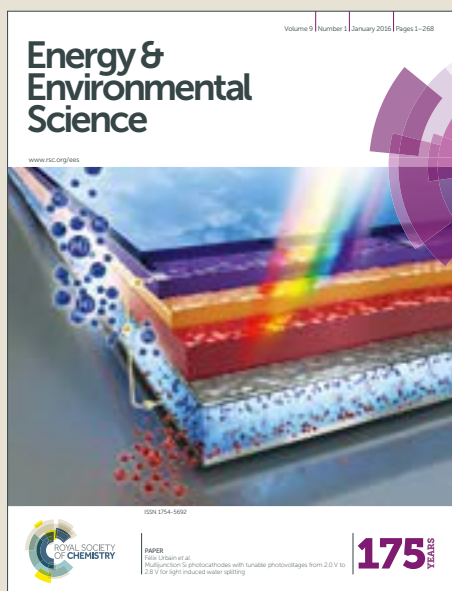


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ARTICLE

Improving the stability and performance of perovskite solar cells via off-the-shelf post-device ligand treatment

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While metal halide perovskite solar cells (PVSCs) have drawn intense attention due to their high solar-to-power conversion efficiency (PCE), their practical application is hampered by the poor long-term stability against moisture. Although strategies have been reported to solve this issue, these methods are introduced during core-device fabrication processes which will increase the risk of introducing unexpected impurities during the fabrication. Herein, we introduce the first kind of simple post-device ligand (PDL) treatment to significantly improve PCE of completely fabricated PVSCs from 18.7% to 20.13%. Meanwhile, the stability of the treated devices without any encapsulation remarkably improves that 70% PCE is maintained in ambient conditions after 500-hour maximum-power-point tracking test while the control unencapsulated device will completely break down within 100 hours. Equally important is that this post-device treatment shows a special 'stitching effect', namely repairing the as-fabricated 'poor devices' by healing the defects of perovskite active region and can improve PCE by over 900%. We also experimentally and theoretically study the fundamental mechanism of the improvement. Consequently, our approach greatly improves the production yield of high-quality PVSCs and their module performances as well as the reduction of lead-waste. Additionally, the treatment is an off-the-shelf post-device approach that can be integrated into any existent perovskite-device fabrication, offers a general strategy to improve the stability and performance of perovskite optoelectronic devices.

Broader context: Moisture stability has been a fundamental challenge for metal halide perovskite solar cells (PVSCs). Although strategies have been reported to solve this issue, these methods are introduced during the core-device fabrication processes which will increase the risk of introducing unexpected impurities during the fabrication. Besides, in the future mass-production process, the completely fabricated 'poor' devices will hamper the cell module performance, reduce the production yield as well as bring a large amount of additional lead waste. To address these issues, we introduce a simple off-the-shelf ligand treatment to simultaneously improve the performance and stability of completely fabricated PVSCs. Equally important is that this post-device modification shows a special 'stitching effect', namely repairing the as-fabricated 'poor devices' by healing the defects of perovskite active region and significantly improve the efficiency by over 900%. Consequently, the ligand treatment greatly improves the production yield of high-quality PVSCs and their module performance as well as the reduction of lead-waste. Our work offers a new strategy of simple off-the-shelf process to improve the stability and performance of perovskite-based optoelectronic devices.

Introduction

In the past few years, perovskite solar cells (PVSCs) have drawn enormous attention with remarkably high efficiency and prospective for low-cost fabrication.¹⁻¹⁴ A new certified efficiency has recently reached 22.7%¹⁵, which enables them as a very promising candidate to be used for next-generation photovoltaics.^{16,17} However, PVSCs still suffer from poor

stability caused by moisture^{18,19}, oxygen²⁰⁻²², light illumination²², applied electric field²³, thermal stress^{24,25}, and defects in perovskite films²⁶⁻³⁰. Among them, moisture has been demonstrated as the most prominent factor for perovskite degradation due to the strong interaction with water molecule.^{19,31-33} Some strategies have been reported to solve this issue. For example, encapsulation [e.g., hydrophobic materials³⁴, epoxy resins³⁵, fluoropolymers³⁶] and interface engineering [e.g., using metal oxides to replace organic carrier transport layers³⁷⁻⁴⁰ and moisture-resistant carrier transport layer⁴¹] have been reported to enhance the moisture stability of PVSCs by blocking the away moisture, but the device still degrades at high humidity environment⁴². Besides, the intrinsic moisture-sensitivity of perovskite films remain an unsolved problem. Recently, other strategies have been reported to solve this issue, e.g. forming water-resisting layer⁴³, adding water-proofing additives⁴⁴, and using two-dimensional (2D)/ three-dimensional (3D) perovskite mixtures^{45,46}. While the stability is improved, these approaches incorporate insulating moieties in

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the perovskite lattice or film surfaces, which may affect the charge separation and transport processes in perovskites or charge extraction from perovskite to carrier transport layers. Besides, these methods are introduced during the core-device fabrication and thus increase the risk of introducing unexpected impurities during the fabrication. More importantly, up to now, how to handle the completely fabricated poor devices during the future mass-production process is still an open question, which is critical to improve the performance of cell module performance, production yield as well as the reduction of additional lead-waste.

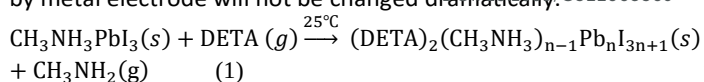
In this work, we introduce the first kind of simple post-device ligand (PDL) treatment to simultaneously improve the performance and stability of completely fabricated PVSCs. The ligand vapours will induce chemical modification in the selected lateral regions particularly that of perovskite layer which prevent the diffusion of water molecules into the protected active perovskite region for enhancing PVSC stability. This post-device treatment could also passivate the surface defects of perovskites in active region for improving the PVSC performance. Interestingly, this PDL treatment strategy shows a special 'stitching effect', namely repairing the as-fabricated 'poor devices' by healing the defects of perovskite in the operation region, which greatly improves the production yield of PVSCs and their module performance as well as the reduction of lead-waste. It should be noted that the off-the-shelf PDL treatment, completely separated from the fabrication process of common perovskite devices, provides a general strategy to improve the stability of different completed perovskite optoelectronic devices (e.g. solar cells, light-emitting diodes, and photodetectors) without introducing any undesirable impurities during device fabrication.

Results and discussion

Post-device ligand treatment and characterization

Fig. 1a shows the process for improving the performance and stability of PVSCs via post-device ligand (PDL) treatment. The PVSCs have the p-i-n configuration of ITO/NiO_x/CH₃NH₃PbI₃/PCBM:C₆₀/Zracac/Ag, where room-temperature solution-processed NiO_x nanostructure³⁴, PCBM:C₆₀ mixture, and zirconium acetylacetonate (Zracac) as hole transport layer (HTL), electron transport layer (ETL), and interface layer, respectively. In this study, diethylenetriamine (DETA) with three amine groups is taken as the ligand example to treat PVSCs as depicted in **Fig. 1a**. Specifically, the ligand vapors are employed to directly treat the as-prepared (completed) PVSC devices (Note: not to treat perovskite nor ETLs/ HTLs during core-device fabrication as reported by others⁴³⁻⁴⁹). In our work, the DETA molecule can interact with CH₃NH₃PbI₃ perovskite by substitution of the surface CH₃NH₃⁺ ion, resulting in a modified CH₃NH₃PbI₃ or a stable non-CH₃NH₃PbI₃ phase (e.g., layered perovskite). With this in mind, the perovskite layer in lateral regions (uncovered by metal electrode) of PVSC (see **Fig. 1a**) would directly react with ligand vapors to form a stable low-dimensional perovskite complexes

(see **Equation 1**), while the perovskite in active region covered by metal electrode will not be changed dramatically.



By the PDL treatment, we aim for improving the air-stability of PVSCs by stabilizing the material in active region and enhancing the water molecule diffusion barrier from lateral region to active region. Meanwhile, the ligand vapors will also passivate the defects of perovskite in active region. As shown in **Fig. 1b**, the three-dimensional (3D) perovskite layer in lateral region changes after the PDL treatment, which can be clearly confirmed from the color change and X-ray diffraction (XRD) patterns (**Fig. 1c**). The new XRD peaks below 10 degree show the dramatic change of low-dimensional perovskite complexes formation in the lateral regions. Interestingly, thanks to the protection of covered electrode, the perovskite in active region was not changed significantly as evidenced from the absorbance spectra of PVSCs with and without PDL treatment as shown in **Fig. 1b** and **Fig. S1**. There are some new XRD peaks below 10 degree that appeared in the active region as shown in **Fig. 1c**, which indicates that some low-dimensional perovskites also form in the active region of PVSCs (which are some nanodots on surface of perovskite active region as discussed later). To gain insight into the post-device treatment, we investigate the perovskite materials in lateral region and active region by using scanning electron microscopy (SEM). To prepare perovskite films for SEM measurement, the Ag electrode and fullerene ETLs in PVSC devices were removed by tape and chlorobenzene washing, respectively. As illustrated in **Fig. S2, S3**, the perovskite materials in lateral region change from nanometer-sized grains (**Fig. 1d**) into micrometer-sized nanorods. Distinctly, as shown in **Fig. 1e**, the morphology (e.g., grain size) of perovskite materials in active region (protected by electrode) after PDL treatment shows no obvious damage and some small nanodots appeared on the grains. These nanodots are the low dimensional perovskites, which can be confirmed from the XRD results in **Fig. 1c**.

The surface composition of perovskite film in active region with and without PDL treatment, was investigated by X-ray photoelectron spectroscopy (XPS). The preparation method of samples for XPS was like that for SEM test. The chlorobenzene washing treatment has negligible effect on the surface composition of perovskite film as illustrated in **Fig. S4**. As shown in **Fig. 1f,g**, the C 1s peak at 284.8 eV of PDL treated perovskite is more pronounced than that of control perovskite. Meanwhile, a new N 1s peak at 400.0 eV illustrates that some additional amine groups (NH₂ or NH) on the surface of PDL treated perovskite. These results can be explained by the absorption of DETA molecules on the surface of CH₃NH₃PbI₃ films or partially substitution of CH₃NH₃⁺ with DETA molecules to form [DETA]⁺ cations (the nanodots on perovskite surface as shown in **Fig. 1e**). Besides, the XPS in **Fig. S5** shows Pb 4f spectra, which contain two main peaks Pb 4f 7/2 and Pb 4f 5/2 at 138.5 and 143.3 eV, respectively. The two small peaks located at 136.6 and 141.6 eV are attributed to the presence of metallic Pb⁵⁰. Interestingly, the metallic Pb peak is greatly reduced for the covered (active-

region) perovskite with PDL treatment. A lower level of Pb defects can reduce the non-radiative recombination and increase the PL lifetime,⁵⁰ which will be discussed later. Besides, Pb 4f spectra of covered perovskite of PDL-treated sample in Fig. S5 shows a slightly red shift, which also confirm the strong interaction between DETA molecules and $\text{CH}_3\text{NH}_3\text{PbI}_3$

perovskite films. Furthermore, we found that the DETA only modify the surface of active perovskite layer (see Fig. S6). Consequently, PDL treatment modulates the surface properties of active region perovskite which will offer the improved device performance described later.

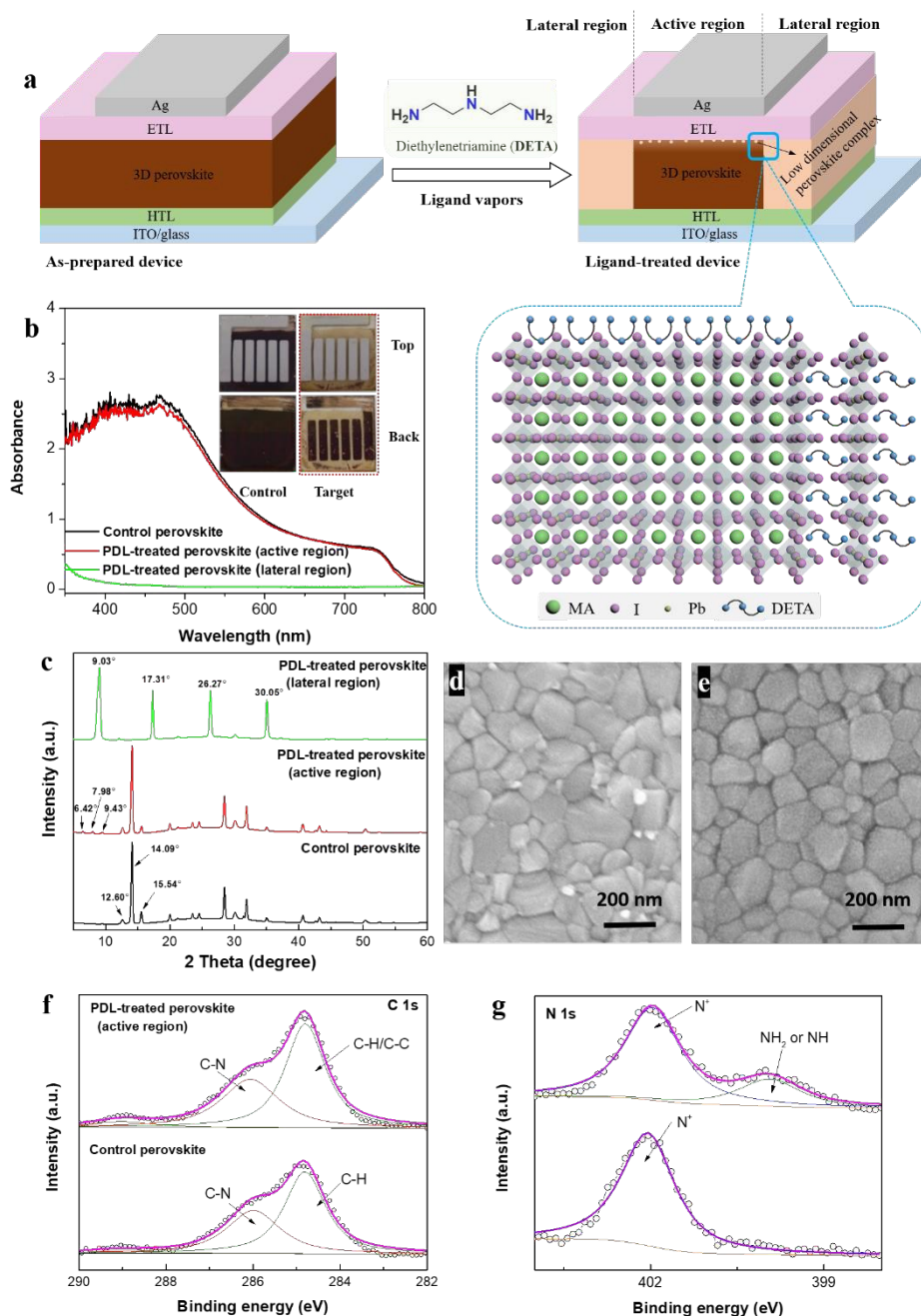


Fig. 1 Processing scheme and characterization of post-device ligand (PDL) treatment. (a) Schematic illustration of the PDL treatment process and the relevant device configuration, the molecular structure of DETA, and a possible model for DETA interaction with the MAPbI_3 cage. (b) UV-vis spectra and (c) X-ray diffraction (XRD) patterns of the perovskite film without (control) and with PDL treatment. The insertion of (b) is the photographs of the real devices before and after PDL treatment. Top-view SEM images of perovskite films in active region of (d) control device without any treatment and (e) the device with PDL treatment. XPS peak of C 1s (f) and N 1s (g) obtained from the surface of control perovskite film without any treatment and the covered (active-region) perovskite with PDL treatment.

Improved photovoltaic performance and stitching effect

The photovoltaic performance of PVSCs before and after PDL treatment have been investigated. To avoid the edge effect, a black shadow mask was employed to define the active area during the measurement under illumination. As shown in **Fig. 2a, 2b** and **Table 1**, the control device A without PDL treatment showed typical performance with short circuit current density (J_{sc}) of 22.12 mA cm⁻², open circuit voltage (V_{oc}) of 1.06 V, fill factor (FF) of 79.6%, PCE of 18.67% and the stabilized PCE of 18.11%. In striking contrast, the device A with PDL treatment (with the optimized modification time of 10 minutes, see **Fig. S7**) showed a significantly improved performance with J_{sc} of 23.47 mA cm⁻², V_{oc} of 1.08 V, FF of 79.4%, PCE of 20.13%, and the stabilized PCE of 19.90%. As shown in **Fig. S8** and **Table S1**, the PDL-treated PVSCs also showed a lower hysteresis than the control devices, which may be related to the suppressed ion migration by the formation of low dimensional perovskite nanodots⁵¹ at the interface of CH₃NH₃PbI₃/fullerene. The IPCE spectrum is shown in **Fig. 2c**. The integration of the IPCE over the AM 1.5 solar emission spectrum produces photocurrent that is consistent with the J_{sc} derived from the J - V curve, showing negligible spectral mismatch of our solar simulator with the standard solar light.

To investigate the reproducibility of the PVSCs, 37 separate devices were fabricated and tested. The histograms of the

device efficiencies are presented in **Fig. 2d**. The PDL treatment significantly improves the device reproducibility with a standard deviation of only 1.94% in PCE which is over 220% improvement over the control (without treatment) of 4.46%. Approximately 80% of the treated cells show PCE over 18%. Furthermore, our PDL treatment strategy can also be applied to other types of perovskites (e.g., Cs₅(MA_{0.17}FA_{0.83})₉₅Pb(I_{0.83}Br_{0.17})₃ mixed perovskite, see **Fig. S9**).

Interestingly, the PDL treatment strategy shows a special 'stitching effect', namely 'repairing' the defect points in the 'poor' PVSC and dramatically improves its photovoltaic performances. Some sample cases are presented in **Fig. S10**. Taking device B as an example. As shown in **Fig. 3a** and **Table 1**, the J - V responses show a significant increase in photovoltaic parameters (J_{sc} : from 22.97 mA cm⁻² to 23.43 mA cm⁻²; V_{oc} : from 1.01V to 1.07 V; FF: from 44.0% to 74.8%) and the overall PCE increases from 10.20% to 18.75% by PDL treatment. For some other poor devices shown in **Fig. S5**, the PCE of repaired PVSCs can improve by over 900% (like device C). Regarding the cause of stitching effect in the PDL treatment, the produced CH₃NH₂ gas (see **Equation 1**) can heal the defects of perovskite films in active region as shown in **Fig. S11** and thus improve the performance of PVSCs⁵².

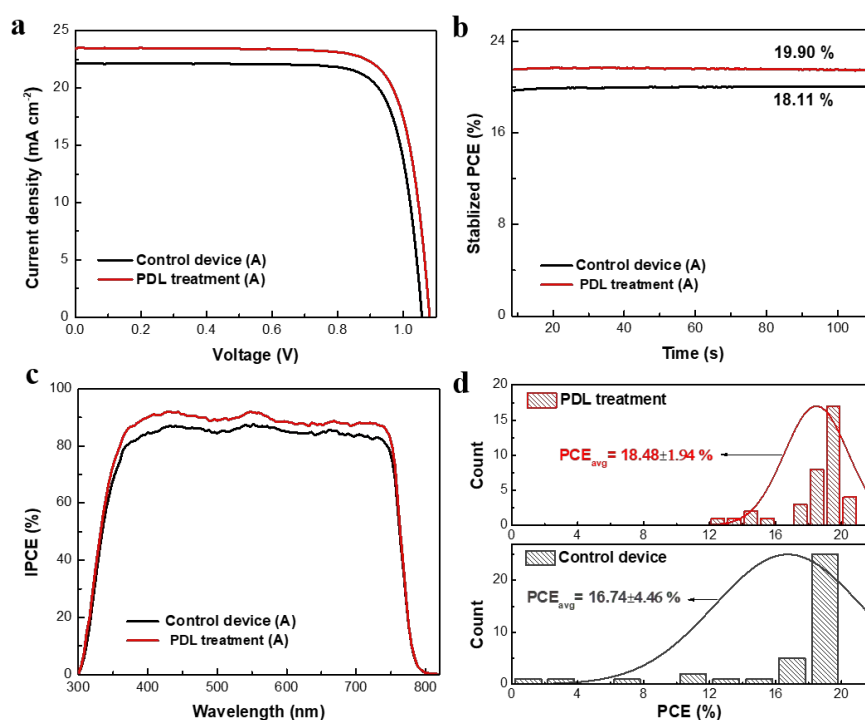
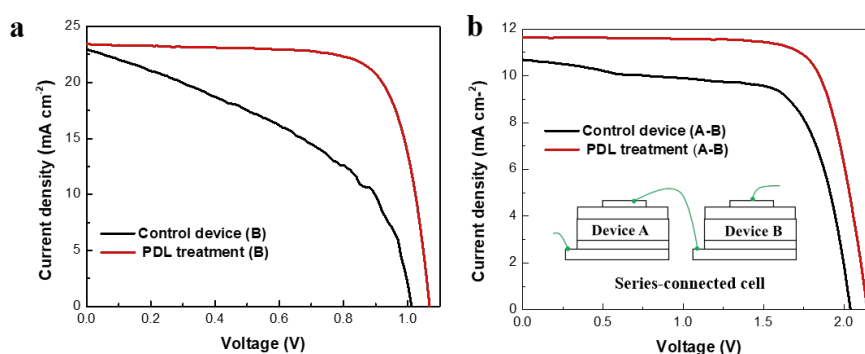


Fig. 2 Enhanced device performance and reproducibility. J - V curves (a), the steady-state PCE (b), IPCE spectra (c) of the champion PVSCs (device A) without (control) and with PDL treatment. (d) Histograms of the device efficiencies (37 cells were fabricated and tested).



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Fig. 3 Stitching effect. *J-V* curves of a 'poor' PVSC (a) and two series-connected devices (b) without (control) and with PDL treatment.

In practical applications, solar panels are typically formed by connecting solar cell units in series. As we know, the poor solar cell unit will govern and greatly harm the overall performances of a PVSC module due to the unmatched photovoltaic parameters of individual devices. In this study, we further find that the PDL treatment can significantly improve the performance of PVSC module by significantly repairing the 'poor' devices. A series-connected device (A-B) was fabricated by connect the two representative devices (A and B) with series model. The corresponding *J-V* curves and photovoltaic parameter summary are shown in **Fig. 3b** and **Table 1**. The series-connected device without PDL treatment shows a mismatched properties and poor photovoltaic performance. After PDL treatment, the PVSC module shows dramatic enhancement in the FF from 68.6% to 76.5% and overall PCEs from 14.95% to 19.07%. As a result, PDL treatment shows enormous potential application in the commercialization of perovskite-based photovoltaic cells.

We further investigated the origin of PDL treatment on the improved photovoltaic performance. Firstly, we performed time-resolved photoluminescence (TRPL) measurements to study the carrier transport and recombination of the perovskite layer in active region. We deposited the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films on bare quartz substrates. Other fabrication procedures are same as the normal PVSCs (see Methods). As illustrated in **Fig. 4a**, the perovskite film with PDL treatment had a threefold stronger photoluminescence intensity and a longer lifetime (τ , 411.6 ns) than that of the control sample (τ , 304.2 ns). This indicates the nonradiative recombination channels in perovskite film have been suppressed by PDL treatment, which was further demonstrated by studying the defect density in perovskite films.

As illustrated in **Fig. S12**, the estimated defect density is considerably reduced from $1.8 \times 10^{16} \text{ cm}^{-3}$ (control) to $9.9 \times 10^{15} \text{ cm}^{-3}$ for the samples with PDL treatment.

We also conducted first-principles density functional theory (DFT) to simulate the defect passivation of perovskite by PDL treatment. For the control perovskite (without treatment), a Pb vacancy (V_{Pb}) defect induces band edge state located near surface (**Fig. 4b**), which increases the intrinsic band gap of the perovskite (**Fig. S13a,b**). Besides, these trap states can capture holes and become nonradiative recombination centres (**Fig. S13c**). To simulate PDL treatment, the initial structure of DETA molecule is constructed and relaxed by Hellman-Feynman forces until the net force on each atom is less than $0.01 \text{ eV/\AA}$. Then the relaxed DETA molecule is put above the V_{Pb} defect. The atom positions of DETA molecule and four upmost atomic layers are fully relaxed with the left bottom layer fixed. After PDL treatment, the V_{Pb} defect becomes much shallower and more delocalized (**Fig. 4c**). Overall, the DETA molecule produced by PDL treatment can passivate the V_{Pb} defect sites near band edge and therefore reducing band gap of the perovskite in active region and the nonradiative recombination centers, which slightly contribute to the improved J_{sc} and V_{oc} , respectively.

To understand the V_{oc} enhancement in PDL treated devices, we firstly estimated the ideality factor (n), which is an indicator of the dominant recombination mechanism occurring within a working device⁵³. Generally, if n is equal to one, bimolecular recombination (the recombination of free electrons and holes in the photoactive layer) is dominant. When n approaches 2, trap-assisted Shockley-Read-Hall (SRH) recombination dominates in the device. By linearly fitting V_{oc} versus log-scaled light intensity (**Fig. 4d**) using the equation: $n = \frac{q}{kT} \frac{dV_{\text{oc}}}{d \ln(\phi)}$, we

Table 1. The characteristic parameters from *J-V* curves of PVSCs without (control) and with PDL treatment.

Device	PDL treatment	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)	γ (s^{-1})	R_{s} ($\times 10^{-5}$ Ohm m^2)	R_{sh} (Ohm m^2)
A	W/O	22.12	1.06	79.6	18.67	8.63	5.15	192.81
	W/	23.47	1.08	79.4	20.13	5.88	5.87	12246.32
B	W/O	22.97	1.01	44.0	10.20	10.81	10.65	8.12×10^{-3}
	W/	23.43	1.07	74.8	18.75	7.09	14.87	100.71×10^{-3}
A-B	W/O	10.69	2.04	68.6	14.95	-	-	-
	W/	11.65	2.14	76.5	19.07	-	-	-

A-B refers to device A and device B series-connected device. γ , R_{s} and R_{sh} are the non-radiative recombination rate, series resistance, and shunt resistance, respectively.

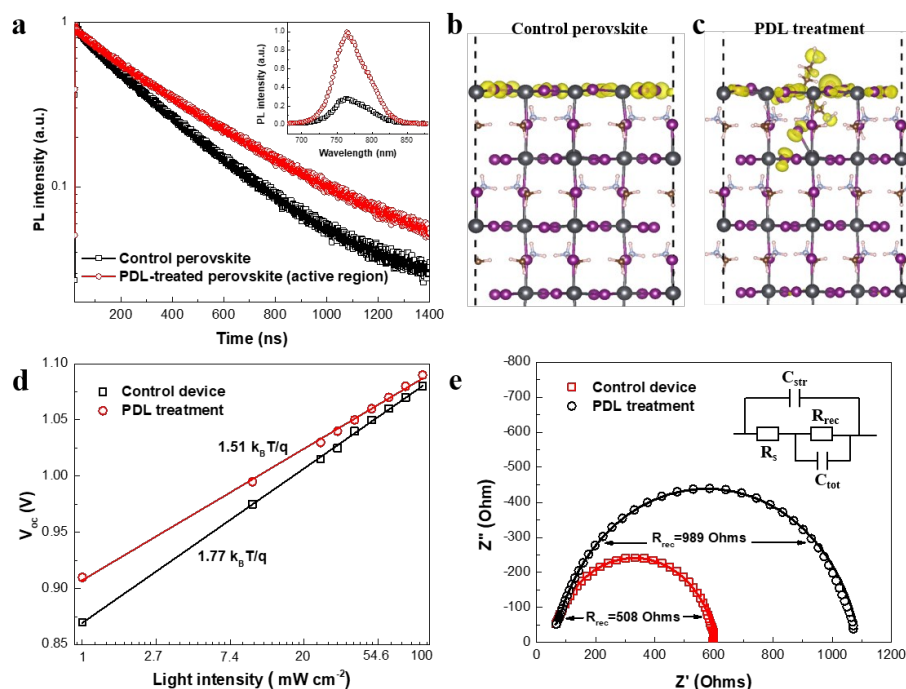


Fig. 4 Charge dynamics and recombination. Time-resolved PL decay of perovskite (active region) with and without PDL treatment. The insertion is the relevant steady-state PL spectra. (b) Trap-like localized Pb vacancy defects form near the valence band edge for the control perovskite surface. (c) Shallow and delocalized Pb vacancy defects are seen for the DETA-passivated perovskite surface. (d) V_{oc} as a function of illumination light intensity for PVSCs without and with PDL treatment. (e) Nyquist plots of PVSCs measured at a bias of 0.1 V under illumination and the equivalent circuit of a planar PVSC with elements representing the recombination resistance (R_{rec}), cell capacitance (C_{tot}), series resistance (R_s), and the stray capacitance (C_{str}).

estimated n of 1.51 and 1.77, respectively, for the PVSCs with and without PDL treatment, which indicates that the PDL treatment could effectively reduce the trap-assisted SRH recombination, which contributes to the improved device performance. Electrical impedance spectroscopy (EIS) is a powerful tool to understand the carrier dynamics in solar cells.⁵⁴ As shown in **Fig. 4e** and **Fig. S14**, the PDL treated PVSC exhibits a much larger recombination resistance (989 Ohms) than that of the control devices (508 Ohms), which indicates the PDL treatment effectively reduces the recombination paths and thus V_{oc} losses. The V_{oc} enhancement of the PDL treated devices could also be related to the formation of a new band structure between the ETL and the perovskite, which forms higher fermi (or quasi-fermi) level and thus increased V_{oc} (see **Fig. S15**). The slightly increased fermi level may attribute to the doping effect of [DETA]⁺.

We also investigated and quantified the efficiency loss of PVSCs without and with PDL treatment by using a modified detailed balance model as described in our previous study⁵⁵. For a $J-V$ curve, our model will adopt the nonlinear Newton's method to retrieve only the three parameters including the non-radiative recombination rate γ , the series resistance R_s , and the shunt resistance R_{sh} . **Fig. S16** depicts the theoretically fitted and experimentally measured $J-V$ curves (with the forward scanning). All the relative fitting errors are below 3% for device A and device B. This small fitting error suggests the modified detailed balance model well captures the device

physics of PVSCs. The fitting results are summarized in **Table 1**. In the case of PDL treated devices, the increase in efficiency can be attributed to the reduced non-radiative recombination rate and improved shunt resistance, which is well consist with experimental results and the first-principle studies of perovskite properties (**Fig. 2** and **Fig. 3**). Consequently, PDL treatment can significantly reduce the defect density and suppress the nonradiative charge recombination in the perovskite in active region, which enables the enhanced performance from the corresponding PVSCs.

Enhanced long-term operational stability

Without the protection of metal electrode, the perovskites in the lateral region can easily react with moisture, which accelerates the degradation of the whole devices by forming iodine-containing compounds.^{26,56} Low dimensional perovskites show higher moisture stability than conventional 3D perovskites.^{57,58} Meanwhile, recent study shows that the low-dimensional perovskites slow ion migration properties. Bearing this in mind, we propose the molecular encapsulation of 3D perovskite of active region by using low-dimensional perovskites (**Fig. 1a**) may be a good strategy to improve the stability of PVSCs. To verify this, the moisture stability of PVSCs was monitored by putting the unencapsulated devices in an ambient atmosphere at room temperature and relative humidity of 50-85%, and the device performances are summarized in **Fig. 5a**. It is clearly that the control devices show

a very fast degradation after exposure to ambient atmosphere. Interestingly, the PDL treated devices retained almost 100% of the initial PCEs after storage in ambient conditions for two weeks. Fig. 5b,5c shows the corresponding XRD results of aged devices. The much slower reduction of the perovskite (110) plane peak and the slower appearance of the PbI_2 peak in the PDL treated PVSCs further demonstrate the better moisture resistance capability enabled by the post-device modification. This result conclusively confirmed that the PDL treatment could effectively improve the moisture stability of PVSCs. The improvement in moisture tolerance will substantially relax encapsulation requirements as demonstrated in Fig. S17. We then investigated the operation stability of unsealed PVSCs by the maximum power point (MPP) tracking. As shown in Fig. 5d,

the control device completely degraded within 100h. In contrast, the LPD treated device maintained ~70% of the initial PCE under 1 sun continuous illumination for 500h. This result reveals that the PDL treatment could also improve the stability of PVSCs under light-soaking and E-bias stress. The post-device passivation enhances the long-term stability of the PVSCs through molecular encapsulation of 3D perovskite of active region achieved by: (i) forming the low-dimensional perovskites in the lateral region, which block the moisture diffusion into the operational region; (ii) forming the low-dimensional perovskites at the interface between 3D perovskites and ETLs, which neutralized and suppressed the ion migration preventing damages to the electrode^{51,56} (see Fig. S18).

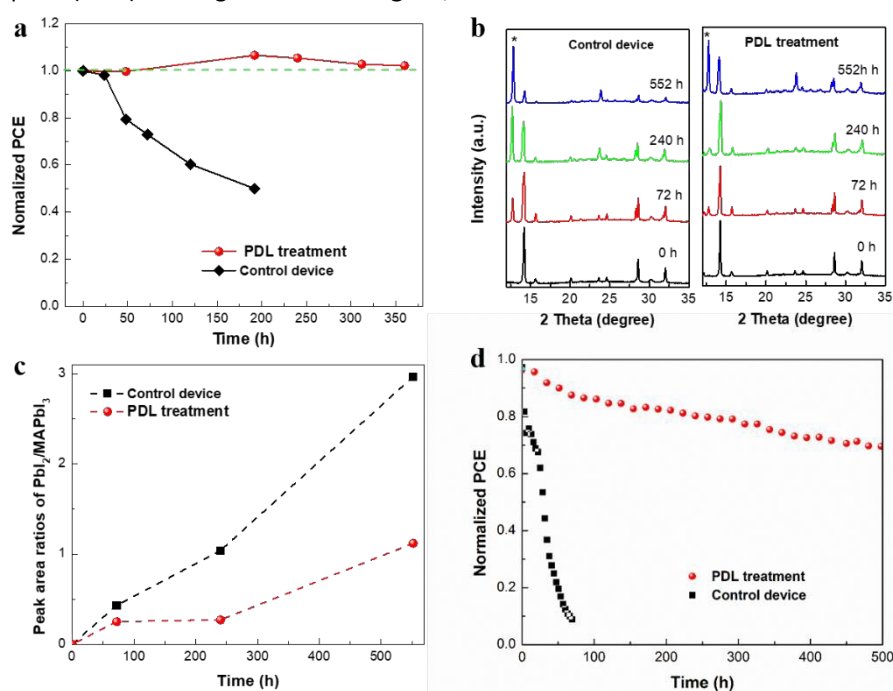


Fig. 5 Stability of PVSCs with and without PDL treatment. (a) Evolution of PCE relative to the initial parameters for the unencapsulated devices with and without PDL treatment over 15 days of storage in air. (b) XRD patterns of the unsealed devices with and without PDL treatment stored in ambient environment for various times. The humidity and temperature are $50 \pm 5\%$ and $25 \pm 1^\circ\text{C}$, respectively. Peaks labelled with asterisk correspond to PbI_2 . (c) Plots of the XRD peak area ratio of the PbI_2 (001) plane to the perovskite (110) plane for the unsealed devices with and without PDL treatment stored in ambient environment as a function of time. (d) Maximum power point (MPP) tracking for 500h of the unencapsulated devices under continuous 1 sun illumination. The humidity and temperature are $50 \pm 5\%$ and $25 \pm 1^\circ\text{C}$, respectively.

Conclusions

In summary, we have demonstrated a novel room-temperature post-device ligand (PDL) treatment to simultaneously improve the performance and stability of completely fabricated PVSCs. Equally important is that this post-device modification shows a special 'stitching effect', namely repairing the as-fabricated 'poor devices' by healing the defects of active region perovskite, which greatly improves the production yield of PVSCs and their module performance. Our theoretical and experimental results offer a fundamental understanding of the performance and stability improvement due to the inhibition of nonradiative charge recombination in the active region and molecular

encapsulation of 3D perovskite of active region, respectively. Furthermore, the PDL treatment, completely separated from the fabrication process of common perovskite devices, provides a general strategy to improve the stability of different completed perovskite devices (e.g., solar cells, light-emitting diodes, and photodetectors).

This work also opens the prospect for other ligands, such as alkylamine, arylamine, and thiols, to be explored as passivators for improving the stability and performance of PVSCs. Dimensionality engineering is also suggested to further improve the device stability via facile design of ligand molecular structure.

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Experimental

Materials. All the chemicals and materials were purchased and used as received unless otherwise noted. $\text{CH}_3\text{NH}_3\text{I}$, $\text{CH}_3\text{NH}_3\text{Br}$, $\text{HC}(\text{NH}_2)_2\text{I}$ (FAI) were purchased from Dyesol and used as received. PbI_2 (99.99%) and PbBr_2 (99.99%) were purchased from TCI. PbCl_2 (99.999%) and CsI (99.9%) were purchased from Sigma Aldrich. NiO_x NCs inks were prepared according to our previous reports^{5, 39, 48}.

Device fabrication. ITO-coated glass substrates were cleaned and then ultraviolet-ozone treated for 20 min. The NiO_x NCs ink (20 mg/mL in DI-water) was spin-coated to obtain 20 nm NiO_x film. The resultant NiO_x films will be used to fabricate devices without annealing process or other treatments. The perovskite solution were prepared by reacting the $\text{CH}_3\text{NH}_3\text{I}$ (190 mg) with PbI_2 (500 mg) and PbCl_2 (30 mg) in anhydrous *N,N*-dimethylformamide (1 ml) at room temperature. To deposit perovskite film, the precursor solution was first dropped onto a NiO_x /ITO substrate. The substrate was then spun at 5000 rpm and after six seconds anhydrous chlorobenzene (180 μl) was quickly dropped onto the center of the substrate, and dried on a hot plate at 100 °C for 10 min. Subsequently, the fullerene mixture (8 mg PCBM + 12 mg C60 in 1mL dichlorobenzene) and zirconium(IV) acetylacetonate (Zracac) (2 mg/mL in anhydrous ethanol) were then sequentially deposited by spin coating at 1000 rpm for 60 s and 4000 rpm for 40 s, respectively. Finally, the device was completed with the evaporation of Ag contact electrodes (120 nm) in a high vacuum through a shadow mask. The $\text{Cs}_5(\text{MA}_{0.17}\text{FA}_{0.83})_{95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ mixed perovskite was prepared according to the previous report¹⁴. For MPP tracking, copper electrode was deposited. All devices were fabricated in glove box.

PDL treatment. The as-prepared PVSCs were covered by a glass petri dish. Around 10 μl diethylenetriamine (DETA) was added at the edge of the petri dish. Since the boiling point of DETA is 204 °C, DETA vaporized the petri dish and modified the perovskite devices moderately at room temperature. The duration of PDL treatment is range from 10 min to 30 min.

Measurement and Characterization. The XRD spectrum was obtained using D5005 X-ray diffraction system ($\text{CuK}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$). UV-vis absorption spectra were obtained from a home-build system with a xenon lamp as a light source and an integrated sphere associated with charge-coupled device (Ocean Optics QE Pro) as a detector. SEM images were recorded using a LEO 1530 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) of perovskite films was measured in the ultrahigh vacuum environment using Physical Electronics PHI 5802 with a monochromatic Al $\text{K}\alpha$ X-ray source. Ultraviolet photoelectron spectroscopy (UPS) were characterized by using a He discharged lamp (He I 21.22 eV, Kratos Analytical). The *J-V* curves were recorded from 0 to 1.2 V using a Keithley 2635 apparatus with scan rate being 0.10 V s^{-1} . Solar-simulated AM 1.5 sunlight was generated using a Newport AM 1.5G irradiation (100 mW/cm^2), calibrated with an ISO 17025-certified KG3-filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1%. To avoid the side edge effect, a black mask with an aperture area of 3.36

mm^2 was employed during the *J-V* measurement. The scan speeds for all *J-V* curves are 0.10 mV/s . The IPCE measurement was performed by a system combining xenon lamp, a monochromator (SpectraPro-2150i, Acton Research Corporation), a chopper, two optical filters (320 and 570 nm), and a lock-in amplifier (SR830, Stanford Research Systems) together with a calibrated silicon photodetector (Hamamatsu mono-Si cell). The impedance measurement was carried out by Zahner electrochemistry station (Zennium Pro) with a DC bias of 0.1 V and a frequency range from 1 Hz and 1 MHz with AC amplitude of 10 mV under illumination with white LED array (100 mW cm^{-2} intensities). The steady-state and time-resolved photoluminescence of perovskite on glass were investigated using PicoQuanta FluoTime 300. A picosecond 375 nm pulse laser (LDH-P-C-375) with a pulse width of <40 ps and a repetition rate of 2 MHz was used to excite the perovskite. The time-resolved single was measured by a time-corrected single photon counting (TCSPC, PicoHarp 300E) module with photomultiplier (PMA-C 192-M) detector. The obtained data were fitted using a bi-exponential function below:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

First-principles calculation

All calculations are performed based on the density functional theory as implemented in the VASP code. For the exchange-correlation functional, we use the generalized gradient approximation (GGA) within the Perdew Burke Ernzerhof (PBE). The plane wave cut-off energy is 500 eV. For the (001) surface of β -MAPbI₃, *k*-points mesh is $4 \times 4 \times 1$ based on Γ point. With the introducing of a vacancy of Pb and the IDEA passivation, the surface is enlarged to $2 \times 2 \times 1$ of the perfect (001) surface and *k*-points mesh is $2 \times 2 \times 1$ based on Γ point.

Conflicts of interest

There are no conflicts to declare.

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Author contributions

W.C. conceived and supervised the project. W.C. and H.Z. conceived the idea and designed the experiment. H.Z. fabricated most of the devices and conducted the characterization. R.X.G. conducted the device simulations. X.W.C. and W.J.Y. conducted the DFT calculations and analyzed the results. J.M. performed the TRPL measurement and assisted the IPCE measurement. J.Q.C. synthesized the NiO_x NCs and assisted the data analysis. Y.Z. assisted the device optimization and stability test. Y.L. and M.J. discussed the results. H.Z., W.C. and M. G. wrote the paper. All authors commented on the manuscript.

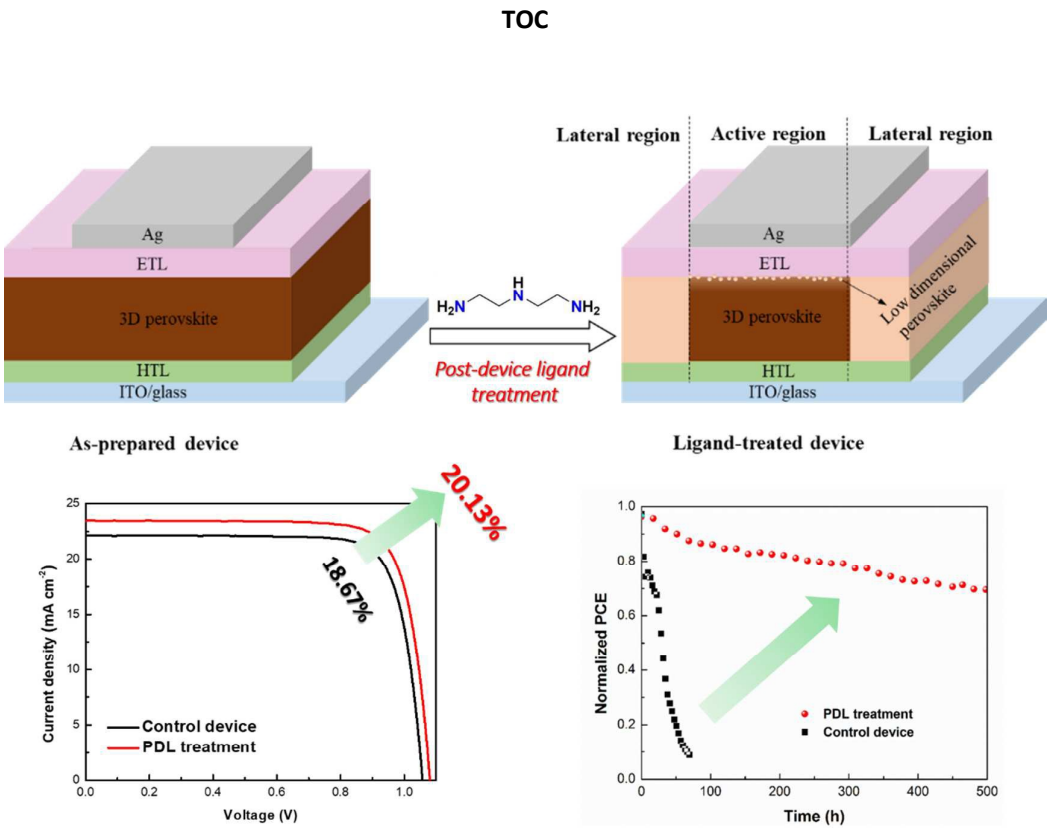
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A simple off-the-shelf post-device ligand treatment is developed to simultaneously improve the performance and air stability of perovskite solar cells as well as repairing the ‘poor device’ for the first time.