

Perovskite Solar Cells Hot Paper

 How to cite:
 Angew. Chem. Int. Ed. 2021, 60, 8303-8312

 International Edition:
 doi.org/10.1002/anie.202017148

 German Edition:
 doi.org/10.1002/ange.202017148

Dually-Passivated Perovskite Solar Cells with Reduced Voltage Loss and Increased Super Oxide Resistance

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Abstract: In recent years, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has witnessed rapid progress. Nevertheless, the pervasive defects prone to nonradiative recombination and decomposition exist at the surface and the grain boundaries (GBs) of the polycrystalline perovskite films. Herein, we report a comprehensive dualpassivation (DP) strategy to effectively passivate the defects at both surface and GBs to enhance device performance and stability further. Firstly, a fluorinated perylene-tetracarboxylic diimide derivative is permeated in the perovskite metaphase during antisolvent treatment, and then a fluorinated bulky aromatic ammonium salt is introduced over the annealed perovskite. The reduction of defect density can be unambiguously proved by the superoxide species generation/quenching reaction. As a result, optimized planar PSCs demonstrate a decreased open-circuit voltages deficit from 0.47 to 0.39 V and the best efficiency of 23.80% from photocurrent scanning with a stabilized maximum power output efficiency of 22.99%. Without encapsulation, one typical device can maintain over 85% of the initial efficiency after heating on a hot plate at 100°C for 30 h under relative humidity (RH) of 70%. When the device is aged under 30 ± 5 % RH, over 97 % of its initial PCE is retained after 1700 h.

Introduction

Within a short time, the certified power conversion efficiency (PCE) of laboratory-made hybrid lead halide perovskite solar cells (PSCs) has reached 25.5%,^[1] on par with that of polycrystalline silicon and copper indium gallium selenide (CIGS) solar cells. However, the poor stability of PSCs under operating conditions remains an obstacle toward industrial-level fabrication and the consumer market.^[2-5] Generally, commercial solar cells must be able to operate continuously for nearly 25 years in an outdoor environment before they can truly occupy a market advantage.

It is known that the degradation of perovskite is normally initialized from the defect sites existing at either surface or grain boundaries (GBs) due to the high reactivity toward moisture and oxygen.^[6-8] Firstly, the surface is the place where defects are most easily formed. Then, the existence of GBs makes the infiltration of moisture and oxygen in the ambient environment into perovskite films easier and thus accelerate the destruction of perovskite.^[9] Perovskite films fabricated via traditional solution process are prone to produce defects at the surfaces and GBs, which serve as non-radiative recombination centers leading to an overall reduction of efficiencies and poor stability of the device.^[10] The chemical passivation of those defects can be rationalized into two main strategies: i. mixing additive substances in the precursor solutions^[11,12] or antisolvents^[13-16] to control perovskite growth and/or passivate defects in perovskite GBs; ii. surface modification via coating functional molecules on the preformed perovskite layer. Various organic molecules^[17-20] and polymers^[21-24] have been applied to chemically passivate the defects on the perovskite surface in PSCs.^[25-27] Albeit the success of the two methods, an optimal combination of them is needed to achieve maximized passivation effects for further improving efficiency and long-term stability.

Previous studies have demonstrated that exposure of MAPbI₃ (MA⁺ = CH₃NH₃⁺) with site vacancies to light and oxygen can lead to the formation of superoxide (O₂⁻) species, which will trigger the cascade photodegradation reaction of the perovskites.^[28-30] For example, the active O₂⁻ species can deprotonate the MA⁺ of photo-excited MAPbI₃*, leading to the formation of PbI₂, H₂O, CH₃NH₂, and I₂. Although early work has demonstrated the importance of faster electron extraction in reducing the yield of O₂⁻ generation, it is doubtful that this problem can be completely solved by charge extraction alone.^[28] Meanwhile, density functional theory (DFT) calculations revealed that iodide vacancies are the preferred sites in mediating the photo-induced formation of

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 $O_2^{\,-}$ species from oxygen.^{[29]} To date, efforts have been devoted to reducing the generation of $O_2^{\,-}$ via passivating the defects on perovskite surface and $GBs^{[30-32]}$ for a more stable perovskite structure.^{[33,34]}

In this context, we introduce a comprehensive dualpassivation (DP) strategy to realize the passivation of defects both inside the GBs and over the surface. Firstly, a solution of conjugated N, N'-bis-(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro dodecan-5-yl)-perylene-3,4,9,10-tetracarboxylic diimide (FPD) in chlorobenzene (CB) is used as the antisolvent (anti-solution), to implant the FPD inside the film during the nucleation of perovskites. This protocol ensures that the defects (e.g., noncoordinating Pb²⁺) at GBs be passivated by the carbonyl groups (C=O), and the fluorine atoms can form hydrogen bonds with MA⁺ to immobilize the cations, thus ensuring thermal stability.^[13–15,35] Secondly, a hydrophobic 2D perovskite layer is formed in situ on the 3D perovskite layer by successively depositing 2-(2-Fluorophenyl)ethylamine iodide after the antisolvent-treatment to passivate the defects on the surface. As a result, the novel DP strategy prolongs carrier lifetime through defect passivation and, hence, lifts the $V_{\rm OC}$ from 1.10 V to 1.18 V, corresponding to a $V_{\rm OC}$ deficit of 0.39 V. In the complete devices, we achieved a champion stabilized PCE as high as 23.80%. It is found that besides the excellent thermal and moisture resistant proper $ties^{[9,14,18,33,36,37]}$ provided by the DP strategy, the effective passivation of site-vacancy-type defects (e.g., iodine vacancy) successfully suppressed the generation of O_2^- species. Especially, this is the first time to observe the decrease of destructive O_2^{-} species by forming a 2D perovskite layer. Therefore, the DP strategy-based PSCs also showed remarkable long-term stability, retaining over 85% of the initial efficiency after heating on a hot plate at 100 °C for 30 h under relative humidity (RH) of 70% and over 97% of the initial PCE after 71 days under a 30% RH environment conditions without encapsulation.

Results and Discussion

The cross-sectional scanning electron microscopy (SEM) image of one typical device is shown in Figure 1a, representdevice а structure of glass/FTO/SnO₂/ ing perovskite/Spiro-OMeTAD/ $FA_{0.92}MA_{0.08}Pb(I_{0.92}Br_{0.08})_3/2D$ Ag. The judiciously designed device is featured by embedding the FPD (Figure 1b) in the 3D perovskite during antisolvent treatment and capping an in situ formed 2D perovskite layer on top with 2-(2-Fluorophenyl)ethylamine iodide^[37] (ortho-FPEAI, hereinafter referred to as oFPEAI) as the bulky cation. (Figure 1c) These measures are adopted to not only passivate the defects at the GBs and on the surface but also form multiple hydrophobic structures for superior performance and stability of the devices (Figure 1 d).^[14,36]

The concentration $(mgmL^{-1})$ of FPD in the CB was optimized by scrutinizing its effect on the surface morphology and crystallinity of the perovskite films. No additional peaks and distinct shifts were observed from the X-ray diffraction (XRD) patterns of the perovskite films treated by antisolution of FPD as compared to the pristine perovskite film, indicating that the FPD molecules do not change the cubic perovskite structure and only exist at GBs and/or on the surface of perovskite film (Figure S1a).^[38,39] However, the stronger diffraction intensity and lower full-width at halfmaximum (FWHM) of the diffraction peak at 14.1° from the



Figure 1. a) Cross-sectional SEM image of the device with FPD/oFPEAI passivation. b) Molecular structures of FPD and oFPEAI. c) The device architecture adopted in this study. d) Schematic illustration of possible passivation and enhanced stability mechanism for FPD/oFPEAI-passivated devices. e) UV-vis absorption and f) steady-state PL spectra of the pristine perovskite and FPD incorporated perovskite with different concentrations.

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films with FPD suggest the higher crystallinity or larger grain size (Figure S1b). From the top-view SEM images, when FPD is incorporated into the perovskite films, the average grain size (1.46 μ m) of the perovskite film treated by CB containing 0.04 mgmL⁻¹ FPD is much larger than that of the pristine perovskite film (1.19 μ m), in agreement with the XRD patterns. (Figure S2,3)

To further study the light absorption and assess the passivation effect of FPD, UV-vis absorption spectroscopy, and steady-state photoluminescence (PL) were conducted. As shown in Figure 1e, the UV-vis absorption spectra show a slight absorption enhancement over the region from 450 to 760 nm, which can be ascribed to the better crystallization and higher film quality. It should be noted that there is no noteworthy difference in absorption band edge, suggesting a negligible impact of FPD molecules on the bulk crystal structure of pristine perovskite. An excitation wavelength of 470 nm from the Xe lamp was used for the steady-state PL measurement to probe the surface properties. As shown in Figure 1 f, the PL intensities of the FPD containing perovskites with varied FPD concentrations of 0.02, 0.04, and 0.06 mg mL⁻¹ in the anti-solvent are significantly enhanced, indicating much suppressed non-radiative recombination centers due to the effective passivation by FPD molecules at the GBs. In addition, the blue shift of 2 nm, 11 nm, and 4 nm, respectively, for 0.02, 0.04, and 0.06 mg mL⁻¹ of FPD in CB further verified the effect of defect passivation.^[40]

To confirm the positive effect of FPD on device performance, the PSCs were fabricated by dripping CB antisolvent without/with the FPD molecule on the 3D perovskite layer. After optimization steps, a concentration of 0.04 mg mL⁻¹ for FPD in CB was set to achieve high-efficiency devices. The best-performing PSC exhibited a high PCE of 21.68 % under reverse scan, with a $V_{\rm OC}$ of 1.11 V, a $J_{\rm SC}$ of 23.75 mA cm⁻², and an FF of 82.0%. The control device without FPD additive had a PCE of 20.72%, with a $V_{\rm OC}$ of 1.09 V, a $J_{\rm SC}$ of 23.18 mA cm⁻², and an FF of 82.0% (as shown in Figure S4 and Table S1).

The encouraging results above could be attributed to the benign effect of FPD in improving the film quality and effective passivation of the bulk defects in the perovskite film. Despite the improvement in PCEs, the devices incorporating FPD still suffer from a high $V_{\rm OC}$ deficit of 0.46 V. This voltage loss is strongly related to the recombination at defects on the surface of the perovskite films. In this context, we expect to further reduce surface defects on the 3D perovskite when using the FPD additive as the inside passivator. According to our previous report,^[37] the introduction of oFPEAI isopropanol (IPA) solution onto the surface of the 3D perovskite could in situ form a 2D perovskite passivating layer. Figure 2 a shows XRD patterns for the 3D perovskite (C), the 3D perovskite incorporating FPD (C-FPD), the 3D perovskite only treated with the oFPEAI (C/oFPEAI), and the 3D perovskite incorporating FPD before treating with the oFPEAI (C-FPD/oFPEAI). Compared to sample C, the C/ oFPEAI and C-FPD/oFPEAI samples show additional peaks at 5.4° and 10.7° (marked with #), which correspond to the diffractions of the 2D perovskite (oFPEA)₂PbI₄. The weak



Figure 2. a) XRD of pristine perovskite with different compositions, # corresponds to the $(oFPEA)_2PbI_4$ diffraction peak. The steady-state PL spectra of pristine perovskite with corresponding compositions b) without HTM and c) with HTM. d) Time-resolved photoluminescence (TRPL) curves of the corresponding samples without HTM and e) with HTM.

Angew. Chem. Int. Ed. 2021, 60, 8303-8312

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diffraction peak from PbI_2 (marked with *) indicates that the (oFPEA)₂PbI₄ perovskite was generated separately on the 3D perovskite film. We estimated the FHWM of the (110) diffraction of the 3D perovskite phase for all the samples and found that the C-FPD/oFPEAI sample has a smaller FHWM than the C/oFPEAI sample, suggesting again an increased crystallite size (Figure S5).

Atomic force microscope (AFM) and SEM measurements were further examined to scrutinize the surface of the perovskite films (Figure S6). The SEM results of the C/ oFPEAI and C-FPD/oFPEAI samples agreed with previous reports showing an in situ formed 2D perovskite layer over the 3D perovskite surface. To further get the information of surface crystals shown in SEM, the microscale analysis of the surface was carried out on all the samples of four conditions by confocal laser scanning fluorescence microscopy (CLSM). This measurement can map the emissive chemical constituents spatially by exploiting the differences in their emission spectra.^[41] For pristine 3D perovskite film, we found remnant PbI₂ phases (shown as green color)^[41,42] presenting at the GBs of perovskites (shown as red color). (Figure S7a) In contrast, the CLSM images of the C-FPD film show less PbI₂ phase and lightened dark regions at GBs. (Figure S7d) This indicates that the FPD can passivate the trap states near the surface and along the GBs, resulting in enhanced overall film quality. In the CLSM images of the C/oFPEAI and C-FPD/oFPEAI films (Figure S7g-m), the (oFPEA)₂PbI₄ phase forms a continuous layer showing as evenly distributed highly emissive spots on the 3D perovskite, which is in agreement with our previous reports.^[36]

To get insight into the passivation effect of the DP strategy, we monitored the steady-state PL and time-resolved photoluminescence (TRPL) decay of the perovskite films with different compositions. It is known that the typical characteristics for successful defect passivation include higher PL intensity and longer TRPL lifetime because of the reduced non-radiative recombination sites in the perovskite films.^[43,44] As shown in Figure 2b, we found that the PL intensity of the C-FPD and C/oFPEAI samples obviously increased compared with the pristine 3D perovskite film (C), indicating that the recombination in the perovskite layer is effectively suppressed. Besides, for the samples with oFPEAI treatment (C/oFPEAI and C-FPD/oFPEAI), new peaks corresponding to the $(oFPEA)_2PbI_4$ phase at 506 nm were measured when illuminating from the top side of the film. While from the bottom side, only one peak at 768 nm could be observed (Figure S8), indicating that the (oFPEA)₂PbI₄ formed only on the top of the 3D perovskite. This was echoed by the significantly prolonged average TRPL lifetime from 17.3 to 55.8, and 129.3 ns when FPD and oFPEAI were introduced, respectively, as shown in Figure 2d, implying suppressed charge trapping in C-FPD and C/oFPEAI films.

As expected, the C-FPD/oFPEAI sample with the DP strategy showed the most intensive PL and longest average TRPL lifetime (513.3 ns, Table S2), which confirms the synergetic passivation effect of the two passivators on different defect sites on perovskites. We also did PL and TRPL measurements on the samples with the HTM layers deposited on the four kinds of perovskites. As shown in Figure 2 c, e, the

further reduced PL intensity and shortened TPPL lifetimes of the samples after passivation illustrate that the charge transport dynamics between the perovskite and HTM layers are also improved.

To investigate the chemical interaction between FPD and perovskite as well as the defect-passivation at GBs and the surface, we performed high-resolution X-ray photoelectron spectroscopy (XPS) analysis. Firstly, the characteristic fluorine element from the FPD and oFPEAI was identified in the corresponding samples confirming the existence of the passivating agents. The single peaks located in the F 1s spectra at binding energy (BE) of 687.2 eV belong to fluorosubstitution on the phenyl group of oFPEAI (Figure S9a, blue and green).^[36] However, the signal of F 1s was not detected for the C-FPD sample (Figure S9a, red), which may be associated with the low FPD concentration or illustrating the inexistence of the FPD molecule on the surface of the perovskite film. As shown in Figure 3a, the BE at 143.5 and 138.7 eV were assigned to $4f_{5/2}$, $4f_{7/2}$ of divalent Pb^{2+} , respectively, and the two weaker peaks at 141.8 and 137.0 eV were associated with metallic Pb^{0,[45]} We calculated the intensity ratio of Pb⁰/ (Pb⁰ + Pb²⁺) for three modified samples and the pristine to observe a notable tendency (Table S3). Obviously, this ratio in the perovskite films with FPD (C-FPD and C-FPD/oFPEAI) was reduced to 4.4% and 6.5%, respectively, indicating that the FPD could better passivate the noncoordinated Pb²⁺ thereby reducing the formation of metallic lead. Interestingly, as shown in Figure 3 a,b, the BE of Pb 4f core level and I 3d core level shifted about 0.3 eV to lower energy for oFPEAI treated perovskites (C/oFPEAI and C-FPD/oFPEAI), indicating that the thin 2D perovskite layer facilitates charge transfer at the interface because the core levels are closer to the Fermi level.[20,46]

To further evaluate the passivation effect of different molecules, we conducted depth profiling XPS spectra for Pb 4f of the pristine perovskite (C) and C-FPD/oFPEAI samples. As shown in Figure 3 c,d, sample C shows the vertical composition uniformity for the Pb element. For the C-FPD/ oFPEAI sample, since the formed 2D perovskite layer is as thin as 20 nm, the depth profile of XPS spectra shows a clear transition into the underlying 3D perovskite after Ar etching for 30 s (1 cycle, as shown in Figure S9b). After 2 cycles of Ar etching, the Pb⁰ intensity ratio (Pb⁰/ (Pb⁰ + Pb²⁺)) in sample C reached 13.4%, which is higher than that of the C-FPD/ oFPEAI sample (6.2%). This clearly showed that the metallic Pb⁰ was reduced due to the successful passivation of FPD on perovskite GBs defects (i.e., noncoordinating Pb²⁺).

The passivation of defects should considerably influence the $V_{\rm OC}$ of the devices due to the consequently enhanced carrier concentration and suppressed non-radiative recombination. To evaluate the effect of this DP strategy on the photovoltaic performance, we fabricated complete solar cells based on perovskite films with and w/o the corresponding passivating procedures. The champion device with pristine perovskite (C) shows a higher PCE of 21.22 % under reverse scan (Figure 4a). The solar cells based on C-FPD and C/ oFPEAI perovskites exhibited improved $V_{\rm OC}$ of 1.11 and 1.13 V and PCE of 21.62 % and 22.52 %, respectively (seen in Table 1). After optimization, the dually-passivated (based on



Figure 3. Compositional characteristics of perovskite films with corresponding compositions. High resolution surface XPS a) Pb 4f, b) I 3d. High-resolution depth profiling XPS of c) the pristine 3D perovskite (C) and d) C-FPD/oFPEAI samples.

Devices	<i>V</i> _{oc} [V]	$J_{\rm SC}$ [mA cm ⁻²]	FF	PCE [%]	$\int_{SC} [mA cm^{-2}]^{[a]}$	PCE _{MPP} [%] ^[b]		
Control	1.10 (1.088 \pm 0.017 ^[c])	23.93 (23.65±0.32)	0.805 (0.808±0.010)	21.22 (20.60±0.43)	22.50	18.60		
C-FPD	1.11 (1.106±0.009)	24.20 (23.72±0.28)	$0.807 (0.816 \pm 0.012)$	21.62 (21.40±0.20)	23.01	20.10		
C/oFPEAI	1.132 (1.128 \pm 0.016)	23.73 (23.70±0.09)	0.838 (0.832±0.010)	22.52 (22.19±0.31)	23.14	20.76		
C-FPD/oFPEAI	1.163 (1.164±0.010)	24.77 (23.88±0.09)	0.825 (0.830±0.009)	23.80 (23.36±0.24)	23.36	22.99		

Table 1: Photovoltaic parameters of solar cells.

[a] Calculated J_{sc} from the EQE spectrum; [b] the steady-state PCE was measured under constant voltage of the maximum power point; [c] \pm represents the standard deviation of the mean.

C-FPD/oFPEAI perovskite) devices showed the best efficiency of 23.80% under reverse scan, with a negligible hysteresis (Figure S10, Supporting Information). In addition, for one of our highest performing devices, we measured an outstanding $V_{\rm OC}$ of 1.18 V with a PCE of 23.11% (Figure S11a, Supporting Information). The corresponding external quantum efficiency (EQE) of the champion devices are shown in Figure S11b, which shows an integrated $J_{\rm SC}$ of 23.36 mA cm⁻² for the dually-passivated device.

The stabilized efficiency output of the devices based on pristine (C) and C-FPD/oFPEAI perovskites were measured and shown in the inset of Figure 4a. The best-performing device with C-FPD/oFPEAI perovskite showed a stabilized efficiency of 22.99%, while the best cell employing pristine perovskite (C) exhibited a stabilized efficiency of 18.6%. To check the reproducibility of the device performances with different passivating procedures, we collected the photovoltaic parameters of 20 devices from four batches (Figure 4b). The statistics of the $V_{\rm OC}$ and PCE distribution confirm the repeatability of our results and that the DP strategy can undoubtedly increase the $V_{\rm OC}$ value and improve the performance of PSCs. We also tested the solar cell devices operating as LED in the dark and under a voltage bias. The dually-passivated (C-FPD/oFPEAI) devices showed much more intensified electroluminescence (EL) under 1.5 V and an emission peak located at 781 nm (Figure 4c), which is





Figure 4. a) Current density-voltage (J-V) curves of the optimized devices w/o and with FPD/oFPEAI passivation under reverse scan (1.2 to -0.1 V), testing under 1 Sun AM 1.5 simulated illumination. The inset shows the steady-state measurement of PCE of the champion devices. b) Statistical deviation of the photovoltaic parameters for the corresponding solar cells. c) The electroluminescence spectra (EL) of the corresponding devices under 1.5 V bias in the dark operating as LEDs. Inset: EL image of the C-FPD/oFPEAI device. d) Electron and hole trap density of these devices. e) Charge recombination resistance (R_{rec}) for the different devices versus applied potential from impedance measurement in the dark. f) Transient photocurrent decay, g) measured DOS extracted from the EIS, and (h) IMVS derived carrier recombination lifetimes for the four kinds of devices.

direct evidence that the non-radiative recombination losses in the perovskite layer have been significantly suppressed after passivation by FPD/oFPEAI.

We next characterized solar cells via various optoelectronic methods. We estimated the trap-state density of electron-only and hole-only devices based on a space-charge limited current (SCLC) measurement model (Figure 4d and Figure S12). The pristine perovskite film (C) has an electron trap density of 1.05×10^{16} cm⁻³ and a hole trap density of 1.05×10^{16} cm⁻³. The electron trap densities are estimated to be 5.07×10^{15} and 7.57×10^{15} cm⁻³ for the C-FPD and C/ oFPEAI perovskite films, respectively. Similarly, the corresponding hole trap densities are estimated to be 6.85×10^{15} and 8.16×10^{15} cm⁻³. A further lower electron (1.14×10^{15} cm⁻³) and hole (4.75×10^{15} cm⁻³) trap density is derived for C-FPD/oFPEAI based devices, which can be interpreted as a better passivation effect on the defects.

Electrochemical impedance spectroscopy (EIS) measurement shows more enormous charge recombination resistance (R_{rec}) values for all passivated devices than that seen in the control devices (Figure 4e). The charge transport properties in control (C), C-FPD, C/oFPEAI, and C-FPD/oFPEAI perovskite-based devices, were further investigated by transient photovoltage (TPV) and transient photocurrent (TPC) decay measurement (Figure 4f and Figure S13). Transient photovoltage showed a decay lifetime of 0.24, 1.11, 1.19, and 29.9 ms for the control, FPD-, oFPEAI-, and FPD/oFPEAIpassivated devices, respectively, indicating that the process of interfacial charge recombination is indeed slowed down. We measured the photocurrent decay lifetime of 25.37, 6.41, 3.73, and 4.03 µs for the same sequences of conditions, respectively. These results are consistent with the TRPL results in the perovskite films covered with HTMs, as discussed above.[47]

Besides, we measured the distribution of the density of states (DOS) in perovskite films to explore the passivation

effect of this DP strategy using the EIS method. The measurement details and the equivalent circuit model used for the fitting of EIS can be found in Figure S14. As shown in Figure 4g, a relatively smaller DOS in the order of 10^{17} to 10^{18} cm⁻³ can be derived from the C-FPD/oFPEAI device, which further confirms the reduction of trap states in the perovskite film made from DP strategy.

Intensity-modulated photovoltage spectroscopy (IMVS) was employed to evaluate further the mean charge carrier recombination lifetime of each device, which provided information about the electron lifetime and electron-hole recombination dynamics under open-circuit conditions.^[48,49] Figure S15 shows complex plane IMVS data of the best device recorded under different DC light intensities. As light intensity increases, the semi-circle radius decreases. Figure 4h shows the voltage-dependence of the recombination lifetime (τ_n). The τ_n of the C-FPD and C/oFPEAI devices are much larger than that of the pristine (C) device. Furthermore, with the DP strategy, the C-FPD/oFPEAI device showed the most enormous τ_n , meaning that the C-FPD/oFPEAI device has better transport and less recombination due to the more efficiently passivated defects at interface and GBs.

It is found that the perovskites made by the DP strategy exhibited superior stability under ambient air with high relative humidity (RH) of up to 70%. In Figure 5 a, the XRD pattern of C/oFPEAI and C-FPD/oFPEAI perovskites remained almost the same as the fresh one after 20 days. However, for the pristine (C) and C-FPD perovskites, pronounced peaks at 11.7° were observed, demonstrating the formation of a δ -phase FAPbI₃. The observed bleaching of dark color in Figure S16a indicates the decomposition of the 3D perovskite. In contrast, after the treatment by oFPEAI, films of C/oFPEAI and C-FPD/oFPEAI showed higher resistance to moisture than the control. (Figure S16a)

In one set of experiments, the PCEs of the control, FPD-, oFPEAI-, and FPD/oFPEAI-passivated devices were monitored during heating the corresponding devices on a hot plate at 100 °C, in the air of RH 70 %, under ambient light, for 30 h. As shown in Figure 5b, the devices based on the C-FPD and C/oFPEAI perovskites retained nearly 84% and 76% of the original PCE after thermal aging at 100°C for 30 h, respectively. In contrast, the pristine device shows a rapid degradation with a maximum loss of 35% of the initial PCE. Furthermore, after the thermal aging test for 30 h, the PCE of the C-FPD/oFPEAI device remained 85% of the initial value. To identify the reason behind the different stability behavior of perovskite material and devices, we assessed the thermal resistance of the unencapsulated devices at about 100°C in ambient conditions with a prevalent humidity of 70%. The variation in XRD patterns and a series of photographs of the pristine and passivated perovskite films after thermal treatment (100°C) for 180 h are shown in Figure 5c and Figure S16b. The XRD patterns of the pristine perovskite film exhibit a more distinct diffraction peak of PbI₂ than the C-FPD film. Moreover, the pristine 3D perovskite (C) started to bleach after 132 h and turned completely yellow after 180 h. The C-FPD perovskite shows superior thermal stability compared to the control, suggesting that the FPD significantly retarded the degradation of perovskites. According to the previous discussion, the FPD additive can enhance the thermal stability of perovskite^{[14,50]} since strong hydrogen bonding (F…H–N) between fluorine atoms and MA⁺ can immobilize MA⁺.^[14]

Besides, the long-term moisture stability of the passivated perovskite films was evaluated in contrast to the pristine 3D perovskite film (C) when all devices were stored in a cabinet with an RH of $30 \pm 5\%$. The moisture resistivity of C/ oFPEAI devices has been thoroughly studied in our previous works,^[36,37] where the hydrophobic fluorophenyl groups acted as the moisture barrier to prevent the invasion of H₂O from ambiance in high humidity environments. In this case, after 71 days, the C-FPD/oFPEAI devices retained over 97% of their initial efficiency, which was similar to the C/oFPEAI device (96%), while the PCE of the PSC based on pristine perovskite (C) dropped to 85%. (Figure 5d)

As we have discussed before, the formation of superoxide (O_2^{-}) near the perovskite film is detrimental to the stability of the devices. To unveil the mechanism of enhanced stability after the passivation strategies, we determined the yield of photo-induced O₂⁻, which is an indicator of the density of vacancies in perovskite films, for the four kinds of perovskite films. Here the yields of $\mathrm{O_2^-}$ for all perovskite films were determined using a fluorescence dye 1,3-diphenylisobenzofuran (DPBF) probe, as shown in Figure 5e (see Experimental section).^[51,52] In the current experiment, the fluorescence quenching of the DPBF probe was monitored at regular time intervals throughout 150 s with the perovskite films exposed to light and dry oxygen (Figure S17). Figure 5 f shows the measured rate of increase of O2- species in these four perovskite films. We found that the yield of O_2^- can be reduced in the C-FPD perovskite compared with the pristine perovskite film. This phenomenon can be interpreted by the fact that the films of C-FPD perovskite exhibited larger crystallites with fewer defects and hence explain the better stability.^[29] Incredibly, all the oFPEAI treated perovskites (C/ oFPEAI and C-FPD/oFPEAI) displayed a significantly lower yield of O_2^- species than the pristine (C) and C-FPD perovskite films. Our previous work^[25] and other studies^[17,31] proved that the ammonium iodide could effectively passivate defects like iodide vacancies, which were proven to be the main incentives to form the destructive O2- species.[29] Therefore, we infer that the in situ formed 2D perovskite layer ((oFPEA)₂PbI₄) passivated the vacant iodide sites on the surface of perovskites, which otherwise will lead to decreased stability by promoting the formation of O₂⁻. This is the first time to find that the 2D perovskite layer can effectively inhibit the formation of the O_2^- species.

Conclusion

In conclusion, this work explores a practical approach for the comprehensive passivation of the traps on the perovskite films in n-i-p planar PSCs. We have demonstrated that the conjugated FPD additive with fluorinated alkyl substitutions can increase the grain size of perovskite and reduce chargecarrier recombination via GBs passivation. Beyond the modified anti-solvent treatment, we put forward a practical

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Figure 5. Stability testing result of perovskite devices without encapsulation. The XRD of aged devices (a) stored under room temperature and 70% RH environment for 20 days, δ corresponds to the δ -phase FAPbl₃ and (c) stored under 100°C heating in the air with an RH of 70% for 180 hours. Normalized PCE of devices (b) (stored in the air RH of 70%) aged and annealed at 100°C over 30 hours and (d) stored in a 30% RH environment over 71 days. e) Oxidation of DPBF by O_2^- (formed on perovskite film under illumination) to form colorless 1,2-dibenzoylbenzene. f) The fluorescence intensity of DPBF aliquots in which films were aged under light and oxygen blow at 455 nm, representing the yield of O_2^- .

method to reduce the generation of O_2^- inside or near the perovskite film. This includes introducing a fluorinated aromatic cation and forming a capping 2D perovskite layer to reduce the defect on the surface of the 3D perovskite. The comprehensive dual-passivation (DP) strategy with FPD and oFPEAI could effectively passivate the defects (i.e., non-coordinating Pb²⁺) at GBs and the iodide vacancies at the surface of the 3D perovskite. As a result, the perovskite

devices with DP strategy delivered a high efficiency of 23.80% with a minimum $V_{\rm OC}$ deficit of 0.39 V. We showed the first observed reduction of the O_2^- by introducing the 2D perovskite capping layer and the significant stability enhancement. This study provided new insight into the strategies for enhancing thermal, moisture, and oxygen stability of perovskite materials and could help develop new passivation methods.

Acknowledgements

P.G. acknowledges the financial support from the National Natural Science Foundation of China (Grant No. 21975260, and 51863012).

Conflict of interest

The authors declare no conflict of interest.

Keywords: defects \cdot dual-passivation \cdot perovskite solar cells \cdot stability \cdot superoxide

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Manuscript received: December 25, 2020 Accepted manuscript online: January 25, 2021 Version of record online: March 4, 2021