements

The authors would like to extend thanks for the financial support from the European Commission, Marie Curie Actions—Intra-European Fellowships (IEF) “SECQDSC” No. 626852 and European Research Council, ERC Starting Grant “HySPOD” No. 306983. The work of TSS is part of the Industrial Partnership Programme (IPP) “Computational sciences for energy research” of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). This research programme was cofinanced by Shell Global Solutions International B.V. The authors thank Dr. L.-H. Lai for fruitful discussions. The technical support of A. Kamp is also highly appreciated.

Received: May 21, 2016

Revised: August 19, 2016

Published online: October 4, 2016

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