Barrier Reinforcement for Enhanced Perovskite Solar Cell Stability under Reverse Bias

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Abstract

Stability of perovskite solar cells (PSCs) under light, heat, humidity, and their combinations, have been significantly improved recently. However, PSCs have poor reverse bias stability that limits their real-world application. Herein, we report a systematic study on the degradation mechanisms of p-i-n structure PSCs under reverse bias. The oxidation of iodide by injected holes at the cathode side initialize the reverse-bias induced degradation, then the generated neutral iodine oxidizes metal electrode like copper, followed by drift of Cu^+ into perovskites and its reduction by injected electrons, resulting in localized metallic filaments and thus device breakdown. A reinforced barrier with combined lithium fluoride, tin oxide, and indium tin oxide at the cathode side reduces device dark current and avoids the corrosion of Cu^0. It dramatically increases breakdown voltage to above −20 V and improved the T_{90} lifetime of PSCs to ~1000 hours under −1.6 V. Modified minimodule also maintained over 90% of its initial performance after 720 hours shadow tests.

Main text

Introduction

Metal halide PSCs have attracted tremendous attention from both academy and industry with their promising future in further reducing solar cell energy cost. The efficiency of single junction perovskite solar cells already exceeds 26% for small area devices and 22% for minimodules[1]. Very promising stability for small area PSCs, particularly those tested under accelerated conditions such as 1 sun illumination and 75-85 °C, have also been shown with T_{90} lifetime exceeding 1000 hours[2-5]. Long operational stability of several thousand hours have been demonstrated for both monofacial and bifacial perovskite minimodules[6,7]. These rapid advances come from global efforts in engineering perovskite ink formulations, device structures and advanced device encapsulations, etc.[8-11] However, low reverse bias stability of perovskite solar cells, which is a big threat to all thin film solar cells, has remained unsolved[12,13]. Many reported perovskite solar cells could withstand reverse bias for only a few minutes[14-16]. Since perovskite subcells are connected in series in all developed perovskite modules, partial shading, caused by various environmental factors such as trees, clouds, animal stools, etc., will induce reverse bias and accelerate the degradation of shaded perovskite subcells. Therefore, enhancing the reverse bias stability is critical for better module shading stability.

Different from covalent bonding semiconductors such as silicon, perovskite materials are more susceptible to reverse bias degradation. Although the improved reverse bias stability has been demonstrated in perovskite/silicon tandems due to the large voltage drop on silicon cell[13,17,18], the reverse bias caused perovskite degradation, such as band bending, ions migration, electrochemical reactions, defects generation, and even thermal breakdown, should not be ignored[12,19-25]. Our early study showed that electric bias could drive ion migration, and the accumulated ions caused self-doping of perovskites close to electrodes, causing the flip of perovskite diodes regardless of the work function of metal electrodes[26]. Electrochemical reaction was later identified for perovskite device under long term bias[27]. The iodide oxidization to neutral halogens (I^0), which was caused by the tunneled holes through sharply bended energy band near cathode, was identified to be new charge recombination centers that reduced the device efficiency under reverse bias[15,28]. Using depth dependent defect profiling, we directly observed that injected holes oxidized iodide interstitials from negatively charged ones (i.e. I_i^-) to positively charged ones (I_i^+), which cause deeper charge traps and thus severe charge recombination[16]. Jeangros et al. pointed out that halides could migrate into electron transport layers under reverse bias and change the energy levels, which induced S-shaped current density-voltage (J-V) curves. Metal ions from electrodes were also reported to migrate into perovskites to form shunts[29]. Metal ion migration induced shunts were directly tied with the appearance of local hot spots observed in PSCs[30]. In perovskites with mixed halides or cations, reverse bias induced phase segregation reported by multiple research groups[15,29], which was recently explained by halides (especially I^-) oxidation[25,31]. These studies clarified many aspects of reverse bias induced perovskite solar cell degradation, but unfortunately, have not resulted in a device design to overcome the reverse bias instability problem. Some strategies, such as increasing grain size[32], grain passivation[33], devices architecture modification[14,34], etc. were reported to improve the reverse bias stability of perovskite devices, however the reported best lifetime under relatively large reverse bias is still no more than 1 hour[14]. A recent study using solution processed iodide barrier substantially improved the reverse bias stability of small area devices[35]. However, it is not known when these solution process would yield a compact and continuous iodide barrier layers at large area module level. Therefore, enhancing the long-term reverse bias stability of PSCs and modules without compromising their efficiency and stability under other stressors is urgent for perovskite photovoltaic technologies to enter market.

Here, we investigated the irreversible degradation mechanism of p-i-n structure PSCs under reverse bias for both instant breakdown and long-term degradation. In addition to the broadly observed ion migration, the redox reaction of neutral iodine with metal electrode played an important role in reverse bias induced breakdown and degradation. Addressing it needs to consider hole injection suppression, iodide migration, neutron iodine diffusion, and electrochemical reaction of Cu^+ and drift of ions. We found a stacking layer of dense SnO_2, indium tin oxide (ITO) and the high-resistance interface layer LiF could dramatically enhance the reverse bias stability. The resulting PSCs with power conversion efficiency (PCE) above 24% retained over 90% of their initial efficiency (T_{90}) after aging under a reverse bias of -1.6 V for 1000 hours. Perovskite minimodule retained over 90% of its initial efficiency after shadowing test for 720 hours.

Degradation behavior under reverse bias

We first differentiate the reverse bias induced device breakdown and long-term degradation. The former refers to the instant burning of devices under a large reverse bias, which is manifested by an abrupt increase of dark current resembling the breakdown of diode. Such severe breakdown is generally permanent and reduces the efficiency of perovskite solar cells to nearly zero. In this study, we applied PSCs with a p-i-n structure of ITO / Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine (PTAA) / $FA_{0.9}Cs_{0.1}PbI_3$ / fullerene (C_{60})/ Bathocuproine (BCP) /Copper (Cu) to study the breakdown behavior, where FA is Formamidinium and Cs is cesium, as illustrated in **Fig. 1a**. PSCs with this structure and perovskite composition were demonstrated to be very stable under operation conditions with T_{90} lifetime over 3000 hours measured under 1 sun light at open circuit voltage (V_{OC}) condition and 60 °C[6]. We applied a constant reverse bias of −3.5 V on the PSCs without notable defects such as dust. The devices quickly lost their efficiency to almost zero within several minutes (**Fig. 1b** and **Supplementary Table 1**). The dark current density (J_D) of the PSCs measured at −1 V dramatically increased from $(1.39 \pm 1.16) \times 10^{-3}$ mA/cm^2 by 6 orders of magnitude to $(2.61 \pm 0.89) \times 10^{3}$ mA/cm^2 (**Fig. 1c**). As shown in **Fig. 1d**, some dark spots with size 10s-100s micrometers were observed on the Cu side after device breakdown, the perovskites at these regions turned to yellow seen from the ITO side, suggesting that large Joule heating occurred in these regions, leading to quick local perovskite decomposition.

Local breakdown indicates the formation of highly conductive filament channels. Here we hypothesize a process illustrated in **Fig. 1a** to explain the filament formation under large reverse bias in p-i-n structure solar cells with Cu electrode. Under reverse bias, I^- ions migrate from the perovskite through non-compact fullerene layer toward Cu side, while positive ions (e.g., Pb^{2+}, Cs^+, FA^+) migrate to ITO side. Injected holes from Cu electrode can oxidize I^- to neutral I^0, which was established in previous study[15,16]. The as-formed I^0 may either be further oxidized by holes to generate I^+ or react with Cu electrode to form I^- and Cu^+ ions instantly. Driven by the electric field from reverse bias, Cu^+ ions can quickly drift into the perovskites due to its small size and thus high diffusivity. At high conductive local areas where there is a large density of injected electrons, Cu^+ may be again reduced by electrons back to metallic Cu^0, which forms highly conductive filaments and thus causes local breakdown. The standard electrode potential for Cs^+, Pb^{2+} and Cu^+ are −3.026 V, −0.126 V, and 0.518 V, respectively[36], making Cu^+ easiest to reduce to Cu^0. The locations where breakdown occurs maybe the regions with initially high diffusivity pathways, which allows large charge injection, such as thinner perovskite locations, pinholes, scratch, or voids in perovskites. Therefore, extended defects should be minimized in device fabrication process for better reverse bias stability of PSCs.

We emphasize that the conversion of Cu^0 to Cu^+ is a critical step for the reverse bias induced breakdown because charge neutral Cu^0 does not drift under electric field. To verify the contribution of Cu drift during breakdown process, time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurement was conducted on fresh and breakdown devices to profile the Cu distribution. The observed Cu signal even after a sputtering depth of a few hundred nanometers (nm) as shown in **Fig. 1e** can be explained by the strong diffusion of Cu during sputtering process in ToF-SIMS measurement[37] or roughness of the sample (**Supplementary Fig. 2-3** and **Supplementary Note 1**). Nevertheless, we observed distinctly stronger Cu signal in perovskites close to ITO interface from the breakdown sample, indicating that Cu^+ ions have drifted into perovskite films during breakdown process. Moreover, strong Cu^0 signal was observed at the buried interface (near the ITO side) by the X-ray Photoelectron Spectroscopy (XPS) measurement (**Fig. 1f**), when we peeled off the perovskite films after aging the device at −3.5 V for 6 min to expose the embedded surface (**Supplementary Fig. 4**). This further proves that Cu^0 has penetrated the entire films to contact ITO and form conducting paths. X-Ray diffraction (XRD) measurement (**Fig. 1g**) also revealed that CuI (~25.5°) and PbI_2 (~12.7°) were generated after device breakdown, proving the oxidation of Cu^0 electrode by I^0 and the decomposition of perovskites by local Joule heating.

When the reverse bias was reduced, breakdown did not occur immediately, and the devices could survive for a much longer time. After aging at −2.5 V for ~24 h, some dark spots gradually appeared on the Cu side covering nearly 50% of the device area (**Fig. 2a**), and there was no apparent formation of dark CuI on the Cu side observed by naked eyes after aging at −1.6 V even for ~200 h, despite this bias is already larger than device V_{OC} (**Fig. 2b**). Nevertheless, the J_D of devices still increased by 4-5 orders of magnitude to $(3.13\pm2.06)\times10^2$ mA/cm^2 after aging at −2.5 V and $(6.73\pm3.82)\times10^1$ mA/cm^2 after aging at −1.6 V (**Fig. 2c**), leading to obvious efficiency drop of PSCs dominated by fill factor (FF) and V_{OC} reductions (**Fig. 2d** and **Supplementary Table 2**). It should be noted that such a performance decline is irreversible, because we have put these aged samples under 1-sun LED light (~12 h) for recovery before the J-V measurements. We already considered that the efficiency could be partially recovered after forward bias or light soaking (**Supplementary Fig. 5**), due to the reversible ion migration[29], therefore the observed efficiency reduction here is permanent. In these cases, PbI_2 was rarely observed in the XRD patterns (**Fig. 2e**), indicating that reduced reverse bias dramatically slow-down perovskite decomposition, most likely due to the much lower local leakage current density and thus lacks breakdown filament. To prove it, we performed XPS measurement on the buried interface of perovskite which has been aged under −2.5 V for 200 h. The perovskite films were peeled off ITO substrate to expose the bottom surfaces using the established method reported previously[38]. No apparent Cu signal was observed (**Supplementary Fig. 6**), indicating that Cu^0 filament has not yet formed. However, CuI still appeared in the XRD pattern after sufficient bias and aging time (i.e., −2.5 V for ~24 h, **Fig. 2f**), indicating that I_2 generation and reaction with Cu^0 occurred even under lower reverse bias which didn't induce instant breakdown. No apparent CuI phase was observed in −1.6 V aged sample (**Fig. 2f**), this could be attributed to the slower degradation process under such condition.

We noticed that CuI formation is orders of magnitude faster under reverse bias than under regular operation conductions. Our prior study showed that it took more than 300 hours even at 90 °C for Cu^0 to react with perovskite when Cu^0 was directly deposited on perovskites in the dark, and it takes over 20 years at 40°C based on the derived activation energy[39]. This is reasonable because I^- does not react with Cu^0, but I^0 or I_2 does. CuI forms in a few seconds when Cu^0 film was exposed to I_2 vapor at room temperature (**Fig. 2g** and **Supplementary Fig. 7**). Light may accelerate the reaction of Cu^0 with perovskites, because light helps the conversion of I^- to I^0 [40]. Nevertheless, iodine generation under light is still drastically slower than under reverse bias. For instance, when we deposited Cu^0 directly on perovskites, and then placed the devices under 1 sun illumination at 85 °C for 24 hours in N_2 atmosphere, we could still not observe the formation of CuI as shown by the XRD pattern in **Fig. 2g**. Therefore, the oxidization of I^- to I^0 is the critical rate limiting step that determines the Cu^+ formation, which is part of both breakdown and reverser bias degradation process of PSCs, pointing out that suppressing this step is crucial to stabilize PSCs under reverse bias.

Since electrons are injected under reverse bias from ITO side, one question arises is whether the reduction of cations occurs in perovskites close to ITO. To investigate this issue, we conducted XPS measurements on the buried interface of the perovskite films after the devices were aged under −2.5 V for 24 hours. We first investigated Pb^{2+}, because its electrode potential of −0.126 V is much less negative than that of Cs^+, making it more likely to be reduced if that would occur. As shown in **Fig. 2h**, no notable difference was observed for the Pb peak signal. Furthermore, no characteristic Pb^0 peak was observed. Increasing bias voltage (−3.5 V for 6 min, device has been breakdown) or bias time (−2.5 V for 200 h) still could not generate Pb^0 peak at the anode side (**Supplementary Fig. 8**), suggesting that reduction of Pb^{2+} unlikely occur under these conditions. Measuring metallic Cs is difficult by this method as it can be easily oxidized by oxygen or moisture when the surface is exposed to air. Nevertheless, the highly negative electrode potential (−3.026 V) indicates the difficulty to reduce Cs^+ in regular experimental or device operation conditions. Therefore, we examined whether FA^+ could be reduced instead.

The electrochemical reaction of FA^+ may change the stoichiometry of perovskite composition and thus bandgap of perovskites. To verify it, we conducted photoluminescence (PL) mapping measurements of the PSCs aged at −2.5 V for 24 hours with incident exciting light from ITO side. The darker regions in the aged sample exhibited lower PL intensity than fresh samples (**Fig. 2i**). These regions were identified to rich of CuI close to the Cu side (**Supplementary Fig. 9** and **Supplementary Note 2**), so their lower PL intensity may result from an increased defects density[41]. Nevertheless, the PL peak wavelength was unchanged even at the dark regions (**Fig. 2j**), indicating the absence of electrochemical reaction of FA^+ under reverse bias. Nuclear magnetic resonance (NMR) study (**Fig. 2k** and **Supplementary Fig. 10-11**) further confirmed the absence of FA^+ reduction, because there was no chemical shift nor new peak generation regarding hydrogen signals from the aged sample. When the PSCs aged at −1.6 V for 200 hours, there was still no apparent PL peak shift across the whole region of the perovskite buried interface (**Supplementary Fig. 12**). These data conclude that reduction reaction of Pb^{2+} or FA^+ did not occur before the devices lost most of their PCEs, and oxidization of I^- at cathode side is dramatically faster than the reduction of cations at anode size in perovskite solar cells under reverse bias. Other reactions, such as water splitting, which was observed in dye sensitized solar cells[42], may occur under sufficiently high reverse bias and duration. However, it should not dominate perovskite degradation under reverse bias due to limited amount of residual water (more discussion can be found in **Supplementary Note 3).**

Ions and charge barrier reinforcement

Based on the degradation mechanism, the effective approach to enhance the reverse bias stability of PSCs should consider two aspects: 1) suppressing the degradation of PSCs caused by the electrochemical reaction of I^- when devices show no breakdown. This needs effective hole injection barrier onto perovskite to avoid iodine generation; 2) preventing the formation of breakdown channels caused by the migration of Cu^+ ions into perovskite, and subsequent reduction into Cu^0 filaments. This needs robust Cu^+ blocking layers under the Cu electrode. Our control devices use C_{60} and BCP as the electron transport layers (ETLs) which can serve as a barrier to block ion migration and reduce hole injection from Cu electrode. However, this barrier may have pinholes or not compact enough to prevent I^- and Cu^+ migration through it. Here we introduced other ETL and ion blocking layers to enhance the breakdown voltage. The J-V curves showed that the breakdown voltage was −6.69±0.39 V for the control devices with C_{60}/BCP as ETLs (**Fig. 3a-b**). It should be noted that the current sweeping in J-V curve measurement only takes seconds, so a much larger reverse bias is needed to cause the breakdown during current sweeping than a constant reverse bias shown in **Fig. 1**. The breakdown voltage was increased to −10.69±1.03 V after replacing BCP with a much more compact layer of SnO_2 (10 nm) grown by automatic layer deposition (ALD)[2,7,43-50]. ALD-SnO_2 is much denser than very thin BCP (6 nm), which may not only reduce local hole injection but also blocks I^- and Cu^+ migration through it. Since the breakdown process involves Cu electrochemical reactions ($Cu^0 \rightarrow Cu^+ \rightarrow Cu^0$), using ITO layer to replace Cu^0 or insert ITO layer between Cu^0 and ALD-SnO_2 should avoid the Cu related electrochemical reactions. As shown in **Fig. 3a-b**, inserting a sputtered ITO layer between ALD-SnO_2 and Cu^0 further increased the breakdown voltage to −14.66±0.57 V. No breakdown was observed at −20 V upon the removal of Cu^0 from the devices. This again confirms that the migration of Cu^+ ions into the perovskite plays a crucial role in reverse bias induced breakdown.

While minimizing breakdown is enabled by avoiding Cu^+ electrochemical reactions and migrations, the creation of I^0 and I^+ via hole injection and induced perovskite damage can still lead to irreversible perovskite degradation under reverse bias. To further reduce hole injection, additional charge blocking layer is needed. This layer should have large bandgap materials to block holes and needs to be ultrathin (1-2 nm) to enable electron extraction during operation. Metal fluorides are considered here, not only because they have large bandgap and can be thermally evaporated to obtain uniform coverage on perovskite in a thin layer, superior to solution method, but also it has been demonstrated to be chemically stable and useful in reducing non-radiative recombination between perovskite and ETL[51,52]. Dielectric material LiF was chosen in this work, the relatively larger bandgap (~13.6 eV) and higher dielectric constant (~9) made it to be a promising hole blocking layer under reverse bias (**Supplementary Table 3**). LiF has been broadly used in PSCs, perovskite/Si tandems, and light emitting diodes (LEDs) to improve the devices performance[53-55]. Previous studies have pointed out its work function tuning capability[51,56] and passivation ability[57,58]. Taking advantage of good passivation effect of LiF, we further investigated its ability to reduce shunting for PSCs under reverse bias. As shown in **Fig. 3b-c**, even though the breakdown voltage was not further increased after LiF insertion, the J_D at −1 V decreased to (1.60±0.02) $\times 10^{-4}$ mA/cm^2 in LiF-contained devices compared to (6.15±1.80) $\times 10^{-4}$ mA/cm^2 in control devices (**Supplementary Table 4**). Since the oxidization of iodide is the first step of the chain reaction, hole injection blocking layer LiF plays the critical role in reducing hole injection and thus stabilize perovskites under reverse bias.

We monitored the evolution of J_D and PCE for devices under continuous reverse bias of −1.6 V in the dark, because dark current reflects shunts in devices. **Fig. 3d-e** showed that the control devices exhibited a huge increase of J_D from (6.15±1.80) $\times 10^{-4}$ mA/cm^2 by nearly five orders of magnitude to (7.22±4.01) ×10 mA/cm^2 after 200 hours of aging (**Supplementary Table 4**), accompanied with a PCE decrease from (22.9±0.2) % to (5.5±2.3) %. The PCE reduction was dominated by the V_{OC} decrease from 1.14±0.01 V to 0.52±0.14 V and FF decrease from (79.6±0.5) % to (43.0±12.9) % (**Supplementary Table 5**). The increase of J_D and decrease of V_{OC} and FF can be attributed to the enhanced shunting pathways (**Supplementary Table 6**), which may originate from the perovskite degradation caused by I^- migration and oxidation, as well as the migration of Cu^+ and associated reduction. Replacing BCP with SnO_2 delayed the formation of shunting pathways: After 200-hour aging, J_D of the devices only slightly increased to (3.51±1.79) $\times 10^{-2}$ mA/cm^2, which is four orders of magnitude smaller than the devices without ALD-SnO_2. The corresponding PCE slightly decreased from (23.3±0.3) % to (20.5±0.5) % (**Supplementary Fig. 13** and **Supplementary Table 5**). When ITO was inserted between SnO_2 and Cu^0, the device J_D after 200-hour aging was (1.83±0.97) $\times 10^{-2}$ mA/cm^2, and the device efficiency remained to be (22.5±0.1) % (**Supplementary Table 4-5**). Lastly, applying LiF onto perovskites maintained the device J_D at (3.44±2.81) $\times 10^{-3}$ mA/cm^2 after 200-hour aging, and the PCE only slightly reduced to (22.9±0.2) %, or 98% of the initial efficiency (**Supplementary Table 4-5**). A clear correlation was observed between the J_D suppression and the PCE degradation among these devices (**Fig. 3f**), indicating that less shunting pathways generation under reverse bias is critical to improve the reverse bias stability of PSCs. Note that the reverse bias stability of our devices is better than previous reported devices with similar device stacking[28,29]. This may be caused by the optimized crystallinity and grain size of perovskites in this study which dramatically suppress ion migration[6].

In addition, the application of pure iodide perovskite avoids the electric field induced phase separation which was observed in mixed halide perovskites[25,29,31]. However, even with the improved perovskite quality, the barrier layer (C_{60}/BCP) in control devices still could not effectively inhibit ions migration and electrochemical reactions at the interface. This indicates that the combination of LiF, SnO_2 and ITO can block hole injection and inhibit the migration of I^-/I^0 and Cu^+, eventually stabilizing the devices under reverse bias, as shown in **Fig. 3g**.

Photovoltaic performance of PSCs

The photovoltaic performance of PSCs was tracked based on different device architectures. Both devices had an averaged PCE over 23%, as shown in **Fig. 4a, Supplementary Fig. 14** and **Supplementary Table 7**, and there was no apparent J-V curves difference among PSCs with different structures (**Fig. 4b**). This indicates that the replacement of BCP with SnO_2 and the insertion of an additional layer of LiF and ITO have no adverse effects on devices when operating under light. The target device, which combined LiF on perovskite, SnO_2 and ITO on fullerene at ETL side, achieved a highest PCE of 24.5%, which is slightly higher than the best-performing control device (24.0%).

We then assessed the stability of these devices by subjecting them to continuous −1.6 V bias aging (details in Methods), where the applied reverse bias is larger than that of ISOS-V-1 protocols[59] ($-V_{OC}$ at ~23 °C, **Supplementary Table 8**) for accelerated test. The control devices had the poorest reverse bias stability which only retained 24.0% of their initial PCE after 200 hours of aging (**Fig. 4c**). All PV parameters in control devices, including J_{SC}, V_{OC} and FF, decreased during the aging process (**Supplementary Table 5**). Substituting BCP with SnO_2 enabled the devices to retain 77% of their initial PCE after 400 hours of aging. Moreover, the reverse bias stability of the devices could be improved further by introducing ITO between SnO_2 and Cu^0, which allowed them to maintain 81% of their initial PCE after 600 hours. Finally, the target devices with an additional LiF layer maintained 84% of their initial PCE after 1000 hours of aging. The best target device kept 91.8% of its initial PCE (24.1%) after 1000 hours aging at −1.6 V bias (**Fig. 4e, Supplementary Fig. 15** and **Supplementary Table 9**).

To understand whether the new device structure change device stability under other stressors, we also evaluated the PSCs under continuous 1-sun illumination at open-circuit condition following the testing procedures of the ISOS-L-1 protocols. Both control and target devices demonstrated good operational stability, keeping 98% of their initial PCE after 2060 hours light soaking (see **Fig. 4d, Supplementary Fig. 16** and **Supplementary Table 10**). Moreover, these devices retained over 90% of their initial PCE after undergoing the 85 °C/85% RH tests for 1172 hours (following the testing procedures of the ISOS-D-3 protocols, **Supplementary Fig. 17-18** and **Supplementary Table 11**). Thus, the utilization of LiF, SnO_2, and ITO can extend the reverse bias lifetime of devices without compromising stability under other stressors.

Shadow stability of perovskite solar minimodules

We continued to evaluate the shadowing stability of perovskite minimodules by applying the device design into perovskite minimodules. The minimodules in this study contain 9 subcells connected in series so that the bias on the shaded subcell reaches 8 times of V_{OC}. Applying the new interface layer/electrode did not dramatically change current-voltage (I-V) curves of the minimodules (**Fig. 5a**). The average PCE of the target minimodules with LiF, SnO_2 and ITO layers was (19.7±0.2) %, slightly higher than that of the control minimodules ((19.5±0.3) %, see **Fig. 5b, Supplementary Fig. 19** and **Supplementary Table 12**). Since the efficiency of solar modules is highly sensitive to the homogeneity of the films and interfacial layers, the increased module efficiency indicates that the LiF, SnO_2, and ITO layers are more uniformly deposited on the perovskites over the module area. In addition, both control and target minimodules exhibited good operational stability under 1-sun illumination at open-circuit, which all retained over 95% of their initial PCE after 800 h of aging (**Supplementary Fig. 20** and **Supplementary Table 13**).

We covered one subcell with black tape (**Fig. 5c** and **Supplementary Fig. 21**) and put the minimodules under 1-sun illumination to monitor their current output during operation. As shown in **Supplementary Fig. 22** and in **Fig. 5e**, the output current after 10 min tracking in control devices exceeded 20 mA, which was smaller than the photocurrent of each subcell of ~70 mA (**Supplementary Fig. 23**), regardless which subcell was covered. In contrast, the target devices exhibited less than 1 mA current output under the same testing conditions. In principle, when one subcell is covered, this subcell cannot generate photocurrent and is under reverse bias generated by other working subcells (shown in **Fig. 5d**). Therefore, the large current output observed in control device suggests the severe current leakage of shaded subcell, most likely due to the partial breakdown. The much smaller current leakage upon barrier reinforcement in target device indicates its shaded regions are more robust under reverse bias provided by other working subcells.

When we shaded one subcell in minimodules under continuous 1-sun illumination, the PCE of the control minimodule notably declined, with ~80% of its initial PCE retained after testing for 144 hours (**Fig. 5f, Supplementary Fig. 24** and **Supplementary Table 14**). PL imaging (**Supplementary Fig. 25**) showed that the PL intensity of the shaded subcell was lower than that of the other illuminated but unshaded subcells, which indicates quicker degradation under reverse bias than under illumination. The degradation of the shaded subcell dominated decreased efficiency of the minimodule [60]. In contrast, target minimodule maintained ~93% of its initial PCE after testing for 720 hours (**Fig. 5f, Supplementary Fig. 24** and **Supplementary Table 14**). Therefore, the new interface and electrode design has been successfully applied to solar minimodules to enhance their shadow stability.

Conclusions

In summary, the high electrochemical reactivity of iodide and redox reactivity between iodine and metal electrode dominated permanent degradation of PSCs under reverse bias, while high diffusivity and electrochemical reactivity of Cu^+ ions stimulated devices breakdown. Extended device fabrication defects within perovskite may accelerate the shunting process due to the large charge injection. Nevertheless, nanoscopic defects, such as grain boundaries and amorphous regions, always exist in polycrystalline films. To further improve the reverse bias stability, a combination of LiF, ALD-SnO_2 and ITO was shown here to be both robust ion migration barrier and good hole injection barrier to reduce the device dark current. ALD-SnO_2 and ITO have been shown to be great combination as transparent ETL and electrode in bifacial devices and perovskite-silicon tandem solar cells. The dense packing of metal oxides, particularly the SnO_2 grown by ALD process, effectively blocks ion migration and then stabilize them for devices under damp heat, light and heat testing. This study highlights the importance of SnO_2 in stabilizing perovskite devices under reverse bias, adding its another function in enhancing stability of perovskite solar cells. The substitution of opaque metal electrodes by ITO further enhanced their resistance to breakdown. LiF, which was also explored in perovskite-silicon tandem cells and single junction devices, was found to reduce hole injection under reverse bias. Overall, the combining these three layers improved the reverse bias stability of PSCs without compromising their efficiency or stability under other stressors. Although it is possible to find other barrier materials, the compatibility of these materials in both single junction and tandem perovskite solar cells allow a straightforward transition to manufacturing.

Methods

Materials

All solvents used in this work were purchased from Sigma-Aldrich with purity of 99.9%, including 2-methoxyethanol (2-ME), dimethyl sulfoxide (DMSO), and toluene (TL). PbI_2 (99.999%) was purchased from Advanced Election Technology Co., Ltd. Formamidinium iodide (FAI), formamidinium chloride (FACl), guanidinium iodide (GAI), phenylammonium tetrafluoroborate ($PEABF_4$) were purchased from GreatCell Solar. PTAA (average Mn 7,000-10,000), CsI (99.999%), $ZnCl_2$ (99.999%), carbohydrazide (CBH, 98%), bathocuproine (BCP, 96%), LiF were purchased from Sigma-Aldrich. C_{60} was purchased from Nano-C Inc. FAH_2PO_2 was synthesized in our lab according to our previous publications[61].

Devices fabrication

$FA_{0.9}Cs_{0.1}PbI_3$ solution (with a concentration of 1.1 M) was pre-prepared by directly mixing $FAPbI_3$ (dissolved in 2-ME), $CsPbI_3$ (dissolved in DMSO) and other additives (dissolved in 2-ME) and diluting with 2-ME solvent prior to blade coating. Additives include: 0.23% FAH_2PO_2, 2.5% FACl, 0.07% $PEABF_4$, 2% $GAPbI_3$, 0.2% CsI, 0.5% $ZnCl_2$ and 0.2% CBH, which were used to improve the film quality and optoelectronic properties as mentioned in our previous publications[6].

Glass/ITO substrates (15 Ω sq^{-1}) were pre-cleaned by acetone in an ultrasonic machine. Then the substrates were treated by UV-ozone for 15 min before using. The PTAA and perovskite layer were fabricated by blade-coating (at a speed of 20 mm s^{-1}) at room temperature (19-21 °C) inside a fume hood. PTAA solution with a concentration of 2.2 mg mL^{-1} (in TL, with additional 2% w.t. BCP) was firstly blade-coated onto ITO substrates with a coating gap of 150 μm. Subsequently, the $FA_{0.9}Cs_{0.1}PbI_3$ solution was blade-coated onto the PTAA-covered ITO substrates with a coating gap of 300 μm. The wet perovskite films were then transferred onto hot plate and annealed at 150 °C for 4 min in air (~20% RH). The Ref solar cells were completed by thermally evaporating C_{60} (45 nm, 0.15 Å s^{-1}), BCP (6 nm, 0.1 Å s^{-1}), and copper (150 nm, 1 Å s^{-1}). For Tar devices, LiF

(1.5 nm, 0.05 Å s^{-1}) was thermally evaporated onto perovskite, SnO_2 (~10 nm) was deposited onto C_{60} by automatic layer deposition (ALD), ITO (120 nm) was sputtering coated onto SnO_2. Other processes were same with Ref devices. Finally, 100 nm MgF_2 layer was evaporated onto the glass side of ITO substrates as an anti-reflection layer. The active area of solar cells is 0.08 cm^2 (0.4 cm × 0.2 cm determined by a metal shadow mask).

The minimodules were fabricated on pre-patterned large ITO glass substrates with P1 width of 30 μm followed by the same procedure as the small solar cells. The laser scribing was performed twice with a Keyence laser marker (MD-U1000C, 355 nm). The width of each subcell is 6 mm, while the final P2 and P3 widths were measured to be ~110 and ~75 μm, respectively. The total width of the dead area was measured to be ~320 μm, giving a GFF of 94.7%. A polydimethylsiloxane (PDMS) layer was attached to the front side of the perovskite solar cells as an anti-reflection coating. The aperture area of minimodules (with 9 sub-cells) is 29.7 cm^2.

The small-area PSCs used for ISOS-L-1 and ISOS-V-1 stability tests and minimodules used for shadow tests were encapsulated with cover glass and epoxy resin (Devcon epoxy Tube 14250) on the Cu side. The small-area PSCs used for ISOS-D-3 stability tests were encapsulated by polyisobutylene (PIB, HelioSeal PVS 101) blanket. Minimodules used for high temperature (85 °C) shadow tests were encapsulated by polyolefin elastomer (POE) and PIB edge-sealing.

Devices characterization

J-V measurements: The J-V curves of small-area PSCs and mini-modules were performed using a Xenon-lamp based solar simulator (Oriel Sol3A, Class AAA Solar Simulator) and the light intensity was calibrated to 1-sun light (100 mW cm^{-2}) by a silicon reference cell (Newport 91150V-KG5). All devices were measured using a Keithley 2400 source meter with a scan rate of 0.1 V s^{-1} in air at room temperature (reverse scan, from 1.2 V to −0.1 V). There was no preconditioning before measurement. No temperature controlling was used for J-V curve measurement. Devices area were determined by the shadow mask.

Stability measurements: The light source used for stability monitor was the LED flood light (SOLLA, 200 W, 6000K daylight white). The spectrum of LED light source was shown in **Supplementary Fig. 1**, and the light intensity was calibrated to 1-sun (100 mW cm^{-2}) by a silicon reference cell (Newport 91150V-KG5).

For light operation stability (following the testing procedures of the ISOS-L-1 protocols[59]), the devices were put under the LED light at the open-circuit (OC) state without any cooling system. The humidity was around 45-55% RH, and the measured temperature was around 55-65 °C. After light soaking for different durations, the devices were taken to solar simulator for J-V measurement.

For 85 °C/85% RH stability (following the testing procedures of the ISOS-D-3 protocols), the devices were put into environment chamber with the temperature of 85 °C, humidity of 85% RH under dark. After aging for different durations, the devices were taken to solar simulator for J-V measurement.

For reverse bias stability (following the testing procedures of the ISOS-V-1 protocols) of small area PSCs, the devices were loaded with different reverse bias through the DC-power supply (LongWei Ltd.) under dark. The humidity was around 45-55% RH, and the temperature was around 25-35 °C. After biasing for different durations, the devices were taken to LED light for 12 h light stabilization, then measured J-V under solar simulator.

For shadow stability of minimodules, one sub-cell of the module was fully shaded with black tape, then the module was put under LED light at 8 V (the voltage at maximum power point (MPP) of device) without any cooling. The humidity was around 45-55% RH, and the measured temperature was around 55-65 °C. After light soaking for different durations, black tape was removed, and the devices were taken to solar simulator for J-V measurement.

Other measurements: XRD were carried out with a Rigaku SmartLab diffractometer using Cu Kα radiation (λ = 1.5418 Å), and the height of samples was calibrated before each measurement. XPS data was collected on a Kratos Supra+ system with a monochromatic Ka x-ray source operated at 150 W. A charge neutralizer was used, and all spectra were corrected to the C 1s peak at 284.6 eV. Surveying and high-resolution scans were acquired at pass energies of 80 eV and 20 eV, respectively, and the analyzed spot size was 300 × 700 um. PL mapping was conducted with PicoQuant MicroTime 100 and FluoTime 100 system at room temperature. PicoQuant PDL 828 “Sepia II” multichannel diode laser was used as the laser source and 405 nm pulsed laser was used for the measurements. ^{1}H-NMR spectra were acquired with a Bruker AVANCE III 600 MHz NMR Spectrometer. For the samples used for ^{1}H-NMR measurement, $FA_{0.9}Cs_{0.1}PbI_3$ solution was directly blade-coated onto ITO substrate (7.5×8 cm^2) to form the perovskite film, then C_{60} (45 nm, 0.15 Å s^{-1}) and copper (150 nm, 1 Å s^{-1}) were thermally evaporated on perovskite to finish devices fabrication (The goal of PTAA and BCP removal is avoiding the hydrogen influence from them). The powder was collected by scratching the perovskite from ITO substrates. These scraped powders were then transferred into NMR tubes filled with deuterium oxide (D_2O) to dissolve before test. TOF-SIMS measurements were conducted utilizing a 3-lens 30 keV BiMn primary ion gun[62]. High mass resolution depth profiles were completed with a 30 KeV Bi^{3+} primary ion beam (0.8 pA pulsed beam current), a 50×50 µm area was analyzed with a 128:128 primary beam raster. Sputter depth profiling was accomplished with 1 kV Cesium ion beam (6 nA sputter current) with a raster of 150×150 microns.

Data availability

All data generated or analyzed during this study are included in the published article and its supplementary information. Source data are provided with this paper.

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Author contributions statement

N.L. and J.H. conceived the idea. N.L. fabricated and characterized perovskite films and devices. Z.S. performed the PL mapping and NMR measurements. C.F. and H.G. optimized the devices fabrication and laser scribing process. H.J. carried out device encapsulation and performed PL mapping measurements. M.L. conducted XRD measurements. S.P.H, Y.D. and M.C.B. conducted TOF-SIMS measurements. N.L. and J.H. wrote the manuscript, and all authors commented on the manuscript.

Competing interests statement

The authors declare the following competing interests: Tandem PV has a license for the following technologies used or evaluated in this paper: an ink formulation for fast coating of perovskites and BHC for reducing iodine. J.H. is an inventor of the technologies and has or could receive royalties. These relationships have been disclosed to and are under management by UNC-Chapel Hill.

Figure captions

Fig. 1 Breakdown of PSCs under reverse bias. **a**, Iodide migration and oxidation (step 1), redox reactions (step 2), the formation of conducting pathways (step 3 and 4) which occurs under reverse bias in PSCs. **b**, The J-V curves of PSCs before and after −3.5 V bias aging (tested under 1-sun illumination). **c**, The dark current of PSCs (measured at −1 V) before and after biasing at −3.5 V for 6 minutes. Eight devices were tested for each condition. The inset shows the equivalent circuit of the device after aging. **d**, Photograph of fresh PSC (left) and PSC aged under −3.5 V for 6 min (right) from Cu side (up) and ITO side (bottom), respectively. Scale bar: 1 mm. **e**, TOF-SIMS measurement results of fresh and that aged −3.5 V (for 6 min) PSCs, respectively. **f**, XPS spectrum of Cu^0 for the sample aged at −3.5 V for 6 min. **g**, XRD patterns of fresh PSCs and PSCs aged under −3.5 V for 6 min, respectively.

Fig. 2 Long-term degradation of PSCs under reverse bias. **a**,**b**, Photograph (left) and optical micrograph (right) of reverse biased PSCs under (**a**) −2.5 V for 24 h and (**b**) −1.6 V for 200 h. Scale bar: 1 mm (left) and 300 μm (right). **c**, The dark current of PSCs measured at −1 V after biasing at various biases and durations (8 devices for each condition). The inset shows the equivalent circuit of the device after aging. **d**, The J-V curves tested under 1-sun illumination of fresh PSCs and PSCs aging after −2.5 V for 24 h and −1.6 V for 200 h. **e**,**f**, XRD patterns of fresh and reverse bias aged PSCs in the range of (**e**) 12-16°, corresponding to PbI_2 and perovskite signal and (**f**) 25-26°, corresponding to CuI signal. **g**, XRD patterns of fresh Cu^0, Cu^0 after reacting with I_2, and Cu^0 after reacting with perovskite, respectively (Inset: the corresponding photographs, scale bar: 1 mm). **h**, XPS spectra of Pb for fresh and −2.5 V aged (for 24 h) perovskites, respectively. **i**, PL mapping of fresh (left) and −2.5 V aged (for 24 h, right) perovskites, respectively. **j**, PL spectra of different regions shown in Fig. 1I. Inset: Normalized PL. **k**, ^{1}H-NMR measurements of fresh and −2.5 V aged (for 24 h) perovskites.

Fig. 3 The pathways to reinforce ions migration and charge injection barrier. a, J-V curves (from 1.2 V to −20 V) of PSCs with different device architectures (5 devices for each group). The arrow represents breakdown voltage evaluation with different device architectures. **b**, Thermal breakdown voltage of different PSCs (The 25–75% box line with 1.5× interquartile rage whiskers, median line and mean point are calculated for 5 devices under each condition). **c**, The dark current of different PSCs (measured at −1 V, the 25–75% box line with 1.5× interquartile rage whiskers, median line and mean point are calculated for 5 devices under each condition). **d**, The dark current evolution of different PSCs (measured at −1 V) when aging under −1.6 V (5 devices for each group). Error bars represent the standard deviation among devices. **e**, The PCE evolution of different PSCs when aging under −1.6 V (5 devices for each group). Error bars represent the standard deviation among devices. **f**, The correlation between dark current increase ratio (defined as the devices dark current after −1.6 V aging for 200 h divided by the dark current before aging) and PCE decrease ratio (defined as the devices PCE after −1.6 V aging for 200 h divided by the PCE before aging). **g**, The scheme of barrier reinforcement through modified devices architecture.

Fig. 4 The photovoltaic performance of small-area PSCs (0.08 cm^2). a, Statistic PCE of PSCs with different device architectures (The 25–75% box line with 1.5× interquartile rage whiskers, median line and mean point are calculated for 20 devices under each condition). **b**, J-V curves (from 1.2 V to 0 V) of PSCs with different device architectures. **c**, Photovoltaic parameters evolution of encapsulated PSCs with different device architectures (5 devices for each group) under −1.6 V aging in the dark (30±5 °C, 50±5 % RH). Error bars represent the standard deviation among devices. **d**, Photovoltaic parameters evolution of encapsulated control and target PSCs (5 devices for each group) under 1-sun LED light and open-circuit in air (60±5 °C, 50±5 % RH). Error bars represent the standard deviation among devices. **e**, PCE evolution of best-performing target PSC under −1.6 V aging in the dark (30±5 °C, 50±5 % RH).

Fig. 5 The photovoltaic performance of large area minimodules (aperture area of 29.7 cm^2). a, I-V curves of control and target minimodules. **b**, Statistic PCE of control and target minimodules (The 25–75% box line with 1.5× interquartile rage whiskers, median line and mean point are calculated for 6 devices under each condition). **c**,**d**, The scheme of a module when 1 subcell is shaded (**c**) and equivalent circuit diagram (**d**). **e**, The current output at 8 V of control and target minimodules under 1-sun illumination for 10 min when different subcells are shaded with black tape. **f**, PCE evolution of encapsulated control and target minimodules when aged under 1-sun LED light at fixed bias of 8 V, where 1 subcell was shaded with black tape (60±5 °C, 50±5 % RH).

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