Enhancing the efficiency and stability of triple-cation perovskite solar cells by eliminating excess PbI_2 from the perovskite/hole-transport-layer interface

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ABSTRACT. Metal halide perovskites are promising contenders for next-generation photovoltaic applications due to their remarkable photovoltaic efficiency and their compatibility with solution-processed fabrication. Among the various strategies to control the crystallinity and the morphology of the perovskite active layer and its interfaces with the transport layers, fabrication of perovskite solar cells from precursor solutions with a slight excess of PbI_2 has become very common. Despite this, the role of such excess in PbI_2 is still rather controversial, lacking consensus on its effect on the bulk and interface properties of the perovskite layer. In this work, we investigate the effect of removing the excess PbI_2 from the surface of a triple-cation mixed-halide $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite layer by four different organic salts on their photovoltaic performance and stability. We show that treatments with iodide salts such as methylammonium iodide (MAI) and formamidinium iodide (FAI) can lead to the strongest beneficial effects on solar cell efficiency, charge recombination suppression, and stability while non-iodide salts such as methylammonium bromide (MABr) and methylammonium chloride (MACl) can also provide improvements in terms of charge recombination suppression and stability to a moderate extent by comparison to the untreated sample. In the most optimized cases, under continuous solar illumination, the MAI and FAI-treated devices maintained respectively 81% and 86% of their initial PCEs after 100 hours of continuous illumination (*versus* 64% for the untreated solar cell with excess PbI_2). Our study demonstrates that eliminating the PbI_2 excess at the perovskite/HTL interface by treating the perovskite surface with organic salts is a simple and efficient route to enhance the efficiency and in particular the stability of perovskite solar cells.

INTRODUCTION

In the last decade, solution-processed metal halide perovskites have attracted tremendous research interest due to their extraordinary physical properties, including large charge carrier diffusion length, high extinction coefficient, excellent charge carrier mobility, and tunable bandgap.¹⁻⁹ These advantageous properties have resulted in the application of perovskite materials in a range of optoelectronic devices such as solar cells,¹⁰ LEDs,¹¹ sensors,¹² photodetectors¹³ and lasers.¹⁴ In particular, research aiming at enhancing the power conversion efficiency (PCE) of perovskite solar cells has led to tremendous progress, resulting a maximum certified PCE of 25.2% in 2019.¹⁵ Critically important to the optimization of the photovoltaic performance, and that of the device stability, are the quality of the perovskite crystalline film and the perovskite/transport-layer interfaces.¹⁶⁻¹⁹ In particular, the grain boundaries, impurities, and defects located either in the bulk or at interfaces can facilitate ion migration and act as charge carrier recombination sites, leading to efficiency loss and device degradation.²⁰⁻²² So far, triple-cation mixed perovskites with the composition of $\text{Cs}_{0.05}(\text{FA}_{1-x}\text{MA}_x)_{0.95}\text{Pb}(\text{I}_{1-y}\text{Br}_y)_3$ (where $\text{FA}^+ = \text{CH}_5\text{N}_2^+$, and $\text{MA}^+ = \text{CH}_3\text{NH}_3^+$) have been shown to result in solar cells with excellent efficiency and enhanced stability.^{5,23}

Various strategies are currently under extensive investigation in order to precisely control the crystallinity and the morphology of the perovskite layer and its interfaces with the transport layers aiming to obtain a highly crystalline, compact and smooth layer with large crystalline grains.²⁴ Very commonly, a slight increase in the PbI_2 /methylammonium iodide (MAI) concentration ratio above the stoichiometric ratio of 1 was found to be beneficial for the photovoltaic performance.^{10,25-27} The origin of this increase has been proposed to arise from various factors. For example, supported by computations,²⁸ the excess PbI_2 in perovskite films were believed to passivate defects at the perovskite grain boundaries and thus contribute to a lower carrier recombination.²⁹ Alternatively, the excess PbI_2 at the perovskite/electron-transport-layer (ETL)

interface (e.g. TiO_2) was claimed to lead to lower carrier recombination at this interface,^{25,30,31} facilitating electron injection into TiO_2 ^{27,32} possibly due to TiO_2 surface passivation and/or band-edge matching between TiO_2 , PbI_2 , and the perovskite. Similarly, at the perovskite/hole-transport-layer (HTL) interface, excess PbI_2 was proposed to facilitate hole injection, block electrons and reduce carrier recombination.^{25,33} Nevertheless, the beneficial effect of the excess PbI_2 remains controversial. By comparison to PbI_2 -deficient perovskite samples, samples with excess PbI_2 exhibited more pronounced current-voltage hysteresis and significantly lower photostability.^{34,35} Recently, it was identified that the excess PbI_2 is the culprit for the solar cell's accelerated degradation due to the photodecomposition of PbI_2 to metallic lead and volatile I_2 under continuous solar illumination.³⁶ Moreover, some reports show that excess in MAI, rather than PbI_2 , is beneficial for device performance.^{37,38} Following these reports several groups investigated a post-treatment process in which an MAI is introduced to the surface of the perovskite active layer, either by thermal evaporation³⁹ or spin-coated from solution⁴⁰ onto the surface of the perovskite layer generally resulting in an improvement of the photovoltaic performance. In light of these seemingly contradicting results, further understanding on the controversial role of the excess PbI_2 in perovskite solar cells is needed, particularly if one can decouple its effect in the bulk and at the interface.

In this work, based on mixed-cation and mixed-halide $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite solar cells, we provide an experimental comparison on the photovoltaic behavior and the solar cell stability under continuous solar illumination between samples with a slight excess of unreacted PbI_2 (in the bulk and at the interface) and samples with the excess PbI_2 intentionally removed at the perovskite/HTL interface. Four different organic salts including iodide salts and non-iodide salts are applied to treat the perovskite film surfaces in order to remove the excess PbI_2 . The resultant solar cell parameters and stability are compared by combining a series of structural,

optical, and photovoltaic characterization methods. By simultaneously removing the surface excess PbI_2 and passivating surface iodide defects, treatments with iodide salts such as MAI and formamidinium iodide (FAI) lead to the strongest improvements in suppressing charge recombination and boosting solar cell efficiency and stability under continuous illumination by comparison to the untreated samples. For treatments involving non-iodide salts such as MABr and MACl, which in principle remove surface excess PbI_2 without passivating surface iodide defects, the resultant perovskite solar cells exhibit also reduced charge recombination as well as clear improvements in terms of stability. Our study indicates that, at the perovskite/HTL interface, the existence of excess PbI_2 is not beneficial for charge recombination suppression and the stability of the photovoltaic devices.

RESULTS AND DISCUSSION

Mixed-cation mixed-halide $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ thin films were first prepared according to the procedure reported by Saliba et al.⁵ According to this method, a precursor solution, where the sum of FA^+ , MA^+ , and Cs^+ is 1.26 mmol and the sum of Pb^{2+} is 1.3 mmol, was prepared leading to a slight excess of Pb^{2+} (about 3%). We then optimized the concentration of the precursor solutions while maintaining the proportion between each sub-constituent unchanged in order to maximize the average perovskite grain size which should offer a better endurance against degradation (details are described in the METHODS section). All prepared perovskite films were examined by X-ray diffraction (XRD), UV-Vis absorption, and scanning electron microscopy (SEM). As shown in **Figure 1** and **Figure S1** of the supporting information, samples fabricated from different precursor concentrations all exhibited typical perovskite diffraction peaks in agreement with previous reports. A small diffraction peak at 12.7° corresponds to the excess cubic PbI_2 residue in the perovskite film. In agreement with the measured UV-Vis absorbance (Figure

S1), the use of more concentrated precursor solution also leads to a thicker perovskite film and increased perovskite grain size. Functional perovskite solar cells were then fabricated based on these precursor concentrations on planar TiO_2 (p- TiO_2)-coated fluorine doped tin oxide (FTO) glass substrates together with a layer of HTL of 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) and gold top contacts. An optimal precursor concentration was then identified from the photovoltaic characteristics of these devices (Figure S1 and Table S1) and will be applied in all the following experiments as the reference condition. In such an optimized condition, the average perovskite grain size was measured to be approximately 400 nm (Figure S1). Clearly visible from the SEM characterizations shown in Figure 1 (a), those crystals showing a brighter SEM contrast than the rest of the film (sometimes referred as the “white phases” previously⁴¹) and often precipitated at perovskite grain boundaries are assigned as PbI_2 crystals according to previous studies.^{41,42} The higher lead content in PbI_2 than in the perovskite phase leads to the brighter SEM contrast observed. Cross-section SEM characterizations on a typical perovskite solar cell by the optimized condition exhibited smooth interfaces with a majority of large perovskite grains protruding throughout the entire film thickness (Figure 1(b)).

Figure 1. (a) Morphologies revealed by SEM on the $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite thin film on a FTO/glass substrate fabricated by the optimized precursor concentration (which will be used as the reference condition for the following experiments). (b) Cross-section

SEM characterization of a completed perovskite solar cell. (c) XRD patterns of the perovskite thin film shown in (a).

To selectively investigate the effect of eliminating PbI_2 from the perovskite/HTL interface and in contrast to the report by Kogo et al,⁴⁰ we used a dilute methylammonium halide (MAX) or FAI solution (1 to 4 mg/mL in isopropanol) that was spin-coated onto the perovskite surface, followed by a five-minute annealing at 100 °C (**Figure 2(a)**). Here, four different organic salts, including MAI, MABr, MACl, and FAI, were chosen in our experiments in order to distinguish the effect of surface iodide defect passivation from the effect of removing the surface excess PbI_2 . While we expect that the treatments of all these four salts on the perovskite film surface can lead to the removal of the excess PbI_2 crystals on the film surface, non-iodide salts were previously shown to be non-effective to passivate the iodide defects on perovskite surface.⁴³ SEM characterizations, after the treatments of these salt solutions at different concentrations, revealed a clear morphological change (Figure 2 (b) to (m)) by comparison to the reference sample (SEM image shown in Figure 1(a)). The excess PbI_2 crystals, which have a brighter SEM contrast than the rest of the film were completely eliminated from the perovskite surface after the samples were treated by a MAI or FAI solution with a minimum concentration of 2 mg/mL, or by a MABr or MACl solution with a minimum concentration of 4 mg/mL. As the objective here is to remove the surface excess PbI_2 , these minimum salt concentrations were then applied in the experiments described below. Revealed by XRD, only a very small reduction of diffraction peak intensity for the PbI_2 phase (for example, 8929 counts by comparison to 9237 counts for the case of MAI treatment) was found when comparing samples before and after the treatments by the salt solutions (**Figure 3(a)**). This indicates that our treatment procedure by these four salts only removed the excess PbI_2 crystals on the surface of the perovskite film but not those in the bulk or at the bottom interface. UV-Vis

absorbance spectrum was measured on the perovskite films before and after these surface treatments (Figure 3(b)). FAI and MAI-treated perovskite films exhibited identical optical bandgaps by comparison to the reference, untreated sample. In contrast, the MABr and MACl surface treatments led to a ~ 0.01 eV and 0.02 eV increase of optical bandgap of the perovskite film (Figure 3(b) and **Figure S2**), respectively. This increase can be understood as result of the MABr and MACl surface treatments which transform the surface excess PbI_2 respectively into larger bandgap perovskites such as $\text{MAPb}(\text{Br}_x\text{I}_{3-x})$ and $\text{MAPb}(\text{Cl}_x\text{I}_{3-x})$ on the surface of the film. Atomic force microscopy (AFM) characterizations were also performed before and after these four organic salt surface treatments. Results reveal the same order-of-magnitude surface roughness on perovskite films before and after treatments (**Figure S3**). A slight reduction of surface roughness, from 18 nm on untreated samples to 12 - 13 nm on treated samples, can be associated to the removal of the excess PbI_2 crystals on the film surface. Such a surface roughness change is however rather small when considering the total film thickness of about 640 nm. Perovskite films whose surfaces were treated by the four organic salts exhibited an enhanced photoluminescence (PL) intensity by comparison to the untreated sample, with the FAI and MAI treatments leading to the strongest enhancement (Figure 3(c)). A slight shift of the PL peak wavelength was observed in the case of the MABr and MACl-treated samples, which is consistent with the results of the slight bandgap changes of these samples observed in UV-Vis absorbance. These results suggest that, among the four organic salts, the dual functions provided by FAI and MAI treatments in terms of surface excess PbI_2 removal and surface iodide defect passivation likely have the strongest effect suppressing non-radiative recombination centers. By comparison, the MABr and MACl treatments, only removing the surface PbI_2 , can also provide an intermediate PL intensity enhancement. This corroborates with recent calculations⁴⁴ which suggested that PbI_2 -terminated perovskite surface is

sensitive to surface defects which act as recombination centers and it is coherent with the device characteristics and stability results that will be discussed below.

Figure 2. (a) Schematic illustration of treating the surface of perovskite films by methylammonium halide (MAX) or formamidinium iodide (FAI) solution in isopropanol and subsequent spin-coating to remove the excess PbI_2 at the top interface. (b - m) SEM characterizations of the $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite film after (b, c, d) MACl, (e, f, g) MABr, (h, i, j)

MAI, and (k, l, m) FAI isopropanol solution treatments with the organic salt concentration fixed at 1 mg/mL, 2 mg/mL, and 4 mg/mL.

Figure 3. (a) XRD spectrum, (b) UV-Visible absorbance, and (c) photoluminescence (PL) (excitation $\lambda = 365$ nm) of the $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite thin films without (reference) and with the different organic salt solution surface treatments. Dotted lines in (c) indicate the slight shift of PL peak wavelength.

After removing the excess PbI_2 crystals from the surface of the perovskite film by the organic salt treatments, we completed the solar cell fabrication by depositing a layer of Spiro-OMeTAD as the HTL and a layer of gold as the top electrode. The current-voltage (J - V) characteristics, measured under 100 mW cm^{-2} AM 1.5G simulated illumination, of the best-performing perovskite solar cells with and without different organic salt treatments are shown in **Figure 4** and **Table 1**, with the statistics of the photovoltaic parameters shown in **Figure S4**. By comparison to the reference sample without salt treatments, the MAI and FAI-treated solar cells exhibit a clear improvement of photovoltaic performance. Specifically, there is an increase of the solar cell J_{sc} , from 20.60 mA cm^{-2} for the reference sample to 21.12 mA cm^{-2} for MAI-treated and 21.16 mA cm^{-2} for the FAI-treated sample, as well as an increase of FF from 77.50% to 79.29% for the MAI-

treated and 78.60% for the FAI-treated sample. A combination of both leads to respectively a 7% and 5% increase of PCE for the MAI and FAI-treated solar cell compared to the reference sample. As there was no change of optical bandgap in the perovskite film associated with the MAI and FAI treatment (Figure 3b), the increase of J_{sc} observed likely originates from a slightly enhanced absorption due to the transformation of the surface excess PbI_2 into a perovskite phase and/or more charges being able to make their way to the electrodes due to reduced recombination loss. In contrast, MABr and MACl-treated samples exhibit a similar PCE by comparison to the reference sample. Specifically, there is a slight reduction of J_{sc} , from 20.60 mA cm^{-2} for the reference sample to 20.19 mA cm^{-2} for the MACl-treated and 20.32 mA cm^{-2} for the MABr-treated sample, together with a slight increase of V_{oc} from 1.10 V to 1.14 V for the MACl-treated and 1.13 V for the MABr-treated sample. These observations are in agreement with the slight increase of the perovskite optical bandgap associated with the treatments with these two salts (Figure 3b). The external quantum efficiency (EQE) spectra measured on the optimal devices treated by different organic salts are shown in Figure 4b. The short-circuit current densities obtained from integrating their EQE spectra with the AM 1.5G spectrum are in good agreement (with $< \pm 0.2 \text{ mA cm}^{-2}$ of difference) by comparison to the J_{sc} measured in the $J-V$ curves.

To gather further insights into the charge transfer and recombination processes in these devices, they were investigated via electrochemical impedance spectroscopy (EIS) and light-intensity-dependent measurements. Figure 4c shows the Nyquist plots of the perovskite solar cells with and without different organic salt treatments, measured in dark with an external bias holding at their respective V_{oc} . The measured EIS spectra can be fitted well using an equivalent circuit model previously applied on perovskite solar cells (shown in the inset of Figure 4(c)).^{45,46} The inner series resistance (R_s), charge transport resistance (R_{tr}), and the recombination resistance (R_{rec}) obtained

from fitting the experimental data are listed in Table 1. By comparison to the untreated sample, one can observe that there is a clear increase of recombination resistance together with a decrease of charge transport resistance associated with the treatments by the different organic salts. Among the four salts applied, MAI and FAI led to the most significant effects with the recombination resistance of the solar cell increased from 1590 Ω (untreated) to 3665 Ω for the MAI-treated and 3410 Ω for the FAI-treated sample, and with the charge transport resistance reduced from 115.9 Ω to 50.9 Ω for the MAI-treated and 68.8 Ω for the FAI-treated sample. For the MABr and MACl treated samples, similar trends of increased recombination resistance and decreased transport resistance are also observed, but their effects are not as significant as the treatments with MAI or FAI. These EIS results are consistent with the light-intensity-dependent V_{oc} measurement results shown in Figure 4(d). Such light-intensity-dependent V_{oc} measurements have been applied previously to reveal the dominant recombination mechanisms in perovskite solar cells.^{47,48} While the interpretations of such experiments remain complex, for bulk-recombination-limited cases,⁴⁹ the slope of V_{oc} over the natural logarithm of light intensity ($\frac{\delta V_{oc}}{\delta \ln(I_{light})}$) being kT/q has been considered as an indicator for the dominant bimolecular recombination, whereas such a slope being 2kT/q suggests the dominant trap-assisted recombination.^{47,48} Our results show a decrease of this slope upon the application of any of these four salt treatments on the perovskite film surface, with the MAI and FAI treatments leading to the strongest effect decreasing the slope from 2.05 kT/q to 1.65 kT/q for the MAI treatment and 1.68 kT/q for the FAI treatment. A strong reduction of trap-assisted recombination in these MAI and FAI-treated samples should originate from their dual roles, which removes the excess surface PbI_2 and at the same time passivate surface iodide defects. Interestingly, the MABr and MACl-treated samples also exhibit a moderate decrease of ($\frac{\delta V_{oc}}{\delta \ln(I_{light})}$), from 2.05 kT/q to 1.80 kT/q for the MABr treatment and 1.82 kT/q for the MACl

treatment. As these non-iodide salts could not passivate surface iodide defects which were considered as the dominating defects of the perovskite surfaces,⁴³ our observation suggests that the removal of the surface excess PbI_2 alone can help to alleviate trap-assisted recombination. Indeed, such PbI_2 crystallites might hinder charge transport at that interface due to the formation of charge transport barriers³⁴ and recent calculations⁴⁴ even suggested that PbI_2 -terminated perovskite surface being recombination centers. Consequently, the removal of the surface excess PbI_2 can result in the formation of a more intimate perovskite interface with the HTL reducing charge recombination and improving charge transfer to the transport layer.

Figure 4. (a) Current density–voltage (J–V) photovoltaic characteristics measured on the $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite solar cells, with the device architecture shown in

Figure 1(b), fabricated with MACl, MABr, MAI, or FAI surface treatment by comparison to the reference sample (without treatment), under 100 mW cm⁻² AM 1.5G illumination. The solid dots and lines indicate results from the reverse scan (from V_{oc} to J_{sc}), and the dash lines indicate results from forward scan (from J_{sc} to V_{oc}). (b) EQE spectra for the perovskite solar cells shown in (a) and the corresponding integrated J_{sc} of the devices. (c) Typical Nyquist plots (symbols) obtained from the perovskite solar cells shown in (a) tested in the dark and at their V_{oc} . The solid lines represent the fits obtained by applying the equivalent circuit shown in the inset. (d) Light intensity dependence of V_{oc} for these solar cells. The filled symbols and lines represent experimental data and numerical fits, respectively. Fitted values of the slope of V_{oc} over the natural logarithm of light intensity ($\frac{\delta V_{oc}}{\delta \ln(I_{light})}$) are indicated inside the bracket of the label for each curve.

Table 1. Summary of the Photovoltaic Characteristics of the $\text{CS}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ Perovskite Solar Cells, with the Device Architecture Shown in Figure 1(b), Fabricated with and without the Surface Treatments of Different Organic Salts.^a

Sample	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	R_s (Ω)	R_{tr} (Ω)	R_{rec} (Ω)
Reference	20.60	1.10	77.50	17.56	30.77	115.94	1590
MACl	20.19	1.14	76.17	17.53	28.34	75.93	2475
MABr	20.32	1.13	76.97	17.67	27.12	70.96	2895
MAI	21.12	1.12	79.29	18.76	26.76	50.89	3665
FAI	21.16	1.11	78.60	18.46	27.81	68.79	3410

^aResults are presented together with the parameters (inner series resistance R_s , charge transport resistance R_{tr} , and recombination resistance R_{rec}) obtained from fitting the electrochemical

impedance spectroscopy results. J_{sc} : short-circuit current density; V_{oc} : open-circuit voltage; FF: fill factor; PCE: power conversion efficiency.

To illustrate the versatility of the salt treatments described above, we applied the same MAI treatment to $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite solar cells fabricated in an inverted device structure of glass/indium tin oxide (ITO)/poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA)/poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)]-dibromide (PFN)/perovskite/[6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM)/bathocuproine (BCP)/silver. As shown in **Figure 5(a)** and **Table S2**, the MAI treatment clearly improves the photovoltaic performance, leading to a maximum PCE of 20.03% for the treated sample by comparison to the PCE of the untreated sample (19.45%). From the statistics made from the same batch of inverted solar cells (**Figure 5(b)**), one can observe a clear improvement of J_{sc} and a slight augmentation of V_{oc} associated with the MAI treatment, which is in excellent agreement with the reduced trap-assisted recombination by such a treatment observed above from the EIS and light-intensity measurements.

Figure 5. (a) Current density–voltage (J–V) photovoltaic characteristics measured on the best performing $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite solar cells with an inverted device

architecture (glass/ITO/PTAA/PFN/perovskite/PCBM/BCP/silver) with and without the MAI treatment on the perovskite film surface, under 100 mW cm⁻² AM 1.5G illumination. (b) The short-circuit current (J_{sc}), (c) open-circuit voltage (V_{oc}), (d) fill factor (FF), and (e) power conversion efficiency (PCE) of the same batch of Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃ perovskite solar cells in this inverted architecture with and without the MAI treatment on the perovskite film surface.

After studying the impacts of these organic salt surface treatments on the perovskite solar cell photovoltaic parameters, we proceed to characterize their effects on solar cell stability. In recent years, it has been increasingly recognized that the enhancement of the photovoltaic stability of perovskite solar cells is a critically important prerequisite to their integration into industrial applications.^{50–52} Perovskite materials and solar cells have been shown to be sensitive to environmental factors such as oxygen⁵³ or water,⁵⁴ as well as unavoidable exposure to light and temperature.^{55,56} A common point of these four organic salts is that they can all eliminate the perovskite/HTL interfacial excess PbI₂ of the solar cell, with the MAI and FAI treatments capable to passivate surface iodide defects at the same time. Unencapsulated perovskite solar cells with and without these salt surface treatments were measured under continuous AM 1.5G simulated solar illumination at 100 mW cm⁻² inside an Ar-filled glovebox for 100 hours. A global view of these solar cell degradation characteristics under continuous illumination is shown in **Figure 6(a)**. One can notice that, for the untreated sample, the degradation can be described roughly in two stages: (i) A fast “burn-in” degradation, resulting a PCE drop to 77.4% of its initial value, happening during the first two hours (**Figure 6(b)**); (ii) A much slower degradation after this burn-in stage until the end of the experiment when one measured a PCE of 63.5% of its initial value after 100 hours of illumination. Remarkably, by comparison to the untreated sample, solar cells treated by these four

organic salt treatments all exhibit significantly less severe burn-in degradation, with the strongest effect observed in the MAI and FAI-treated cases: For example, after the first two-hours' degradation, the MAI, FAI, MABr and MACl-treated samples exhibited only a slight PCE drop to 98.0%, 98.0%, 96.2%, and 92.1% of their initial values, respectively. Concerning the longer-term degradation after the first two-hours, the slow degradation behaviors until the end of the experiment of the salt-treated samples are similar to that of the untreated case. Nevertheless, mainly due to the improvement made during the burn-in stage, after 100 hours of degradation, the PCE of the MAI-, FAI-, MABr- and MACl-treated solar cells still remained 81.2%, 85.7%, 77.1%, and 75.1% of their initial values, respectively, which is significantly higher than the untreated reference sample. The strong beneficial effect by the MAI and FAI surface treatments can be understood as the combined consequence of interfacial excess PbI_2 removal and surface iodide defect passivation. Interestingly, even without passivating surface iodide defects, just by removing the interfacial excess PbI_2 through the MABr or MACl treatments, a clear improvement of perovskite solar cell degradation behavior can already be observed, in particular for the early burn-in stage. The evolution of each photovoltaic parameters of these perovskite solar cells fabricated with and without the surface treatments of different organic salts during continuous illumination degradation experiments is shown in Figure S5. The beneficial effects of these salt treatments are most significant in the preservation of V_{oc} and FF during degradation. A possible origin of this enhancement can be related to the decomposition of PbI_2 under continuous illumination into iodine (gaseous phase) and metallic lead, which act as recombination centers capable to accelerate degradation.³⁶

Figure 6. (a) Efficiency evolution over 100 hours of the unencapsulated $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite solar cells, fabricated with the device architecture shown in Figure 1(b), with the MAI (blue), FAI (orange), MABr (purple), and MACl (pink) surface treatments by comparison to the reference solar cell without treatment (green) under continuous AM 1.5G illumination at 100 mW cm^{-2} measured inside an Ar-filled glovebox. (b) The zoom-in view of (a) for the first two hours of degradation.

CONCLUSION

In summary, we investigated the role of interfacial PbI_2 excess in $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite solar cells on their photovoltaic performance and stability. Four different organic salts, MAI, FAI, MABr, and MACl, were applied in a diluted solution to treat the perovskite film surface in order to remove the excess surface PbI_2 and the resultant device characteristics were compared. Treatments with iodide salts, such as MAI and FAI, provided the strongest improvements in terms of solar cell efficiency, charge recombination suppression, and device stability under continuous illumination by comparison to the untreated sample, which is likely linked to their dual effects in terms of surface excess PbI_2 removal and

surface iodide defect passivation. Treatments with non-iodide salts, such as MABr and MACl, which remove surface excess PbI_2 without passivating iodide defects, can also provide a clear improvement in terms of charge recombination suppression and device stability. In the most optimized cases, under continuous solar illumination, the MAI and FAI-treated devices maintained respectively 81% and 86% of their initial PCEs after 100 hours of continuous illumination (*versus* 64% for the untreated solar cell with excess PbI_2). Our results show that eliminating PbI_2 at the perovskite/HTL interface by organic salt treatments is highly beneficial for both the efficiency and stability of perovskite devices and can be easily implemented during their fabrication process.

METHODS

Perovskite thin film preparation and solar cell fabrication. The FTO-coated glass substrates and the pre-patterned ITO substrates were cleaned by four sequential ultrasonication baths in 2% hellmanex detergent solution, deionized water, acetone and isopropanol for a duration of 15 minutes in each bath. Blow-dried substrates were then further cleaned by oxygen plasma for 10 minutes. To prepare the compact TiO_2 (cp- TiO_2) ETL, a sol-gel precursor solution based on titanium (IV) isopropoxide was prepared according to a previously reported procedure.⁴⁵ This precursor solution was then spin-coated (at 4000 rpm) onto cleaned FTO substrates followed by substrate annealing in an oven in air first at 120 °C for 15 minutes and then at 450 °C for 1 hour. To achieve mixed-cation and mixed-halide $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ thin films, typically, a 1mL precursor solution was prepared containing FAI (1 M), MABr (0.2 M), PbI_2 (1.1 M), and PbBr_2 (0.2 M) dissolved in a mixture of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (4/1, v/v). 40 μL of a CsI stock solution in DMSO (1.5M) was then added into the above

precursor solution to achieve the $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ composition. This precursor solution was defined as concentration 1 (C1). More concentrated precursor solutions, representing 30%, 60%, and 90% more concentrated than C1, while maintaining the proportion between each sub-constituents unchanged, were also prepared (and defined as C2, C3, and C4, respectively). Optimized precursor concentration was found to be C3 according the photovoltaic characteristics of the resultant devices (Figure S1). The deposition procedure of the perovskite precursor solution onto cp-TiO₂ was performed in an Ar-filled glovebox by two-step spin-coating program first at 1000 rpm for 10 s and then at 5000 rpm for 45 s. During the second step, 100 μL chlorobenzene was dropped on the spinning substrate after 30 s of spinning. The coated substrate was then annealed at 100 °C for 60 minutes on a hot-plate inside the glovebox. To remove the excess PbI₂ crystals on the surface of selected perovskite thin films, inside a glovebox, 50 μL of MAI, or FAI, or MABr, or MACl solution in isopropanol (1 to 4 mg/mL) was drop-cast onto the surface of the perovskite film followed by spin-coating to dry out the solution and a five-minute annealing on a hot-plate at 100 °C. Concerning the HTL, a polymer solution was prepared inside a glovebox by dissolving 72.3 mg of Spiro-OMeTAD in 1 mL chlorobenzene with an addition of 17.5 μL of Li-bis(trifluoromethanesulfonyl)imide solution in acetonitrile (520 mg/mL) and 28.8 μL of tert-butylpyridine. The HTL was then deposited on top of the perovskite layer by spin-coating the polymer solution at 4000 rpm for 30 s. Finally, the gold top contacts (about 100 nm thickness) was thermally evaporated on the top of the HTL through a shadow mask to complete the solar cell architecture. The size of the active area of these solar cells is 0.1 cm². For perovskite solar cells with an inverted architecture, PTAA (1.5mg/ml in toluene) was spin-coated on the cleaned ITO substrates in a drybox (RH<0.5%) at 4000 rpm for 30 s with a thermal anneal of 10 min at 100 °C. After cooling down, PFN-Br (0.5mg/ml in methanol) was then spin-coated on the PTAA at 5000 rpm for 30 s. The perovskite precursor was deposited on the HTL with the same procedure as above

mentioned, followed by a thermal annealing at 100 °C for 30 min. For the MAI-treated samples, the treatment procedure was identical as that mentioned above with a MAI concentration of 2mg/ml. The prepared films were then transferred to a N₂-filled glovebox. PCBM (20mg/ml in chlorobenzene) was dynamically spin-coated on the perovskite layer at 2000 rpm for 30 s, followed by a 10 min anneal at 100 °C. Sequentially, BCP (0.5mg/ml in isopropanol) was spin-coated on the PCBM at 4000 rpm for 30 s as a hole blocking layer. To complete the devices, 80 nm silver was thermally evaporated on top of the films under high vacuum.

Characterization. SEM measurements were performed in a TLD (Through the Lens Detector) mode with a FEI Magellan 400 system equipped with a standard field emission gun source. XRD spectrum were obtained by a PANalytical X'Pert X-ray diffractometer using Cu-K α radiation. UV-Visible absorbance spectra were recorded by a JASCO V770 UV-Vis-NIR spectrometer. Thin film thickness was measured by a Dektak profilometer. AFM was measured by a Digital Instruments Nanoscope III AFM in tapping mode. PL experiments were carried out in air, on perovskite samples deposited directly on glass substrates. The top surfaces (perovskite side) of the PL samples were excited by an LED source ($\lambda = 365$ nm) and the PL spectra were recorded in a reflection mode by an optical fiber connected with a computer-controlled Oceanoptics HR4000 spectrometer. Solar cell current-voltage characteristics were measured in an Ar-filled glovebox by a computer-controlled Keithley 2612B source measurement unit (SMU). Devices were illuminated through the transparent substrate (FTO/glass) side by a class ABB (ASTM E927-10) Newport LCS-100 solar simulator with an AM 1.5G filter operated at 1 sun condition. The light intensity was first calibrated by a calibrated Si reference solar cell (ReRa Solutions B.V.). For the external quantum efficiency (EQE) measurements, a monochromatic light beam was obtained from a white light source coupled with an Oriel Cornerstone monochromator and appropriate order sorting filters. The

monochromatic illumination was calibrated by a NIST-calibrated Si photodiode. The solar cell short-circuit current I_{sc} under each monochromatic wavelength was measured in air by a Keithley 2634B SMU. The EQE spectrum was determined by $EQE(\%) = \frac{I_{sc}(A)}{P(W)} \times \frac{1240}{\lambda(nm)} \times 100$ where $P(W)$ is the power of the monochromatic illumination and $I_{sc}(A)$ is the measured short-circuit current. The EIS measurements were carried out in the dark, in an Ar-filled glovebox, from 20 Hz to 2 MHz with a modulation amplitude of 20 mV, and with an external applied bias holding at the open-circuit voltage of the solar cell, by an electrochemical workstation (Agilent, E4980A). Solar cell degradation measurements under continuous solar illumination was realized under 1-sun illumination (AM 1.5G, 100 mW cm⁻²) on unencapsulated solar cells inside an Ar-filled glovebox at 30°C-35°C. During such a degradation experiment, computer-controlled $J-V$ sweeps were performed every 10 minutes by Keithley 2612B SMU during 100 hours. Concerning shelf-life experiments, unencapsulated perovskite solar cells were stored in dark and in a closed box with controlled humidity (air, ~11% humidity) between test points.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website (PDF). XRD, UV-Vis absorbance, film morphology by SEM, and photovoltaic characteristics of the Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃ perovskite thin films fabricated by different precursor concentrations; Statistics on the measured J_{sc} , V_{oc} , fill factor, and PCE of the Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃ perovskite solar cells fabricated by different precursor concentrations; Tauc plots obtained from UV-Vis absorbance from perovskite thin films treated by different organic salts; Atomic force microscopy (AFM) characterizations on the perovskite thin films treated by different organic salts; Statistics of the photovoltaic parameters of

the perovskite solar cells fabricated with and without different surface treatments; Summary of the photovoltaic characteristics of the perovskite solar cells fabricated by an inverted architecture with and without MAI treatment; The evolution of photovoltaic parameters during degradation experiments under continuous 1-Sun illumination; Shelf-life experiment results where solar cells fabricated with and without the MAI treatment were stored in dark and in a closed box with controlled humidity (air, ~11% humidity) between test points.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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TOC Graphic