

Immediate and temporal enhancement of power conversion efficiency in surface-passivated perovskite solar cells

Yongyoon Cho^{1,2,3}, Jueming Bing^{1,4,5}, Hyung Do Kim², Yong Li¹, Jianghui Zheng^{1,4,5}, Shi Tang^{1,4,5}, Martin A. Green¹, Atsushi Wakamiya⁶, Shujuan Huang^{1,7}, Hideo Ohkita^{2} and Anita W.Y. Ho-Baillie^{1,4,5*}*

¹Australian Centre for Advanced Photovoltaics (ACAP), School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney 2052, Australia

²Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

³Graduate School of Materials Science,
Nara Institute of Science and Technology, Ikoma, Nara 630-0192, Japan

⁴School of physics, University of Sydney, NSW 2006, Australia

⁵The University of Sydney Nano Institute, University of Sydney, NSW 2006, Australia

⁶Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

⁷School of Engineering, Macquarie University, Sydney 2109, Australia

Corresponding Author

*Anita W.Y. Ho-Baillie (anita.ho-baillie@sydney.edu.au)

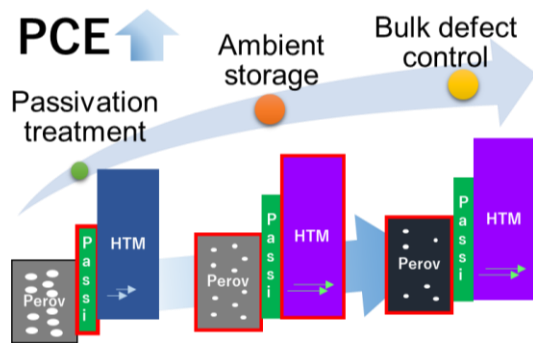
*Hideo Ohkita (ohkita@photo.polym.kyoto-u.ac.jp)

Keywords : Perovskite, Storage, Aging, Passivation, Interface, Bulk, Recombination

ABSTRACT

This work reports strategies for improving power conversion efficiency (PCE) by capitalizing on temporal changes by storage effect and immediate improvements by interface-passivation. It is demonstrated both strategies can be combined as shown by PCE improvement in passivated perovskite solar cells (PSCs) upon ambient storage, due to trap density reduction. By analyzing dominant charge recombination process, we find that lead-related traps in perovskite bulk, rather than at surface, are the recombination centers in both as-fabricated and ambient-stored passivated PSCs. This emphasizes the necessity to reduce intrinsic defects in the perovskite bulk. Furthermore, storage causes temporal change in band alignment even in passivated PSCs contributing to PCE improvement. Building on these findings, composition engineering was employed to produce further immediate PCE improvements due to defect reduction in the bulk achieving a PCE of 22.2%. These results show that understanding the dominant recombination mechanisms within a PSC is important to inform strategies for producing immediate and temporal PCE enhancements either by interface passivation, storage or composition engineering or a combination of all to fabricate highly efficient PSCs.

TOC GRAPHICS



Introduction

Perovskite solar cell (PSC) is the fastest advancing photovoltaic technology. The highest certified power conversion efficiency reported to date is 25.5%, surpassing those of other solution process-able solar cells (e.g. dye-sensitized solar cells and organic solar cells) and reaching those of efficient inorganic solar cells.¹ Despite rapid efficiency growth, there is still room for improvement approaching the Shockley–Queisser limit and there is scope of research for commercialization and for niche applications such as flexible panels, wearable devices and space photovoltaics.^{2–6}

To achieve high power conversion efficiencies (PCE) for perovskite solar cells (PSCs), diverse engineering techniques such as composition engineering, film formation engineering, defect chemistry, and interface engineering have been explored.^{7–13} In particular, interface or surface passivation treatment has been recently identified as an effective tool for enhanced stability and photovoltaic performance.^{10–12,14} In our previous work, we have demonstrated a successful approach of using a mixture of formamidinium iodide (FAI) and *iso*-butylammonium iodide (*i*BAI) that reacts with excess lead iodide from a bulk perovskite layer to form an effective surface passivation layer.¹² These reports have shown that surface defects in as-deposited perovskite can be passivated by additional treatment.^{15,16} However, there has been little investigation and understanding in terms of temporal changes in optoelectronic properties that can occur for these passivated perovskite solar cells and therefore is the focus of this work.

Apart from the immediate and distinct increases in PCE by deliberate fabrication approaches as described above, gradual improvements in PCE for PSCs during the first few days of storage can also occur.^{12,17–23} Several studies have shown that the most common hole-transporting material (HTM), 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD)

contributes to this temporal change after storage due to changes in conductivity²⁴⁻²⁷. Another major contributor is the changes in the properties of the perovskite layer, various explanations include perovskite crystallite coalescence,²⁸ sodium ion diffusion from indium tin oxide (ITO) glass into perovskite grain boundaries,²⁹ and storage-induced recrystallization,³⁰ and perovskite film strain relaxation causing a reduction of trap-assisted non-radiative recombination³¹. In our previous report, we have demonstrated that defect density reduction at the perovskite surface, conductivity increase of the HTM, and the lowering of the highest occupied molecular orbital (HOMO) of HTM are main contributors to efficiency improvement after storage effect for n-i-p mesoporous-structured device.³² Although temporal PCE improvement after storage effect can also be seen in passivated devices as well,^{12,21,22,33} there lacks a systematic investigation with the aim of understanding the underlying mechanisms which will be the focus of this work.

Herein, we first investigated the effect of storage on interface-passivated mesoporous n-i-p (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} PSCs with spiro-OMeTAD. The interface-passivation is implemented by depositing the mixed 3D-2D passivation layer on the perovskite layer prior to the deposition of HTM as reported in our previous work.¹² After one day of ambient (relative humidity (RH) of around 20%) storage, the average PCE of the passivated device increased significantly by more than 2% absolute (from 17.2% to 19.7%) and the champion device has a PCE of 21.2%. New insight into the origin of such storage effect has been found in this study. Firstly, we found that the reduction of defects density occurs after ambient storage even when the perovskite's surface is already well passivated. Through XPS measurement, reduced defects in passivated perovskite bulk is related to the metal Pb⁰, which is different from un-passivated perovskite. However, the dominant recombination process still occurs in the bulk after storage. This motivates the introduction of Cs into the composition for the perovskite bulk

(CsPbI₃)_{0.05}((FAPbI₃)_{0.95}(MAPbBr₃)_{0.05})_{0.95} to test for further improvement. It was found that the PCE's of passivated Cs containing cells achieved further improvement to 19.3% before ambient storage and to 22.2% for the champion cell. Another insight revealed was the sensitivity of energy alignment. The insertion of the passivation layer reduces the band offsets between the perovskite bulk and after storage, the HTM HOMO level was reduced further thereby reducing the band offsets further enhancing charge extraction and enhancing cell's fill factor. Maximum PCE was therefore able to be achieved quickly after only 1 day of ambient storage due to the combined effects. Through this study, we can conclude that it is important to study optoelectronic and chemical properties of passivation materials for interface engineering and to understanding the mechanism of trap density (N_t) reduction in bulk perovskite, in order to design PSCs with higher PCE.

Effect of ambient storage on interface-passivated PSCs

Figure 1 shows the effect of ambient storage (with controlled RH of around 20% in a desiccator) on passivated PSCs with a typical n-i-p structure (**Figure 1a**). For comparison, results of the as-fabricated un-passivated device (dotted line in **Figure 1b** and grey dots in **Figure 1c-f**) are also included. It is evident as-fabricated passivated devices showed immediate PCE improvement (solid line in **Figure 1b** and black dots in **Figure 1c-f**) compared to un-passivated devices and upon storage, improved further from an average PCE of 17.2 to 19.7% with the champion device achieving a PCE of 21.2% after 1 day of storage. To ensure the effect of storage observed is not related to the effect of light and ambient exposure during current–voltage measurements. Repeated measurements were performed and results showed no effect on current density-voltage (J – V) curves (**Figure S1**). The PCE enhancement after storage is attributed to enhancements in open

circuit voltage and fill factor (**Figures 1c-f** and **Table S1**). The time taken for passivated devices to reach maximum PCE is 1 day which is shorter than that (2 days) required by un-passivated device as reported previously³².

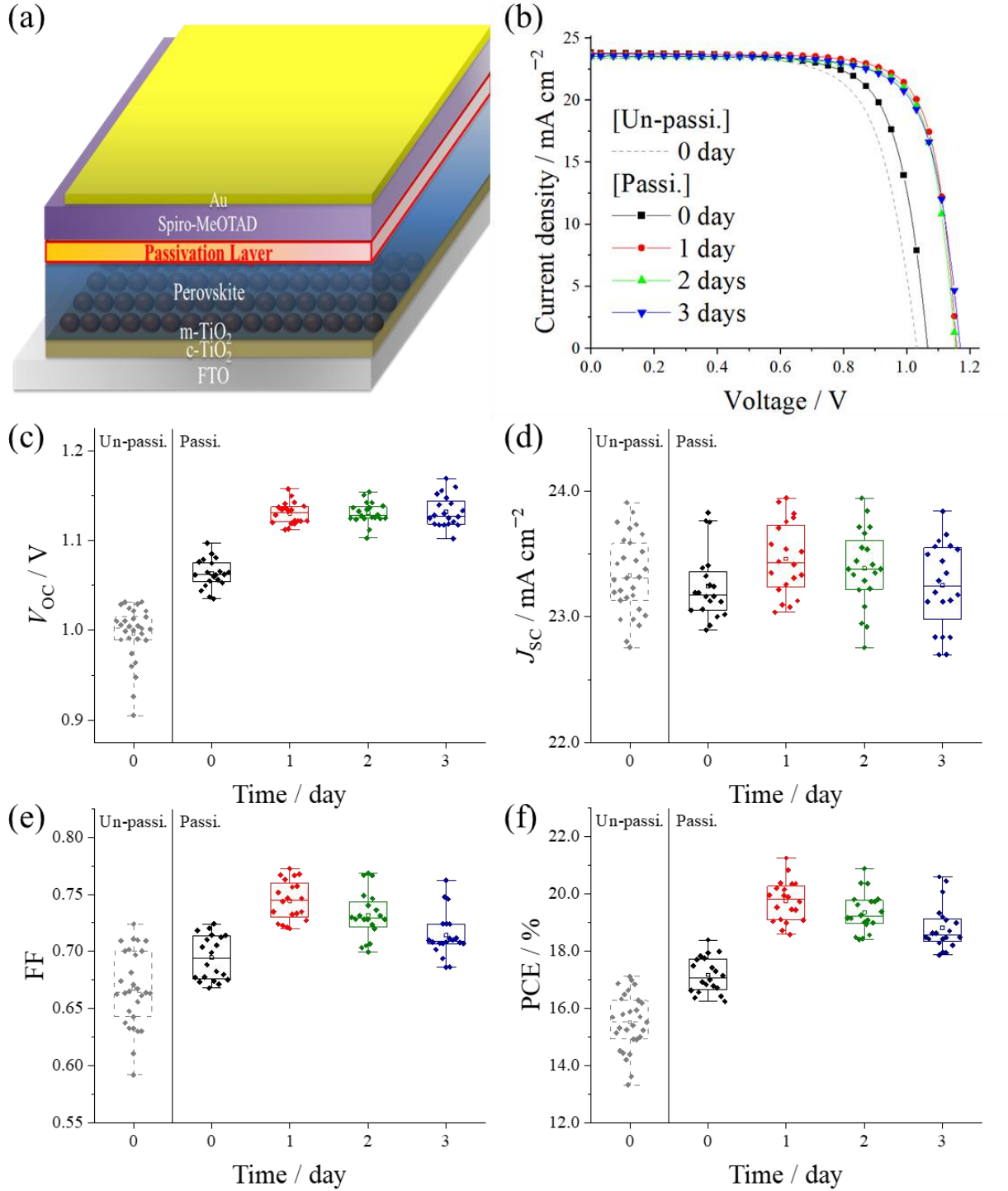


Figure 1. (a) Device structure of PSCs studied in this work. (b) J - V characteristics of the best as-fabricated un-passivated and fresh and ambient-stored passivated $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ devices. (c–f) Distributions of parameters for more than 20 un-passivated³² and passivated $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ devices plotted against storage time. Reprinted with permission from ref 32. Copyright 2021 American Chemical Society.

Table 1. Photovoltaic parameters of the best as-fabricated un-passivated and fresh and ambient-stored passivated $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ devices.

Device	$J_{\text{SC}} / \text{mA cm}^{-2}$	V_{OC} / V	FF / %	PCE / %
Un-passivated	23.4	1.03	70.9	17.1
Passivated	23.8	1.07	72.4	18.4
After 1 day	23.8	1.16	77.2	21.2
After 2 days	23.5	1.15	76.8	20.9
After 3 days	23.6	1.17	74.7	20.6

Temporal change in the passivated perovskite film after storage

In the previous study, temporal changes in both HTM and perovskite layers were found to be the main reasons for the improved device efficiency³² due to i) trap reduction in perovskite, ii) conductivity increase, and iii) lowered HOMO level in HTM. As the same device structure with an additional passivation layer was employed in this work, the same temporal change would take place in the HTM layer. Therefore, as the first step, we studied the HTM-free passivated perovskite layer before and after the ambient storage.^{15,32,34}

We first measured time-resolved photoluminescence (TRPL). Results are shown in **Figure 2a**. As summarized in **Table S2**, the averaged lifetime of the as-fabricated film increased from 172 ns to 497 ns after 2 days of ambient-storage. To evaluate N_t in passivated perovskite film before and after 2 days of ambient storage, we measured their dark J - V characteristics to determine the trap-filled limit voltage (V_{TFL}) using the space-charge-limited current (SCLC) technique (**Figure S2** and see details in the Supporting Information). N_t were estimated to be $(9.58 \pm 1.48) \times 10^{15} \text{ cm}^{-3}$ for the fresh film and $(7.42 \pm 1.53) \times 10^{15} \text{ cm}^{-3}$ for the stored film.^{35–38} We therefore conclude that the PCE improvement due to storage is due to the decrease in N_t in the passivated perovskite layer, consistent with our previous findings.³²

We further investigated the morphological and optoelectronic characteristics of the passivated perovskite layer after storage. In terms of morphology, no crystalline coalescence or grain size growth was observed from scanning electron microscope (SEM) images of passivated perovskite after storage as shown in **Figure S3**. Bandgaps (energy thresholds) E_g were determined from the peak of the differential external quantum efficiency (EQE) of full devices before and after storage (**Figure S4**)^{39,40} showing no change in E_g (1.62 eV) after storage. For the energy level analysis, we measured the ionization potential (valence band (VB) energy level, E_{VB}) of fresh and stored perovskite films with and without passivation by photoelectron yield spectroscopy (PYS). Results are shown in **Figure 2b**. A very small change in the E_{VB} for the perovskite film was observed after storage (from -5.64 eV to -5.61 eV). Although this was also observed in our previous work, this is considered insignificant that could affect cell performance. The change in E_{VB} for perovskite after the introduction of passivation layers has been observed similar to other works such as Formamidinium bromide and n-butylammonium iodide passivation treatments.^{22,41} The reasons for such change are still unclear necessitating further investigations.^{22,41} More importantly,

the insertion of the passivation layer with a higher E_{VB} of -5.44 eV reduces the energy offset for each step change: 0.20 eV between the E_{VB} perovskite layer and E_{VB} passivation layer and 0.27 eV between the E_{VB} passivation layer and the HOMO_{HTM} (see “0 day” for “Passivated” in **Figure 2c**). These “smaller” steps in energy levels lower offset losses and facilitating faster extraction before carriers have the chance of recombining through the sub-bandgap defect states.^{42–44} This is supported by the faster PL decay observed on passivated perovskite/HTM test structures compared to unpassivated counterparts (**Figure S5**).^{45–47} After 1 day of ambient storage, HOMO_{HTM} is reduced from -5.17 eV to -5.42 eV (see “0 day” for “Passivated” in **Figure 2c** and **Figure S6**) further narrowing the gap (0.02 eV) and therefore offset losses between the E_{VB} passivation layer and the HOMO_{HTM}. Such desirable stepwise energy alignments thereby contributes to higher V_{OC} by the same principle in the 1-day-stored device (**Table 1**).³² However, after 2 days of storage, the HOMO_{HTM} went down further to -5.46 eV, lower than the E_{VB} passivating layer (-5.44 eV).³² This forms an energy barrier (see “2 days” for “Passivated” in **Figure 2c**) resulting in poorer FF observed in devices stored for 2 or more days (**Table S1**) due to the worse charge extraction from band-misalignment. Therefore, these results reveal that not only the reduction in N_t in perovskite layers, but also proper cascaded band alignment between the perovskite layer and the HTM are of significance for higher PCE in PSCs. This means that appropriate choices of passivation and transport layers are equally important.

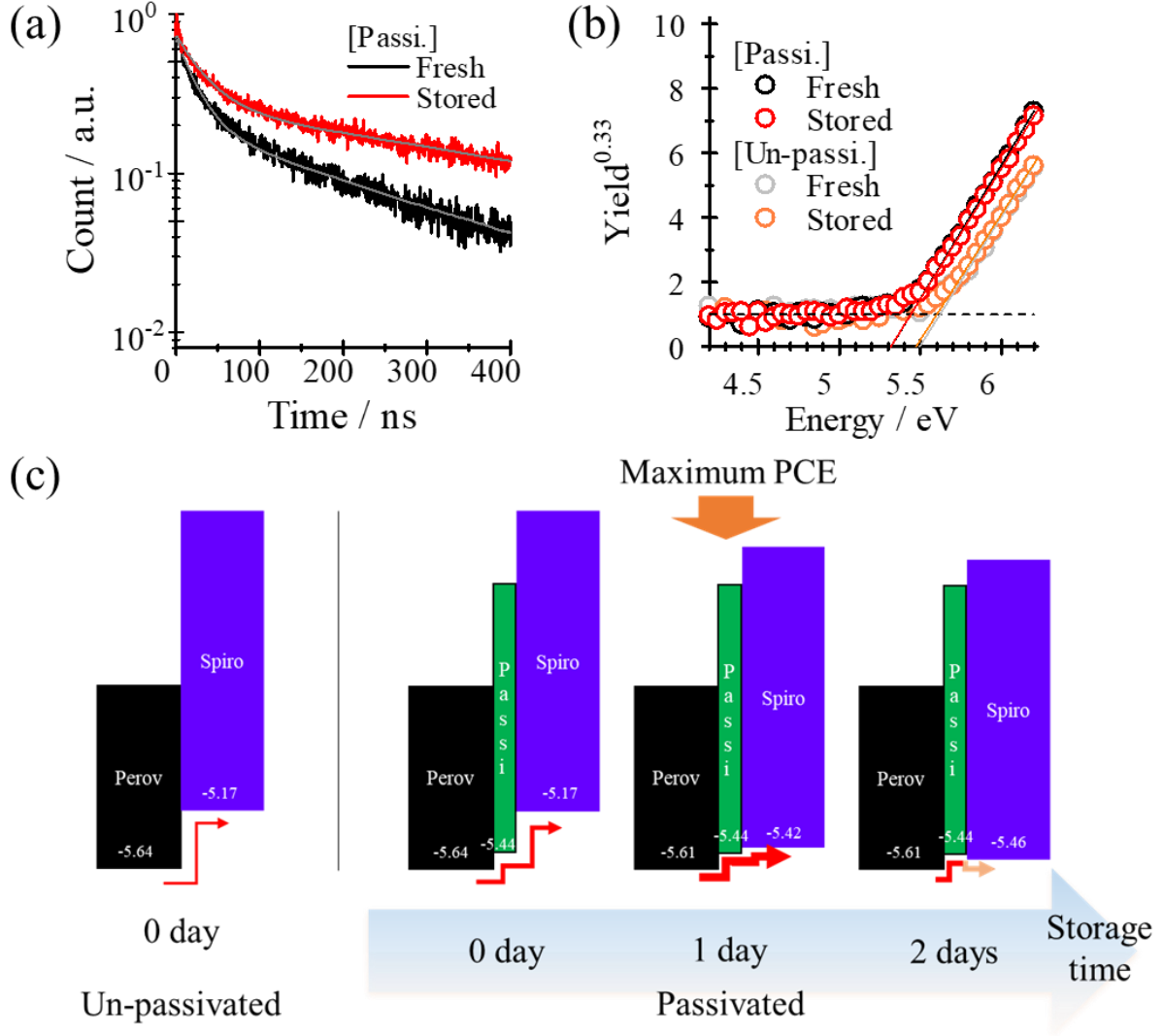


Figure 2. (a) TRPL decay of the passivated (solid) $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ perovskite film before (black) and after (red) 2 days of ambient storage. (b) PYS results of un-passivated and passivated $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ perovskite films before and after storage. The straight lines are fitted lines. (c) Illustration of temporal change in energy levels HTM before and after storage and illustration of the advantage of inserting a passivating layer with higher E_{VB} of -5.44 eV reducing the energy offsets between the various layers.

Dominant recombination in the passivated-perovskite device before and after storage

The reduction in N_t by ambient storage was observed regardless of surface passivation treatment. In our previous work, the reduced N_t resulted in the change of dominant recombination process from surface-dominated to bulk-dominated in un-passivated perovskite.³² However, due to the passivation treatment in this work, the same reduction in N_t by ambient storage does not necessarily produce the same change in the dominant recombination process. To identify dominant recombination mechanism (be it in the bulk or at the surface interface) of the passivated PSCs before and after storage,^{48–53} we measured light intensity dependent and temperature dependent V_{OC} to evaluate n_{id} and the activation energy (E_a) for the recombination current in the device. Background discussion can be found in Supporting Information.

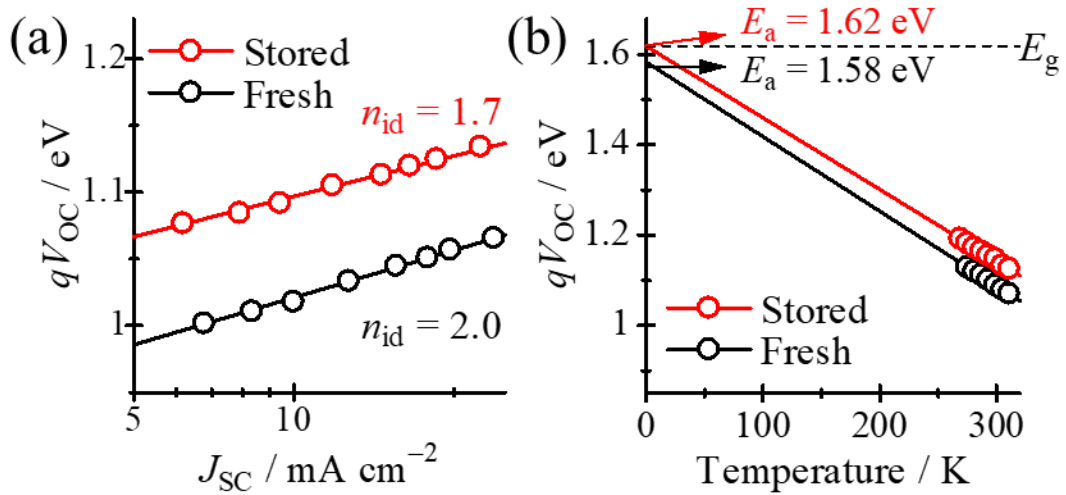


Figure 3. (a) qV_{OC} -log J_{SC} plot and (b) temperature dependent qV_{OC} for the passivated $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ devices before (black) and after (red) ambient storage. n_{id} was evaluated from the slope from (a). E_a determined from y-intercept (0 K) from (b). Dash line in (b) represents E_g determined from Figure S3.

Figure 3a shows the intensity dependent qV_{OC} for the passivated PSCs before (black) and after (red) ambient storage. From the slope, n_{id} was evaluated to be 2.0 for the fresh device and 1.7 for the stored device. The close-to-2 n_{id} value suggests that the typical trap-mediated SRH recombination is dominant in both the fresh and stored devices.^{11,48,51} **Figure 3b** shows the temperature dependent qV_{OC} for the fresh and ambient-stored passivated PSCs. By extrapolating qV_{OC} curves to 0 K, E_a was evaluated to be 1.58 eV for the fresh device and 1.62 eV for the stored device, which are close to the bandgap energy E_g (1.62 eV determined from **Figure S4**). These results in conjunction with the results of light intensity dependent V_{OC} (for determining n_{id}) confirm that recombination in the perovskite bulk is the dominant process for passivated devices both before or after storage^{48,49,53}. This confirms the effectiveness of passivation treatment eliminating surface recombination¹² as being the dominant bottleneck that is otherwise found in fresh un-passivated devices, as reported in our previous work.³² This is further supported by the reduced sub-bandgap signals observed in the EQE of fresh or stored passivated device (black and red), compared to fresh un-passivated device (grey) (**Figure S7**).

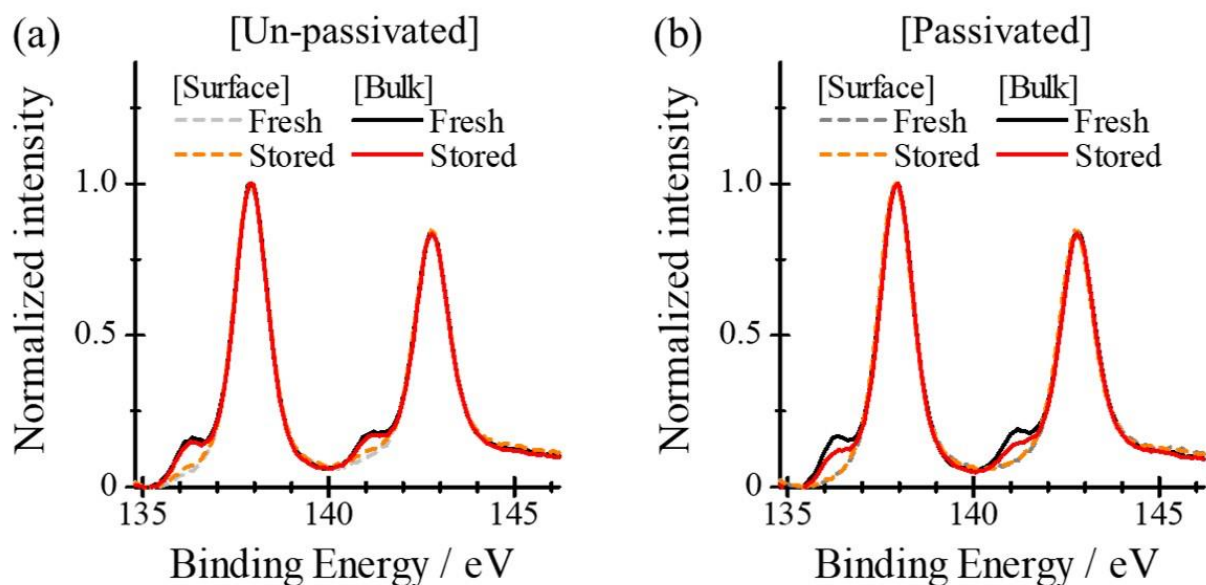


Figure 4. Normalized XPS peaks of Pb4f for the (a) un-passivated and (b) passivated $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ perovskite film before (grey and black) and after (orange and red) ambient storage.

To further investigate the change of passivated perovskite by ambient storage, depth resolved X-ray photoelectron spectroscopy (XPS) was carried out by measuring the surface as well as 150nm into the bulk by argon ion beam etch. Results are shown in **Figure S8**. Most peaks have shown negligible changes after storage except for the lead peaks (see **Figure 4a** for normalized results) in the perovskite bulk. First of all, it is apparent that 136eV and 141eV Pb4f shoulder peaks can be found in the perovskite bulk layer but not at the surface for both un-passivated and passivated perovskites (**Figures 4a & 4b**). Secondly, the intensities of these shoulder peaks decrease in passivated perovskites after ambient storage (**Figure 4b**). Thirdly, the main peaks in the passivated perovskite bulk increase after ambient storage (**Figure S8h**). The shoulder peaks

can be attributed to the metallic Pb^0 (low oxidation state of Pb).⁵⁴ These results indicate the existence of Pb^0 in the bulk layer, implying the formation of under-coordinated Pb defects and importantly, these peaks decrease after ambient storage for the passivated perovskite (**Figure 4b**). This explains the origins of PCE improvement in the passivated PSCs. This is the first time that reduction of lead-related bulk defects by storage is revealed. As to why this particular storage-induced-bulk-improvement only occurs in passivated device and not un-passivated device, more work is required for elucidating the causes.

Further improvement by composition engineering for passivated-perovskite before and after storage

While it is encouraging to see that surface recombination is no longer dominant in passivated devices (whether fresh or stored) and N_t in the passivated perovskite can be reduced by ambient storage, a PCE of 21.2%, and an n_{id} of 1.7 for stored passivated device mean defects in perovskite bulk still exist. This motivates the use of composition engineering to improve the quality of the perovskite layer for further immediate PCE improvement.

Here the perovskite composition is changed from $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ to $(\text{CsPbI}_3)_{0.05}((\text{FAPbI}_3)_{0.95}(\text{MAPbBr}_3)_{0.05})_{0.95}$, taking advantages of Cs incorporation (defect reduction)^{55–58} and increased FA content (higher PCE).^{10,11,59} The result is an immediate PCE improvement by ~1% absolute (cf. Figures 1 & 4 and cf. Tables S1 & S3) due to the increase in J_{SC} (~25 mA cm^{-2} as opposed to ~24 mA cm^{-2} for Cs-free devices) from reduced bandgap (from 1.62eV (**Figure S4**) to 1.58eV (**Figure S9**)). The effect of storage is also studied showing similar PCE improvement (**Figure 5 & Table S3**). The lower $n_{\text{id}} = 1.5$ (inset of **Figure 5**) in Cs-containing films is the result of longer carrier lifetime (**Table S4**) determined from TRPL (**Figure S10**). This

contributes to higher FF of 0.79 in the corresponding champion device (**Figure 5**). As a result, the best PCE of 22.2% was achieved (**Figure 5**).

Aligning with the title of this work, these results show that composition engineering produces an immediate PCE enhancement in surface-passivated cells while further storage can still produce a temporal PCE enhancement in these surface-passivated and bulk-improved devices.

However, we note that the lowered n_{id} of 1.5 is above 1, indicating room for improvement to further reduce trap-mediated recombination process. Future work will also entail investigation into the effect of composition engineering on band alignment between the perovskite layer and the HTM and will elucidate whether storage will cause further changes. Results may prompt for another search for more appropriate passivation and transport layers.

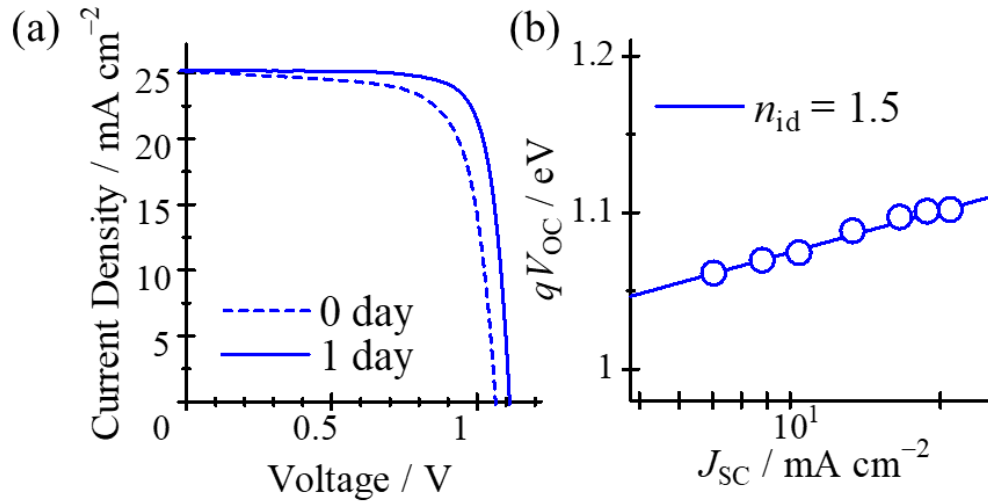


Figure 5. (a) J – V characteristics of the best $(\text{CsPbI}_3)_{0.05}((\text{FAPbI}_3)_{0.95}(\text{MAPbBr}_3)_{0.05})_{0.95}$ perovskite solar cells before (dash) and after 1 day (solid) of ambient storage. (b) Intensity dependent V_{OC} for the same device after storage for determining the ideality factor.

Table 2. Photovoltaic parameters of the best $(\text{CsPbI}_3)_{0.05}((\text{FAPbI}_3)_{0.95}(\text{MAPbBr}_3)_{0.05})_{0.95}$ perovskite solar cells before and after storage.

Device	$J_{\text{SC}} / \text{mA cm}^{-2}$	V_{OC} / V	FF / %	PCE / %
0 day	25.1	1.06	0.72	19.3
1 day	25.2	1.11	0.79	22.2
2 days	25.3	1.11	0.75	21.2

Conclusion

In summary, we demonstrated the combined effects of storage, surface passivation and composition engineering to produce temporal and immediate improvements of PCE for PSCs. It was found that 1 day of ambient storage improved the performance of passivated $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ PSCs from average PCEs of 17.4% to 19.7%. A maximum PCE of 21.2% has been achieved. It was found that the presence of the surface passivating layer with an E_{VB} between those of the perovskite bulk and the HTM are beneficial in reducing the band energy offsets between the three layers enhancing charge extractions. However, excessive ambient storage (more than two days) caused further reduction in the HTM HOMO level resulting in band-misalignment between the perovskite bulk and the HTM which explained the reduced FF of devices that were stored for too long. Charge recombination in the perovskite bulk dominates in passivated devices regardless of storage confirmed by intensity dependent and temperature dependent V_{OC} measurements but lead-related defects can be reduced by storage confirmed by XPS, TRPL and SCLC measurements. Composition engineering (from $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ to $(\text{CsPbI}_3)_{0.05}((\text{FAPbI}_3)_{0.95}(\text{MAPbBr}_3)_{0.05})_{0.95}$) was demonstrated to be effective in producing

immediate performance improvement further even in well surface-passivated devices and if stored for 1 day produced temporal performance improvement further. The best cell had a PCE of 22.2% with a lowered ideality factor of 1.5.

These findings suggest that research on i) the technologies to reduce N_t in the perovskite layer and ii) interfacial passivation layers with appropriate energy level alignment with HTM's are necessary to realize higher PCE for PSCs.

Supporting Information

Supplementary characterizations of materials and devices; tables summarizing previous reports of storage effect; photovoltaic parameters and fitting parameters of TRPL; and figures summarizing results of $J-V$, SEM, XPS, PYS, EQE, SCLC, and TRPL.

Acknowledgements

The Australian Centre for Advanced Photovoltaics (ACAP) encompasses the Australian-based activities of the Australia U.S. Institute for Advanced Photovoltaics (AUSIAPV) and is supported by the Australian Government through the Australian Renewable Energy Agency (ARENA). We thank Associate Professor Tomokazu Umeyama and other researchers at Kyoto University and at the University New South Wales for their technical support. This study is also partly supported by a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO), and Japan Science and Technology Agency (JST) Advanced Low Carbon Technology Research and Development Program (ALCA) Grant Number JPMJAL1603 and JSPS KAKENHI Grand Number JP20F20031.

Experimental section

Materials

All chemicals were purchased from TCI or Sigma–Aldrich/Merck or Alfa Aesar or Lumtec (Luminescence Technology Corp.) and used without further purification.

To prepare 1.2 M FAPbI₃ (or MAPbBr₃) solution, the prepared FAI (or MABr) is mixed with PbI₂ (or PbBr₂) in dimethylformamide (DMF) : dimethyl sulfoxide (DMSO) mixed solvent (4 : 1 volume ratio) at room temperature. For the solution of (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}, prepared FAPbI₃ and MAPbBr₃ solutions are mixed with the corresponding volume ratio. In the case of perovskite solutions, which we used in this study, excess PbI₂ (5 mol% to FAPbI₃) were mixed with the prepared (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} solution and stirred at room temperature for 30 min.

For the solution of (CsPbI₃)_{0.05}((FAPbI₃)_{0.95}(MAPbBr₃)_{0.05})_{0.95} perovskite, the prepared CsI is mixed with PbI₂ in DMF/DMSO mixed solvent (4 : 1 volume ratio), then prepared 1.2 M solutions of CsPbI₃, FAPbI₃, and MAPbBr₃ are mixed with the corresponding volume ratio at room temperature.

To prepare passivation solution, FAI and *i*BAI were dissolved in isopropyl alcohol for 5 mol% concentration solution. Then, mixed passivation solution was prepared by mixing FAI and *i*BAI solutions with 1 : 1 ratio.

Perovskite film deposition

Perovskite film was deposited on the glass, FTO substrate or m-TiO₂/c-TiO₂/FTO substrate. The prepared perovskite solution was spun at 2000 rpm and 6000 rpm for 20 s and 30 s, respectively. During the last 20 s of the second spin-coating step, the anti-solvent chlorobenzene was drop-

casted for 3 s. The films were dried on a hot plate at 100 °C (150 °C for triple cation perovskite) for 20 min. The prepared passivation solution was then spun at 2000 rpm for 20 s. The films were dried on a hot plate at 100 °C for 5 min.

Solar Cell Fabrication

FTO glass was cleaned by toluene, acetone, and ethanol for 15 min each in ultrasonic bath. A compact TiO₂ (c-TiO₂) was deposited by spray pyrolysis (~50 nm) using 12.5 mM titanium diisopropoxide bis(acetylacetonate) solution at 470 °C on the FTO substrate. On top of the c-TiO₂ layer, 150 mg mL⁻¹ of mesoporous TiO₂ paste (m-TiO₂, Greatcell solar 30 NR-D) in ethanol was spin-coated at 4000 rpm for 12 s. Then, the substrates were annealed at 100 °C for 5 min followed by sintering at 500 °C for 30 min, which results in ~200 nm thickness of the m-TiO₂ layer. Then perovskite layer was deposited according to the process above. A solution of spiro-OMeTAD containing 72.3 mg spiro-OMeTAD, 17.5 µL of a 520 mg mL⁻¹ lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 31.2 µL of 4-*tert*-butylpyridine in 1 mL chlorobenzene was spin-coated on the perovskite/m-TiO₂/bl-TiO₂/FTO substrate at 5000 rpm for 40 s which results in ~150 nm thickness of the spiro-OMeTAD layer. All films on m-TiO₂ were deposited in a nitrogen-filled glovebox. A 100-nm gold electrode was deposited by thermal evaporation.

Characterization method

Top-view and cross-section SEM images were obtained using a field emission SEM (Hitachi Regulus8220).

The *J*–*V* characteristics and external quantum efficiency (EQE) of the devices were analyzed by integrated ECT-250D type solar simulator (Bunkoukeiki), under 100 mW cm⁻² (AM 1.5G) simulated sunlight and calibrated monochromic light, respectively. A black and non-reflective aperture (0.09 cm²) mask was used over the cells to avoid overestimation of the device current

densities associated with the active device area. All J – V measurements were undertaken at room temperature in ambient condition. SCLC measurement was carried out under dark condition using test structure of FTO/perovskite/Au.

Time-resolved photoluminescence was measured time-correlated single-photon-counting (TCSPC) fluorescence lifetime system (Horiba Jobin Yvon FluoroCube) at an excitation wavelength of 470 nm. Perovskite and perovskite/HTM films for TCSPC were prepared on the mesoporous TiO_2 substrate (FTO/c- TiO_2 /m TiO_2). Bi-exponential function fitting is used and average lifetime τ_{ave} is defined as $\tau_{\text{ave}} = \sum_i A_i \tau_i^2 / \sum_i A_i \tau_i$.

The valence band of perovskite was measured with a photoelectron emission yield spectrometer (Riken Keiki, AC-3E).

Ideality factor (n_{id}) and activation energy (E_{a})

n_{id} typically lies between 1 and 2 depending on the recombination mechanism under typical conditions. To be more specific, it would be near unity for band-to-band or trap-mediated interface or surface recombination and it would be 2 for trap-mediated SRH recombination.^{S1-S3} In the case of E_{a} , it would be similar to E_{g} , if the recombination current is due to band-to-band recombination or SRH recombination in the light-harvesting absorber layer.^{S1,S4,S5} On the other hand, E_{a} would be smaller than E_{g} if the recombination current is due to recombination at the sub-bandgap tailed states in the bulk and/or recombination at the perovskite/charge transport layer interface, as reported previously.^{S1,S6,S7}

On the basis of a simple equivalent circuit model, V_{OC} is given by the equation (1),

$$V_{\text{OC}} = \frac{n_{\text{id}} k_{\text{B}} T}{q} \ln \left(\frac{J_{\text{SC}}}{J_0} \right) \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, q is the elementary charge, and J_0 is the saturation current density at a reverse bias. Thus, n_{id} can be estimated from the slope of the qV_{OC} - $\log J_{SC}$ plot. The recombination current in the diode J_0 is typically given by the Arrhenius equation (2).

$$J_0 = J_{00} \exp\left(-\frac{E_a}{n_{id}k_B T}\right) \quad (2)$$

where J_{00} is the pre-exponential factor. By combining the equations (1) and (2), we obtain the equation (3).

$$qV_{OC} = E_a - n_{id}k_B T \ln\left(\frac{J_{00}}{J_{SC}}\right) \quad (3)$$

Consequently, E_a of the device can be evaluated from an extrapolated value at 0 K of the temperature dependent qV_{OC} .

References

- (1) Green, M. A.; Dunlop, E. D.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Hao, X. Solar Cell Efficiency Tables (Version 58). *Prog. Photovoltaics Res. Appl.* **2021**, No. May, 657–667. <https://doi.org/10.1002/pip.3444>.
- (2) Han, F.; Luo, J.; Zhao, B.; Wan, Z.; Wang, R.; Jia, C. Cesium Iodide Interface Modification for High Efficiency, High Stability and Low Hysteresis Perovskite Solar Cells. *Electrochim. Acta* **2017**, 236, 122–130. <https://doi.org/10.1016/j.electacta.2017.03.139>.
- (3) Di Giacomo, F.; Zardetto, V.; D’Epifanio, A.; Pescetelli, S.; Matteocci, F.; Razza, S.; Di Carlo, A.; Licoccia, S.; Kessels, W. M. M.; Creatore, M.; Brown, T. M. Flexible Perovskite Photovoltaic Modules and Solar Cells Based on Atomic Layer Deposited Compact Layers and UV-Irradiated TiO₂ Scaffolds on Plastic Substrates. *Adv. Energy Mater.* **2015**, 5 (8), 1401808. <https://doi.org/10.1002/aenm.201401808>.
- (4) Han, T.-H.; Tan, S.; Xue, J.; Meng, L.; Lee, J.-W.; Yang, Y. Interface and Defect Engineering for Metal Halide Perovskite Optoelectronic Devices. *Adv. Mater.* **2019**, 31 (47), 1803515. <https://doi.org/10.1002/adma.201803515>.
- (5) Reb, L. K.; Böhmer, M.; Predeschly, B.; Grott, S.; Weindl, C. L.; Ivandekic, G. I.; Guo, R.; Dreißigacker, C.; Gernhäuser, R.; Meyer, A.; Müller-Buschbaum, P. Perovskite and Organic Solar Cells on a Rocket Flight. *Joule* **2020**, 4 (9), 1880–1892. <https://doi.org/10.1016/j.joule.2020.07.004>.
- (6) Kim, B. J.; Kim, D. H.; Lee, Y.-Y.; Shin, H.-W.; Han, G. S.; Hong, J. S.; Mahmood, K.; Ahn, T. K.; Joo, Y.-C.; Hong, K. S.; Park, N.-G.; Lee, S.; Jung, H. S. Highly Efficient and

- Bending Durable Perovskite Solar Cells: Toward a Wearable Power Source. *Energy Environ. Sci.* **2015**, 8 (3), 916–921. <https://doi.org/10.1039/C4EE02441A>.
- (7) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. Il. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* **2015**, 517 (7535), 476–480. <https://doi.org/10.1038/nature14133>.
 - (8) Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. Il. Solvent Engineering for High-Performance Inorganic–Organic Hybrid Perovskite Solar Cells. *Nat. Mater.* **2014**, 13 (9), 897–903. <https://doi.org/10.1038/nmat4014>.
 - (9) Bing, J.; Kim, J.; Zhang, M.; Zheng, J.; Lee, D. S.; Cho, Y.; Deng, X.; Lau, C. F. J.; Li, Y.; Green, M. A.; Huang, S.; Ho-Baillie, A. W. Y. The Impact of a Dynamic Two-Step Solution Process on Film Formation of $\text{Cs}_{0.15}(\text{MA}_{0.7}\text{FA}_{0.3})_{0.85}\text{PbI}_3$ Perovskite and Solar Cell Performance. *Small* **2019**, 15 (9), 1804858. <https://doi.org/10.1002/sml.201804858>.
 - (10) Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T.-Y.; Noh, J. H.; Seo, J. Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-Hexylthiophene). *Nature* **2019**, 567 (7749), 511–515. <https://doi.org/10.1038/s41586-019-1036-3>.
 - (11) Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. Surface Passivation of Perovskite Film for Efficient Solar Cells. *Nat. Photonics* **2019**, 13 (7), 460–466. <https://doi.org/10.1038/s41566-019-0398-2>.
 - (12) Cho, Y.; Soufiani, A. M.; Yun, J. S.; Kim, J.; Lee, D. S.; Seidel, J.; Deng, X.; Green, M. A.; Huang, S.; Ho-Baillie, A. W. Y. Mixed 3D-2D Passivation Treatment for Mixed-Cation Lead Mixed-Halide Perovskite Solar Cells for Higher Efficiency and Better Stability. *Adv.*

- Energy Mater.* **2018**, 8 (20), 1703392. <https://doi.org/10.1002/aenm.201703392>.
- (13) Bing, J.; Lee, D. S.; Zheng, J.; Zhang, M.; Li, Y.; Kim, J.; Lau, C. F. J.; Cho, Y.; Green, M. A.; Huang, S.; Ho-Baillie, A. W. Y. Deconstruction-Assisted Perovskite Formation for Sequential Solution Processing of Cs_{0.15}(MA_{0.7}FA_{0.3})_{0.85}PbI₃ Solar Cells. *Sol. Energy Mater. Sol. Cells* **2019**, 203 (July), 110200. <https://doi.org/10.1016/j.solmat.2019.110200>.
- (14) Gharibzadeh, S.; Abdollahi Nejand, B.; Jakoby, M.; Abzieher, T.; Hauschild, D.; Moghadamzadeh, S.; Schwenzer, J. A.; Brenner, P.; Schmager, R.; Haghighirad, A. A.; Weinhardt, L.; Lemmer, U.; Richards, B. S.; Howard, I. A.; Paetzold, U. W. Record Open-Circuit Voltage Wide-Bandgap Perovskite Solar Cells Utilizing 2D/3D Perovskite Heterostructure. *Adv. Energy Mater.* **2019**, 9 (21), 1803699. <https://doi.org/10.1002/aenm.201803699>.
- (15) Song, Z.; Shrestha, N.; Wathage, S. C.; Liyanage, G. K.; Almutawah, Z. S.; Ahangharnejhad, R. H.; Phillips, A. B.; Ellingson, R. J.; Heben, M. J. Impact of Moisture on Photoexcited Charge Carrier Dynamics in Methylammonium Lead Halide Perovskites. *J. Phys. Chem. Lett.* **2018**, 9 (21), 6312–6320. <https://doi.org/10.1021/acs.jpclett.8b02595>.
- (16) Yoo, J. J.; Wieghold, S.; Sponseller, M. C.; Chua, M. R.; Bertram, S. N.; Hartono, N. T. P.; Tresback, J. S.; Hansen, E. C.; Correa-Baena, J.-P.; Bulović, V.; Buonassisi, T.; Shin, S. S.; Bawendi, M. G. An Interface Stabilized Perovskite Solar Cell with High Stabilized Efficiency and Low Voltage Loss. *Energy Environ. Sci.* **2019**, 12 (7), 2192–2199. <https://doi.org/10.1039/C9EE00751B>.
- (17) Deng, Y.; Dong, Q.; Bi, C.; Yuan, Y.; Huang, J. Air-Stable, Efficient Mixed-Cation Perovskite Solar Cells with Cu Electrode by Scalable Fabrication of Active Layer. *Adv.*

- Energy Mater.* **2016**, 6 (11), 1–6. <https://doi.org/10.1002/aenm.201600372>.
- (18) Lee, D. S.; Yun, J. S.; Kim, J.; Soufiani, A. M.; Chen, S.; Cho, Y.; Deng, X.; Seidel, J.; Lim, S.; Huang, S.; Ho-Baillie, A. W. Y. Passivation of Grain Boundaries by Phenethylammonium in Formamidinium-Methylammonium Lead Halide Perovskite Solar Cells. *ACS Energy Lett.* **2018**, 3 (3), 647–654. <https://doi.org/10.1021/acsenergylett.8b00121>.
- (19) You, J.; Meng, L.; Song, T. Bin; Guo, T. F.; Chang, W. H.; Hong, Z.; Chen, H.; Zhou, H.; Chen, Q.; Liu, Y.; De Marco, N.; Yang, Y. Improved Air Stability of Perovskite Solar Cells via Solution-Processed Metal Oxide Transport Layers. *Nat. Nanotechnol.* **2016**, 11 (1), 75–81. <https://doi.org/10.1038/nnano.2015.230>.
- (20) De Bastiani, M.; Aydin, E.; Allen, T.; Walter, D.; Fell, A.; Peng, J.; Gasparini, N.; Troughton, J.; Baran, D.; Weber, K.; White, T. P.; De Wolf, S. Interfacial Dynamics and Contact Passivation in Perovskite Solar Cells. *Adv. Electron. Mater.* **2019**, 5 (1), 1800500. <https://doi.org/10.1002/aelm.201800500>.
- (21) Zhou, Y.; Wang, F.; Cao, Y.; Wang, J.-P.; Fang, H.-H.; Loi, M. A.; Zhao, N.; Wong, C.-P. Benzylamine-Treated Wide-Bandgap Perovskite with High Thermal-Photostability and Photovoltaic Performance. *Adv. Energy Mater.* **2017**, 7 (22), 1701048. <https://doi.org/10.1002/aenm.201701048>.
- (22) Cho, K. T.; Paek, S.; Grancini, G.; Roldán-Carmona, C.; Gao, P.; Lee, Y.; Nazeeruddin, M. K. Highly Efficient Perovskite Solar Cells with a Compositionally Engineered Perovskite/Hole Transporting Material Interface. *Energy Environ. Sci.* **2017**, 10 (2), 621–627. <https://doi.org/10.1039/C6EE03182J>.

- (23) Li, N.; Zhu, Z.; Chueh, C.-C.; Liu, H.; Peng, B.; Petrone, A.; Li, X.; Wang, L.; Jen, A. K. Y. Mixed Cation $\text{FA}_x\text{PEA}_{1-x}\text{PbI}_3$ with Enhanced Phase and Ambient Stability toward High-Performance Perovskite Solar Cells. *Adv. Energy Mater.* **2017**, 7 (1), 1601307. <https://doi.org/10.1002/aenm.201601307>.
- (24) Wang, S.; Yuan, W.; Meng, Y. S. Spectrum-Dependent Spiro-OMeTAD Oxidization Mechanism in Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, 7 (44), 24791–24798. <https://doi.org/10.1021/acsami.5b07703>.
- (25) Hawash, Z.; Ono, L. K.; Qi, Y. Recent Advances in Spiro-MeOTAD Hole Transport Material and Its Applications in Organic-Inorganic Halide Perovskite Solar Cells. *Adv. Mater. Interfaces* **2018**, 5 (1), 1700623. <https://doi.org/10.1002/admi.201700623>.
- (26) Hawash, Z.; Ono, L. K.; Raga, S. R.; Lee, M. V.; Qi, Y. Air-Exposure Induced Dopant Redistribution and Energy Level Shifts in Spin-Coated Spiro-MeOTAD Films. *Chem. Mater.* **2015**, 27 (2), 562–569. <https://doi.org/10.1021/cm504022q>.
- (27) Hawash, Z.; Ono, L. K.; Qi, Y. Moisture and Oxygen Enhance Conductivity of LiTFSI-Doped Spiro-MeOTAD Hole Transport Layer in Perovskite Solar Cells. *Adv. Mater. Interfaces* **2016**, 3 (13), 1600117. <https://doi.org/10.1002/admi.201600117>.
- (28) Roose, B.; Ummadisingu, A.; Correa-Baena, J.-P.; Saliba, M.; Hagfeldt, A.; Graetzel, M.; Steiner, U.; Abate, A. Spontaneous Crystal Coalescence Enables Highly Efficient Perovskite Solar Cells. *Nano Energy* **2017**, 39 (June), 24–29. <https://doi.org/10.1016/j.nanoen.2017.06.037>.
- (29) Bi, C.; Zheng, X.; Chen, B.; Wei, H.; Huang, J. Spontaneous Passivation of Hybrid

- Perovskite by Sodium Ions from Glass Substrates: Mysterious Enhancement of Device Efficiency Revealed. *ACS Energy Lett.* **2017**, 2 (6), 1400–1406. <https://doi.org/10.1021/acsenenergylett.7b00356>.
- (30) Fei, C.; Wang, H. Age-Induced Recrystallization in Perovskite Solar Cells. *Org. Electron.* **2019**, 68 (January), 143–150. <https://doi.org/10.1016/j.orgel.2019.02.010>.
- (31) Moghadamzadeh, S.; Hossain, I. M.; Jakoby, M.; Abdollahi Nejand, B.; Rueda-Delgado, D.; Schwenzer, J. A.; Gharibzadeh, S.; Abzieher, T.; Khan, M. R.; Haghighirad, A. A.; Howard, I. A.; Richards, B. S.; Lemmer, U.; Paetzold, U. W. Spontaneous Enhancement of the Stable Power Conversion Efficiency in Perovskite Solar Cells. *J. Mater. Chem. A* **2020**, 8 (2), 670–682. <https://doi.org/10.1039/C9TA09584E>.
- (32) Cho, Y.; Kim, H. Do; Zheng, J.; Bing, J.; Li, Y.; Zhang, M.; Green, M. A.; Wakamiya, A.; Huang, S.; Ohkita, H.; Ho-Baillie, A. W. Y. Elucidating Mechanisms behind Ambient Storage-Induced Efficiency Improvements in Perovskite Solar Cells. *ACS Energy Lett.* **2021**, 6 (3), 925–933. <https://doi.org/10.1021/acsenenergylett.0c02406>.
- (33) Bai, Y.; Dong, Q.; Shao, Y.; Deng, Y.; Wang, Q.; Shen, L.; Wang, D.; Wei, W.; Huang, J. Enhancing Stability and Efficiency of Perovskite Solar Cells with Crosslinkable Silane-Functionalized and Doped Fullerene. *Nat. Commun.* **2016**, 7 (1), 12806. <https://doi.org/10.1038/ncomms12806>.
- (34) García-Fernández, A.; Moradi, Z.; Bermúdez-García, J. M.; Sánchez-Andújar, M.; Gimeno, V. A.; Castro-García, S.; Señarís-Rodríguez, M. A.; Mas-Marzá, E.; Garcia-Belmonte, G.; Fabregat-Santiago, F. Effect of Environmental Humidity on the Electrical Properties of Lead Halide Perovskites. *J. Phys. Chem. C* **2019**, 123 (4), 2011–2018.

<https://doi.org/10.1021/acs.jpcc.8b03915>.

- (35) Son, D.Y.; Kim, S.G.; Seo, J.Y.; Lee, S.H.; Shin, H.; Lee, D.; Park, N.G. Universal Approach toward Hysteresis-Free Perovskite Solar Cell via Defect Engineering. *J. Am. Chem. Soc.* **2018**, *140* (4), 1358–1364. <https://doi.org/10.1021/jacs.7b10430>.
- (36) Guo, Y.; Ma, J.; Lei, H.; Yao, F.; Li, B.; Xiong, L.; Fang, G. Enhanced Performance of Perovskite Solar Cells via Anti-Solvent Nonfullerene Lewis Base IT-4F Induced Trap-Passivation. *J. Mater. Chem. A* **2018**, *6* (14), 5919–5925. <https://doi.org/10.1039/C8TA00583D>.
- (37) Liu, Z.; Qiu, L.; Juarez-Perez, E. J.; Hawash, Z.; Kim, T.; Jiang, Y.; Wu, Z.; Raga, S. R.; Ono, L. K.; Liu, S.; Qi, Y. Gas-Solid Reaction Based over One-Micrometer Thick Stable Perovskite Films for Efficient Solar Cells and Modules. *Nat. Commun.* **2018**, *9* (1), 3880. <https://doi.org/10.1038/s41467-018-06317-8>.
- (38) Zhang, Y.; Kim, S.-G.; Lee, D.; Shin, H.; Park, N.-G. Bifacial Stamping for High Efficiency Perovskite Solar Cells. *Energy Environ. Sci.* **2019**, *12* (1), 308–321. <https://doi.org/10.1039/C8EE02730G>.
- (39) Luo, D.; Yang, W.; Wang, Z.; Sadhanala, A.; Hu, Q.; Su, R.; Shivanna, R.; Trindade, G. F.; Watts, J. F.; Xu, Z.; Liu, T.; Chen, K.; Ye, F.; Wu, P.; Zhao, L.; Wu, J.; Tu, Y.; Zhang, Y.; Yang, X.; Zhang, W.; Friend, R. H.; Gong, Q.; Snaith, H. J.; Zhu, R. Enhanced Photovoltage for Inverted Planar Heterojunction Perovskite Solar Cells. *Science* **2018**, *360* (6396), 1442–1446. <https://doi.org/10.1126/science.aap9282>.
- (40) Green, M. A.; Ho-Baillie, A. W. Y. Pushing to the Limit: Radiative Efficiencies of Recent

- Mainstream and Emerging Solar Cells. *ACS Energy Lett.* **2019**, *4* (7), 1639–1644.
<https://doi.org/10.1021/acsenergylett.9b01128>.
- (41) Mahmud, M. A.; Duong, T.; Yin, Y.; Pham, H. T.; Walter, D.; Peng, J.; Wu, Y.; Li, L.; Shen, H.; Wu, N.; Mozaffari, N.; Andersson, G.; Catchpole, K. R.; Weber, K. J.; White, T. P. Double-Sided Surface Passivation of 3D Perovskite Film for High-Efficiency Mixed-Dimensional Perovskite Solar Cells. *Adv. Funct. Mater.* **2020**, *30* (7), 1907962.
<https://doi.org/10.1002/adfm.201907962>.
- (42) Song, T.; Kanevce, A.; Sites, J. R. Emitter/Absorber Interface of CdTe Solar Cells. *J. Appl. Phys.* **2016**, *119* (23), 233104. <https://doi.org/10.1063/1.4953820>.
- (43) Crovetto, A.; Hansen, O. What Is the Band Alignment of $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ Solar Cells? *Sol. Energy Mater. Sol. Cells* **2017**, *169* (May), 177–194.
<https://doi.org/10.1016/j.solmat.2017.05.008>.
- (44) Shi, J.; Xu, X.; Li, D.; Meng, Q. Interfaces in Perovskite Solar Cells. *Small* **2015**, *11* (21), 2472–2486. <https://doi.org/10.1002/smll.201403534>.
- (45) Gloeckler, M.; Sites, J. R. Efficiency Limitations for Wide-Band-Gap Chalcopyrite Solar Cells. *Thin Solid Films* **2005**, *480–481*, 241–245. <https://doi.org/10.1016/j.tsf.2004.11.018>.
- (46) Kapil, G.; Ripolles, T. S.; Hamada, K.; Ogomi, Y.; Bessho, T.; Kinoshita, T.; Chantana, J.; Yoshino, K.; Shen, Q.; Toyoda, T.; Minemoto, T.; Murakami, T. N.; Segawa, H.; Hayase, S. Highly Efficient 17.6% Tin–Lead Mixed Perovskite Solar Cells Realized through Spike Structure. *Nano Lett.* **2018**, *18* (6), 3600–3607.
<https://doi.org/10.1021/acs.nanolett.8b00701>.

- (47) Minemoto, T.; Murata, M. Theoretical Analysis on Effect of Band Offsets in Perovskite Solar Cells. *Sol. Energy Mater. Sol. Cells* **2015**, *133*, 8–14. <https://doi.org/10.1016/j.solmat.2014.10.036>.
- (48) Tress, W.; Yavari, M.; Domanski, K.; Yadav, P.; Niesen, B.; Correa Baena, J. P.; Hagfeldt, A.; Graetzel, M. Interpretation and Evolution of Open-Circuit Voltage, Recombination, Ideality Factor and Subgap Defect States during Reversible Light-Soaking and Irreversible Degradation of Perovskite Solar Cells. *Energy Environ. Sci.* **2018**, *11* (1), 151–165. <https://doi.org/10.1039/C7EE02415K>.
- (49) Kim, H. Do; Yanagawa, N.; Shimazaki, A.; Endo, M.; Wakamiya, A.; Ohkita, H.; Benten, H.; Ito, S. Origin of Open-Circuit Voltage Loss in Polymer Solar Cells and Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2017**, *9* (23), 19988–19997. <https://doi.org/10.1021/acsami.7b03694>.
- (50) Grover, S.; Li, J. V. Theory and Analysis of Temperature Coefficient of Open-Circuit Voltage (dV_{oc}/dT) in Heterojunction Solar Cells. In *2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC)*; IEEE, 2015; pp 1–3. <https://doi.org/10.1109/PVSC.2015.7356039>.
- (51) Calado, P.; Burkitt, D.; Yao, J.; Troughton, J.; Watson, T. M.; Carnie, M. J.; Telford, A. M.; O'Regan, B. C.; Nelson, J.; Barnes, P. R. F. Identifying Dominant Recombination Mechanisms in Perovskite Solar Cells by Measuring the Transient Ideality Factor. *Phys. Rev. Appl.* **2019**, *11* (4), 1. <https://doi.org/10.1103/PhysRevApplied.11.044005>.
- (52) Kim, H. Do; Miyamoto, Y.; Kubota, H.; Yamanari, T.; Ohkita, H. Open-Circuit Voltage Loss in $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskite Solar Cells. *Chem. Lett.* **2017**, *46* (2), 253–256.

<https://doi.org/10.1246/cl.160994>.

- (53) Zheng, X.; Chen, B.; Yang, M.; Wu, C.; Orler, B.; Moore, R. B.; Zhu, K.; Priya, S. The Controlling Mechanism for Potential Loss in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Hybrid Solar Cells. *ACS Energy Lett.* **2016**, *1* (2), 424–430. <https://doi.org/10.1021/acsenergylett.6b00215>.
- (54) McGettrick, J. D.; Hooper, K.; Pockett, A.; Baker, J.; Troughton, J.; Carnie, M.; Watson, T. Sources of Pb(0) Artefacts during XPS Analysis of Lead Halide Perovskites. *Mater. Lett.* **2019**, *251*, 98–101. <https://doi.org/10.1016/j.matlet.2019.04.081>.
- (55) Hu, Y.; Hutter, E. M.; Rieder, P.; Grill, I.; Hanisch, J.; Aygüler, M. F.; Hufnagel, A. G.; Handloser, M.; Bein, T.; Hartschuh, A.; Tvingstedt, K.; Dyakonov, V.; Baumann, A.; Savenije, T. J.; Petrus, M. L.; Docampo, P. Understanding the Role of Cesium and Rubidium Additives in Perovskite Solar Cells: Trap States, Charge Transport, and Recombination. *Adv. Energy Mater.* **2018**, *8* (16), 1703057. <https://doi.org/10.1002/aenm.201703057>.
- (56) Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M. Cesium-Containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency. *Energy Environ. Sci.* **2016**, *9* (6), 1989–1997. <https://doi.org/10.1039/C5EE03874J>.
- (57) Solanki, A.; Yadav, P.; Turren-Cruz, S. H.; Lim, S. S.; Saliba, M.; Sum, T. C. Cation Influence on Carrier Dynamics in Perovskite Solar Cells. *Nano Energy* **2019**, *58* (January), 604–611. <https://doi.org/10.1016/j.nanoen.2019.01.060>.

- (58) Lee, J.-W.; Kim, D.-H.; Kim, H.-S.; Seo, S.-W.; Cho, S. M.; Park, N.-G. Formamidinium and Cesium Hybridization for Photo- and Moisture-Stable Perovskite Solar Cell. *Adv. Energy Mater.* **2015**, 5 (20), 1501310. <https://doi.org/10.1002/aenm.201501310>.
- (59) Kim, M.; Kim, G.-H.; Lee, T. K.; Choi, I. W.; Choi, H. W.; Jo, Y.; Yoon, Y. J.; Kim, J. W.; Lee, J.; Huh, D.; Lee, H.; Kwak, S. K.; Kim, J. Y.; Kim, D. S. Methylammonium Chloride Induces Intermediate Phase Stabilization for Efficient Perovskite Solar Cells. *Joule* **2019**, 3 (9), 2179–2192. <https://doi.org/10.1016/j.joule.2019.06.014>.