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A full range of defect passivation strategy targeting efficient and stable planar perovskite solar cells

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ABSTRACT

Defects and inferior charge transport dynamics within devices are key issues that inhibit the improvements of photovoltaic performance and stability. Developing facile and feasible strategies for synchronous passivation of defects regarding charge transport layers (CTLs), perovskite films and their interfaces, and precise tuning of energy level structure, is a definite way to solve above problems. Herein, we develop a synergistic passivation strategy for perovskite films and bilateral interfaces to improve device performance. Firstly, an appropriate amount of phenylethylammonium chloride is adopted to modify SnO2 electron transport layer (ETL). The complexation reaction between N atoms in $-NH_2$ and Sn^{4+} improve the agglomeration of SnO_2 nanoparticles and film quality of SnO₂ ETL. The presence of Cl^{-} ions not only effectively fill oxygen vacancies within SnO₂ ETL, but also participate in regulating crystal growth dynamics of perovskite films, thus improving electron transport properties at interface. Subsequently, p-type conducting material N,N'-Bis-(1-naphthalenyl)-N,N'-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) is introduced into anti-solvent chlorobenzene during the preparation of perovskite films to further regulate the crystal quality and achieve full-range defect passivation. Particularly, the introduction of NPB helps to construct a gradient heterojunction between upper perovskite film and SpiroOMeTAD hole transport layer, thus reducing the accumulation of hole carriers near interface and further suppressing current-voltage hysteresis behavior of devices. Additionally, the hydrophobicity of NPB and full range of defect passivation greatly enhance the humidity and thermal stability of devices. Finally, a high power conversion efficiency of 21.88% is obtained with suppressed hysteresis and enhanced long-term stability. This work highlights the role of full-range defect passivation on CTLs, perovskite absorption layers and interfacial charge transport properties, which provide a novel concept for constructing high-performance and stable perovskite devices.

1. Introduction

As one of the fastest developing photovoltaic (PV) devices among the third-generation solar cells, polycrystalline perovskite solar cells (PSCs) have received extensive attention by virtue of the excellent optoelectronic properties of the polycrystalline perovskite material itself and the charge transport materials. Meanwhile, diverse as well as easy solution processing methods are gradually providing strong and reliable technical support for the preparation of large-area and even flexible PSCs [1–4]. Currently, the power conversion efficiency (PCE) of *n*-i-p structured organic–inorganic hybrid PSCs has been as high as 25.8%. [5] However, there is still a gap between it and the maximum theoretical efficiency of 35% given by the Shockley–Queisser limit, and its stability is not comparable with that of silicon-based solar cells, which can be mainly ascribed to the problem of defects that limit the further improvements in efficiency and stability.

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The presence of defects in charge transport layers (CTLs), perovskite films and at their interfaces seriously affects the optoelectronic properties of the films, the growth dynamics of polycrystalline perovskite films, and the transport properties of both electrons and holes. For n-i-p planar structured PSCs, the selection and preparation of high-quality ETLs will provide an ideal platform for constructing high-performance devices. Currently, the most commonly used ETLs are selected from metal oxides with excellent *n*-type semiconductor properties, such as titanium dioxide, zinc oxide and tin dioxide (SnO₂) [1,6-9]. Where, SnO₂ ETL has been widely exploited in rigid, flexible and tandem *n*-i-p structured PSCs due to its unique optoelectronic properties, such as high electron mobility, superior chemical stability and low-temperature preparation properties [10–12]. Nevertheless, there is still a great deal of room for improving the crystalline quality as well as the optoelectronic properties for SnO₂ ETLs prepared at low temperatures using commercial SnO₂ aqueous colloidal dispersions. For example, Yang et al. were the first to adopt the chelating agent ethylenediaminetetraacetic acid (EDTA) to improve the aggregation properties of SnO₂ nanoparticles (NPs), and the introduction of such kind of additives could effectively regulate the quality of SnO₂ ETLs as well as the crystal growth dynamics of polycrystalline perovskite films, resulting in the successful preparation of highly efficient and hysteresis-free planar PSCs [13]. Likewise, we have well learnt that the quality of the perovskite films determines the PV performance and long-term stability of the PSCs. However, during the preparation of polycrystalline perovskite films, a large amount of uncoordinated cations/anions will inevitably accumulate at the grain boundaries or on the surface of the films [14-17]. According to Lewis acid-base theory, atoms containing lone pair of electrons in molecules have been proved to complex with uncoordinated ions in the forms of coordination bonds [18,19]. Noel et al. have demonstrated that the introduction of materials containing lone pair of electrons of N, O, S and P atoms, such as thiourea, graphene derivatives, urea and poly(ethylene glycol) diacrylate can participate in the passivation of uncoordinated Pb²⁺ ions when they are introduced into the perovskite precursor solutions [20]. Recently, researchers have developed some synergistic passivation strategies to achieve effective modulation of defects within perovskite films and ETLs. For example, our group has developed a method to achieve the overall improvement in the PV performance and stability of the devices through adding chelating agents containing mobile alkali metal ions in SnO2 aqueous colloidal dispersions [21]. Liu's group and Zhu et al. employed 1,2dichlorobenzene and potassium chloride (KCl) to modify SnO₂ ETLs, respectively [22]. The introduction of Cl⁻ ions can effectively play a role in filling the oxygen vacancies of SnO₂ ETLs, which can further enhance the electron extraction ability of ETLs, and also effectively regulate the nucleation and growth process of polycrystalline perovskites as Cl⁻ ions diffuse into the interior of perovskite films [23]. Moreover, for n-i-p structured planar type PSCs, some synchronous modification strategy at bottom and top interfaces have also been put forwarded, which usually refers to the construction of dual CTLs, or the interfacial modifications by introducing functional organic groups/compounds on the CTLs to enhance the photovoltaic performance of the device [24-27]. So far, schemes for simplified integrated defect passivation within the devices are rare, which will undoubtedly limit the further improvements in device performance. Thus, a full range of defect passivation strategy is strongly desired to achieve high performance and stable PSCs.

Herein, we employ a bilateral interface passivation strategy, including additive addition and anti-solvent post-treatment approach, to systematically regulate the issues of defects that presented within the SnO_2 ETLs, at the surface/grain boundaries of the perovskite films and at their interfaces, while further improving the charge transport dynamics of polycrystalline perovskites to achieve high-performance *n*-i-p (regular) structured planar PSCs. In detail, on one hand, the organic compound phenylethylammonium chloride (PEACI) is first introduced into the SnO_2 aqueous colloidal dispersions, where N atoms containing lone pairs of electrons can complex with Sn^{4+} ions, thus improving the

agglomeration properties of SnO₂ NPs. Meanwhile, the introduction of Cl⁻ ions can effectively fill the oxygen vacancy defects generated during the preparation of SnO₂ films, which can ultimately improve the optoelectronic properties and film formation quality of SnO₂ ETLs [28,29]. In addition, the presence and diffusion of Cl⁻ ions can not only regulate the crystal growth dynamics of perovskite films, but also participate in the defect passivation at their interface and grain boundaries, which will greatly improve the interfacial transport properties of electrons [30,31]. On the other hand, we have learned that the p-type organic highly conductive molecule N,N'-Bis-(1-naphthalenyl)-N,N'-bis-phenyl-(1,1'biphenyl)-4,4'-diamine (NPB) is soluble in chlorobenzene (CB) but insoluble in N, N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), and it also contains N atoms to provide lone pairs of electrons [32]. Therefore, we then introduce NPB into the anti-solvent CB to passivate the defects on the surface and at grain boundaries of the perovskite films during the preparation of perovskite films using a onestep spin-coating method. In this way, the cross-linked distribution of NPB will allow the formation of a gradient heterojunction (GHJ) structure between the upper perovskite film and the hole transport layer (HTL) 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene(SpiroOMeTAD), which will in turn enhance the hole extraction ability at the interface and further improve the hysteresis behavior of the PSCs [33]. Overall, the above-mentioned series of optimization strategies with PEACl modifying SnO2 ETLs and NPB modulating perovskite will ultimately lead to a full range defect passivation within the devices, which will greatly modulate the charge carrier transport and extraction properties, ultimately improving the PV performance and enhancing the thermal stability of the devices. In particular, the good hydrophobicity of NPB molecules will further hinder the penetration of water vapor from the top of the perovskite film to its interior through the grain boundaries, thus enhancing the humidity stability of the devices [34]. As a consequence, after the careful regulation and optimization of the addition content of the above additives, a high PCE of 21.88% can be achieved through co-modifying the Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb (I_{0.85}Br_{0.15})₃ based PSCs with PEACl and NPB, which is higher than that of the pristine and PEACI-SnO2 based counterparts of 19.17% and 20.59%, respectively. Notably, PSCs co-modified with PEACl and NPB also exhibited negligible hysteresis and dramatically enhanced longterm stability, where the PCE of unencapsulated PSCs can still maintain 88.21% after storage at ambient conditions (25 °C, 40 % RH) for 30 days and 81.56% after aging at 85 °C for 200 h in a glove box.

2. Results and discussions

Targeting the full range passivation of the defect states within the devices and the regulation of charge transport dynamics, we have developed a bilateral interface modulation strategy using additives PEACl and NPB. Herein, thermogravimetric analysis (TGA) and differential scanning thermal analysis (DSC) measurements were first carried out under a nitrogen atmosphere with a heating rate of 10 °C/min and a test range from room temperature (25 °C) to 800 °C to evaluate the thermal stability of PEACl and NPB during the fabrication process of PSCs below 150 °C. As shown in Figure S1a, the DSC curve of PEACl exhibits a series of endothermic peaks throughout the entire test range. The peaks located at 122.48 °C and 158.88 °C can be ascribed to the loss of the water molecules adsorbed within PEACl and the corresponding mass loss at 200 °C is only 3.06%. Then we can see that the PEACl starts to decompose at 186.78 °C and completes decomposition at 293.96 °C. Likewise, we also conducted TGA and DSC measurements on NPB under the above measurement conditions, as shown in Figure S1b. We can find that NPB has a high melting point of 277.79 °C, and the mass loss at this temperature is merely 0.46%. And most of the NPB starts to decompose at 503.97 °C and complete the decomposition at 629.64 °C. The higher decomposition temperatures of both PEACl and NPB guarantee that they play a regulatory role throughout the entire fabrication process of PSCs. In particular, the higher stability of the above additives will also

facilitate to improve the thermal stability of PSCs.

Herein, we first introduced different masses of PEACl into the SnO₂ aqueous colloidal dispersions to address some common issues of SnO2 ETLs, such as the presence of pinholes and oxygen vacancy defects [35,36]. Therefore, the following two functions can be expected. On one hand, PEACl can be considered as a Lewis base due to the existence of amino groups, which allows them to well interact with Sn⁴⁺ ions. In order to visually verify the existence of the above-mentioned interactions on a macroscopic point, physical photographs of the corresponding SnO₂ solutions are shown in Figure S2. It can be found that the pristine SnO₂ solution is in a transparent state. On the contrast, with increasing the addition amount of PEACl, especially when it reaches 12 mg, the color of the solution changes to milky white. Such color change reflects the complexation ability of PEACl on SnO₂ solution, implying that different amount of PEACl will bring different improving impacts on the aggregation properties of SnO_2 NPs [37]. On the other hand, the presence of Cl⁻ ions can also effectively fill the oxygen vacancies within the SnO₂ films, which plays a certain role in regulating the optoelectronic properties of SnO₂ ETL as well as in enhancing the quality of the films [38,39].

To investigate the modulation effect of different amounts of PEACl on SnO_2 ETLs, Fig. 1a and b show the optical transmittance spectra and

electrical conductivity plots associated with different PEACl additions. It is apparent that the introduction of PEACl enhances the optical transmittance of SnO₂ ETLs, and the transmittance reaches a maximum when its adding amount reaches 12 mg. Likewise, the electrical conductivity of the above-mentioned films also follows the same variation trend as that of the transmittance. Moreover, to further characterize the electrical properties of the films, we further performed Hall-effect measurements on the above samples. Where, the resistivity, conductivity and mobility of these films were given in Table S1. We can see that the introduction of appropriate amount of PEACl can enhance the conductivity and mobility of SnO₂ films to a certain extent, which is consistent with the variation trends obtained from the J-V characteristic curves in Fig. 1b. Then we named the 12 mg PEACl-modulated sample with the optimum optoelectronic properties as the PEACl-SnO₂ film. To better investigate the surface morphology and the distribution of each elemental component of the SnO₂ films with and without PEACl treatment, we subsequently collected scanning electron microscopy (SEM), energy dispersive X-ray (EDS) and elemental mapping images of the pristine and PEACI-SnO₂ films, as presented in Figure S3. Compared with the pristine films, the PEACI-SnO₂ films exhibit a more homogeneous and denser surface morphology. However, with further increase the addition amount, the overly sufficient complexation can seriously



Fig. 1. (a) Optical transmittance spectra of ITO, pristine and PEACl-SnO₂ films with different addition amounts of PEACl. (b) Current-voltage (I-V) characteristic curves of pristine and PEACl-SnO₂ films with different addition amounts of PEACl. (c) FTIR spectra of PEACl powder, pristine and PEACl-SnO₂ based aqueous colloidal dispersions. (d) Schematic diagram of the crystal structures of PEACl, SnO₂ and the interaction between them. (e) Schematic diagram of the crystal structures of perovskite, NPB and the interaction between them. (f) Optical absorbance spectra of pristine and PEACl-SnO₂ based films with Tauc plots inset. UPS spectra of SnO₂ film in (g) valence-band edge region and (h) secondary electron cut-off edge. UPS spectra of PEACl-SnO₂ film in (i) valence band edge region and (j) secondary electron cut-off edge.

impair the film-forming quality of the SnO₂ films, especially for the homogeneity, which in turn leads to the degradation of the optoelectronic properties of the SnO₂ ETLs.

To unveil the interaction between PEACl and SnO₂, the Fourier transform infrared (FTIR) spectra of PEACl powder, pristine and PEACl-SnO₂ based aqueous colloidal dispersions were recorded. As shown in Fig. 1c, we can see that the vibration of sn-O and O-sn-O peaks in the PEACl-SnO₂ solution shifts to 950.9 cm⁻¹ and 621.4 cm⁻¹ compared with the locations of 944.1 cm^{-1} and 607.7 cm^{-1} in the pristine solution. Meanwhile, the N-H vibration peak in the PEACl molecule appears at 692.4 cm⁻¹, firmly indicating that some interaction between PEACl and SnO₂ happens [40]. Subsequently, X-ray photoelectron spectroscopy (XPS) measurement technique was used to further probe the interaction between PEACl and SnO₂. From the Sn 3d and O 1s core-level XPS spectra presented in Figure S4a-c, we can observe that the binding energy of the Sn 3d peak in the PEACl-SnO₂ is higher than that of pristine one. Accordingly, the binding energy of O 1s peak in the PEACl-SnO₂ shifts to a lower binding energy with respect to that in the pristine one. These phenomena further proves that the complex reaction occurs between the Sn⁴⁺ ions in SnO₂ and the N atom in the amino group in PEACl, which would lead to the shift of shared pairs of electrons between the Sn and O atoms. In addition, a Gaussian-Lorentzian fitting was carried on the O 1s XPS spectra and the detailed parameters are presented in Table S2. It can be seen that the percentage of peaks associated with hydroxyl/oxygen vacancies is reduced in the PEACl-SnO₂ sample in comparison with that of pristine one, which verifies the deduction that the Cl⁻ ions in PEACl can effectively occupying the oxygen vacancies of SnO₂. Meanwhile, we also detected N 1s and Cl 2p signals in the XPS spectra on PEACl-SnO₂ based film, as presented in Figure S4d and e. To more visually illustrate the interaction, the chemical structure of PEACl and the schematic diagram of the interaction between PEACl and SnO₂ NPs are presented in Fig. 1d. All above analyses confirmed the successful modulation of SnO₂ by PEACl.

To investigate the changes in the energy level structure, the ultraviolet photoemission spectroscopy (UPS) measurements were further performed on the pristine and PEACI-SnO₂ ETLs. Fig. 1f-j show the UPS spectra of both films. The work function (WF) can be obtained by subtracting the cut-off energy of the secondary electrons using the excitation energy of He I. The Fermi levels (E_F) of the pristine and PEACI-SnO₂ ETLs are determined to be -4.39 eV and -4.31 eV, respectively [11]. In addition, the valence band edge (VBE) and conduction band edge (CBE) can be determined with the help of the Tauc curves as well as the valence band region of the UPS spectra. As a result, the PEACI-SnO₂ exhibits a more upshifted CBE (-4.18 eV) with respect to that of -4.29 eV of the pristine one, which in turn achieves a more precise alignment with the CBE of perovskite film. It is more conducive to the efficient extraction of electron carriers at the interface, thus significantly contributing to the increase in open-circuit voltage (V_{OC}) of the PSCs.

In order to further realize full range defect passivation within polycrystalline perovskite films, such as uncoordinated Pb²⁺ ions and iodine vacancy defects existing on the surface and grain boundaries of perovskite films, as well as the modulation of hole carrier transport properties, we introduced a highly conductive p-type additive of NPB into antisolvent chlorobenzene (CB) to prepare high-quality polycrystalline perovskite films [41,42]. Subsequently, we characterized the effects of different masses of NPB on the surface morphology and crystal nucleation dynamics of perovskite films spin-coated on pristine and optimized PEACl-SnO₂ ETLs, respectively. Firstly, as can be seen from the SEM images in Fig. 2a-e, the surface morphology of the perovskite films gradually becomes blurred with increasing the amount of NPB which can be attributed to both the extensive distribution of NPB films on the surface of perovskite films and their penetration to the grain boundaries, since they are involved in the whole growth dynamics of polycrystalline perovskite films [43]. In addition, we have also found that all modified perovskite films exhibited enlarged grain size and reduced pinholes, and the perovskite films shows the optimal surface morphology when the amount of NPB reached 0.6 mg/ml. Similarly, the results of the statistical distribution of grain size of the aforementioned perovskite films are also presented in Figure S5. It can be seen that the perovskite film posttreated with 0.6 mg/ml NPB exhibits the largest grain size as well as the most uniform size distribution. Fig. 2f-j presents the cross-sectional SEM images of pristine, PEACl-SnO2 and PEACl-SnO2 based PSC post-treated with different concentrations of NPB in CB with the device structures of ITO/SnO₂(PEACl-SnO₂)/perovskite(perovskite-NPB)/SpiroOMeTAD/ Ag. All the modified perovskite films exhibit well-grown large grain with



Fig. 2. Top-view SEM images of (a) pristine, (b) PEACI-SnO₂, (c) PEACI-SnO₂-NPB (0.3 mg/ml), (d) PEACI-SnO₂-NPB (0.6 mg/ml) and (e) PEACI-SnO₂-NPB (1 mg/ml) based perovskite films. Cross-sectional SEM images of (f) pristine, (g) PEACI-SnO₂, (h) PEACI-SnO₂-NPB (0.3 mg/ml), (i) PEACI-SnO₂-NPB (0.6 mg/ml) and (j) PEACI-SnO₂-NPB (1 mg/ml) based perovskite films. AFM images of (k) pristine, (l) PEACI-SnO₂, (m) PEACI-SnO₂-NPB (0.3 mg/ml), (n) PEACI-SnO₂-NPB (0.6 mg/ml) and (o) PEACI-SnO₂-NPB (1 mg/ml) based perovskite films.

no obvious cracks. Among them, the perovskite films spin-coated on PEACI-SnO2 ETL and post-treated with 0.6 mg/ml NPB (PEACI-SnO2-NPB (0.6 mg/ml)) possess dense morphology and well-crystallized large grains through the whole spatial region, which can be attributed to the co-modulation effect of PEACl and NPB on the crystal growth dynamics of polycrystalline perovskites, and thus facilitating the efficient transport and separation of charge carriers within the perovskite films. We also recorded atomic force microscopy (AFM) images of the corresponding perovskite films to further investigate the changes in the surface morphological characteristics. As presented in Fig. 2k-o, the PEACl-SnO₂-NPB (0.6 mg/ml) based perovskite film exhibits relatively small roughness with the root mean square (RMS) of 13.5 nm, while the RMS for pristine SnO₂, PEACl-SnO₂, PEACl-SnO₂-NPB (0.3 mg/ml) and PEACl-SnO₂-NPB (1 mg/ml) based perovskite films is 21.1 nm, 18.1 nm, 15.3 nm and 19.7 nm, respectively. The smoother surface morphology greatly improves the interfacial contact between the upper perovskite film and SpiroOMeTAD HTL, which will facilitate the enhancement of hole carrier extraction characteristics [44]. The impacts with or without NPB anti-solvent post-treatment method on the surface properties of perovskite films are further probed by Kelvin probe force microscopy (KPFM) [45,46]. Here, we named 12 mg/ml NPB post-treated perovskite films as perovskite-NPB. Where, the corresponding surface potential images are presented in Figure S6, and we can see that the introduction of NPB has a great impact on the surface work function of the perovskite films. The average surface potentials values of pristine and perovskite -NPB films are -865.1 mV and -925.3 mV as the same positions we selected in the above two images, respectively. We have learnt that along with the increasing of average surface potential, the quasi-Fermi levels will also upshifted, which will minimize the difference of energy levels between perovskite film and SpiroOMeTAD hole transport layer [47]. This phenomenon is beneficial to the enhancement of hole extraction and transport properties within PSCs, and further indicating the reduced trap states near the surface of perovskite films after the NPB post-treatment.

The X-ray diffraction (XRD) patterns of the corresponding perovskite films are presented in Figure S7a. Three major peaks of (101), (202)

and (211) crystal planes appeared without observing other impurity peaks for all films, indicating the formation of the pure black-phase perovskite structure. The diffraction peak intensities of co-modified perovskite films are the strongest when the amount of NPB reached 0.6 mg/ml, which exhibits good agreement with the results presented in the SEM images. Here we would like to point out that a PbI2 peak located at 12.65° can be observed in the XRD pattern of PEACl-SnO₂ based perovskite film, which is caused by the excess amount of PbI2 used during the preparation of perovskite films. But the diffraction peak intensity of PbI2 gradually decreases until disappears with the increase of NPB concentration. Accordingly, the variation tendency of UV-vis absorption spectra in Figure S7b is similar with the XRD results. However, all the perovskite films exhibit similar absorption edges, indicating that the introduction of NPB does not change the band gap of perovskite films. The results of SEM, AFM and XRD characterizations prove that 0.6 mg/ml is the optimized concentration for NPB to modulate perovskite films in our case. Thus, in the following part, we named the PEACI-SnO₂-NPB (0.6 mg/ml) as the PEACl-SnO₂-NPB.

Subsequently, we utilized FTIR and XPS techniques to further probe the effect of NPB post-treatment strategy on the perovskite films. As shown in the FTIR spectra in Fig. 3a, the stretching vibrations of benzene ring around 1500 cm⁻¹ can be found in both NPB powder and PEACl-SnO₂-NPB based perovskite films compared with that of the pristine one, which can well verify the extensive distribution of NPB within the perovskite films. From the high-resolution XPS spectra of Pb 4f and I 3d of the pristine and PEACl-SnO2-NPB based perovskite films present in Fig. 3b and c, we can see that the binding energies of Pb $4f_{7/2}$ and Pb $4f_{5/2}$ 2 of the PEACl-SnO₂-NPB based perovskite films shift from 138.56 eV and 143.42 eV for the pristine one to lower binding energies of 138.39 eV and 143.25 eV, respectively. Likewise, the binding energies of I 3d_{5/2} and I 3d_{3/2} of the PEACl-SnO₂-NPB based perovskite films shift from 619.02 eV and 630.51 eV for the pristine one to lower binding energies of 618.69 eV and 630.18 eV, respectively. According to Lewis acid-base theory, we can ascribe the binding energy shift of both Pb and I peaks to the interaction between N atoms in NPB and uncoordinated Pb²⁺ ions (Fig. 1e), since the N atoms containing lone pairs of electrons in NPB



Fig. 3. (a) FTIR spectra of NPB powder, pristine and PEACl-SnO₂-NPB based perovskite films. High-resolution (b) Pb 4f and (c) I 3d XPS spectra of pristine and PEACl-SnO₂-NPB based perovskite films. (d) Schematic diagram of the device structure. (e) Champion J-V curves of pristine, PEACl-SnO₂ and PEACl-SnO₂-NPB based PSCs measured under reverse and forward scanning directions. (f) EQE spectra of the corresponding PSCs.

molecules can interact with metal ions containing empty orbitals through coordinate bonds, which will reduce the density of defect states within the PSCs [48]. In addition, this interaction also effectively modulate the crystal growth dynamics of polycrystalline perovskites, particularly in terms of retarding the crystallization rate, which is consistent with the results of enlarged grain size and enhanced crystallinity obtained in the above SEM and XRD sections [49]. High PV performance and reduced hysteresis behavior of the devices can be expected due to all these improvements.

Fig. 3d shows a schematic diagram of the device structure with ITO/ $PEACl-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACl-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACl-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACl-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACl-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACL-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACL-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACL-SnO_2/Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})_3-NPB/Spi-Delta PEACL-SnO_2/Cs_{0.95}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}FA_{0.85}$ roOMeTAD/Ag, including a diagram of NPB penetration through the grain boundaries into the interior of perovskite film. Subsequently, we present the current density-voltage (J-V) characteristic curves of the pristine, PEACl-SnO₂ and PEACl-SnO₂-NPB based champion PSCs measured under reverse scan (RS) and forward scan (FS) directions in Fig. 3e. The detailed PV parameters are summarized in Table 1. In addition, Figure S8 and Table S3 show the additional J-V curves of the PSCs with NPB post-treatment under different concentrations from 0.3 mg/ml to 1 mg/ml, where the highest PCE is obtained without surprise when the concentration of NPB reaches 0.6 mg/ml. As shown in Table 1, the best PCEs of 19.17% and 20.59% can be obtained for the pristine and PEACl-SnO₂ based PSCs, respectively. While, the PEACl-SnO₂-NPB based devices exhibits a short-circuit current density (Jsc) of 23.66 mA/ cm^2 , a V_{OC} of 1.16 V and a fill factor (FF) of 79.34%, resulting in a PCE of 21.88%. Fig. 3f further illustrates the external quantum efficiency (EQE) spectra of the pristine, PEACl-SnO2 and PEACl-SnO2-NPB based champion PSCs, and we can see that it yields an integrated JSC of 23.04 mA/ cm² for the PEACI-SnO₂-NPB based device, which is superior to that of 21.62 mA/cm² and 22.11 mA/cm² for the pristine and PEACl-SnO₂ based ones. In addition, all Jsc values match well with the results obtained from the J-V curves. Subsequently, we calculate the hysteresis index (HI) of the devices using the equation $HI = (PCE_{reverse}-PCE_{forward})/$ $\text{PCE}_{\text{reverse}},$ where the HI of the pristine, PEACl-SnO_2 and $\text{PEACl-SnO}_2\text{-}$ NPB based devices decrease from 5.79% to 4.32% and 2.68%, respectively [50].

Based on the above analysis, the improved PV performance and the suppressed hysteresis behavior of the modified PSCs should be ascribed to the full range of defect passivation within the devices and the optimization of carrier transport properties at the ETL/perovskite and perovskite/HTL interfaces [51–53]. To evaluate the density of defect states within the devices, we subsequently perform the space-charge limited current (SCLC) measurements. The SCLC curves in Fig. 4a and b are respectively obtained using electron-only devices with the architecture of ITO/SnO₂(PEACl-SnO₂)/perovskite/PCBM/Ag and hole-only ITO/PEDOT:PSS/perovskite(perovskite-NPB)/ devices with SpiroOMeTAD/Ag under dark conditions to further assess the trap density (Nt) of the perovskite films as well as at the interface with ETL and HTL. By using the equation $N_t = 2\epsilon_0\epsilon_r V_{TFL}/(eL^2)$, the N_t of the pristine and PEACI-SnO2 based electron-only devices can be calculated to be $1.35\times 10^{16}\,cm^{-3}$ and $9.78\times 10^{15}\,cm^{-3}$, respectively, where $\epsilon_0,\epsilon_r,$ V_{TFL} e and L correspond to the vacuum permittivity (8.8 \times $10^{-12}\mbox{ F}$ m⁻¹), the relative dielectric constant of perovskite (62.23), trap filled limit voltage, elementary charge (1.6 \times 10⁻¹⁹ C) and thickness of

Table 1

Detailed PV parameters of pristine, $\rm PEACl-SnO_2$ and $\rm PEACl-SnO_2\text{-}NPB$ based champion PSCs measured under different scanning directions.

Device	Direction	Jsc (mA/ cm ²)	Voc (mV)	FF (%)	PCE (%)
Pristine	RS	22.99	1105	75.47	19.17
	FS	22.69	1090	73.01	18.06
PEACl-SnO ₂	RS	23.35	1136	77.61	20.59
	FS	23.11	1128	75.56	19.70
PEACl-SnO ₂ -	RS	23.69	1163	79.42	21.88
NPB	FS	23.48	1160	78.31	21.33

perovskite layer (450 nm), respectively [54]. Likewise, the N_t of holeonly devices prepared on pristine and NPB post-treated perovskite films is 1.41×10^{16} cm⁻³ and 1.71×10^{16} cm⁻³, respectively. Obviously, it is easy to deduce that the co-modulation of PEACl and NPB results in a decrease in the defect density throughout the devices, which contributes to the reduction of the non-radiative recombination losses and the enhancement of V_{OC} in PSCs [55,56].

Steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements are employed to probe the charge carrier transport/ recombination dynamics. As shown in Fig. 4c, for the perovskite films deposited on ITO/SnO₂ and ITO/PEACl-SnO₂ substrates, a significant PL quenching happens in the perovskite films deposited on ITO/PEACl-SnO₂ substrates, which is caused by the better matching of CBE between PEACl-SnO₂ ETL and perovskite film, the enhanced crystalline quality of both perovskite and SnO₂ films, as well as the passivation of the interfacial defect states, so that ultimately promotes the effective extraction of electron carriers at the interface [57,58]. Moreover, the PL intensity of the NPB post-treated perovskite films prepared on quartz glass substrates is significantly reduced with respect to that of the pristine perovskite one, which mainly reflects that NPB can promote the effective transport of hole carriers from perovskite film to NPB by virtue of its good p-type conducting properties. Meanwhile, we also find that the emission peak of the NPB post-treated film deposited on quartz glass is blue-shifted from 764.2 nm to 761.3 nm, which demonstrates that the defect states within the perovskite films can be effective reduced by adopting NPB post-treatment method [59]. As presented in Fig. 4d, all PL decay curves are fitted by the bi-exponential decay function I = $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where A_1 and A_2 are the relative decay amplitudes, and τ_1 and τ_2 correspond to the fast and slow decay lifetimes, respectively [60]. The detailed fitting parameters were summarized in Table S4. The variation tendency of decay time exhibits good agreement with the results of PL spectra, further proving the improvement of both the electron and hole transport properties within PSCs by the PEACl and NPB co-modulation strategy.

Electrochemical impedance spectroscopy (EIS) measurement is further performed to investigate the charge carrier transport and recombination dynamics within the PSCs [61]. Fig. 4e shows the Nyquist plots of pristine, PEACI-SnO2 and PEACI-SnO2-NPB based PSCs obtained under dark conditions with the bias voltage set to 0 V during the measurements. A simulated equivalent circuit containing series resistance (R_s), transfer resistance (R_{tr}) and recombination resistance (R_{rec}) is adopted to fit the above plots, which is shown in the inset, and the corresponding detailed parameters are summarized in Table S5. It can be seen that the R_s and R_{tr} of the PEACl-SnO₂-NPB based PSC are 15.5 Ω and 345.1 Ω , respectively, while the R_s and R_{tr} of the pristine and PEACl-SnO₂ based devices are 28.57 Ω and 631.43 Ω , and 23.56 Ω and 456.7 Ω , respectively. Such variation trend indicates that the usage of PEACl and NPB not only improves the quality of the SnO₂ ETLs and perovskite films, but also modulates the interfacial properties between the perovskite films and the CTLs, thus greatly improving the charge transport properties within the devices [62]. Likewise, a higher R_{rec} (4554.6 Ω) can also be obtained in the PEACI-SnO2-NPB based device compared with that of 2337.6 Ω and 3145.1 Ω in the pristine and PEACl-SnO₂ based counterparts, which indicates that the non-radiative recombination process is effectively suppressed due to the full range of defect passivation within the devices by PEACl and NPB co-modification [63].

As shown in Fig. 4f, we further investigate the dependence of V_{OC} on the light intensity. Based on the equation $V_{OC} = nkTln(I)/q$, we learnt that the degree of slope deviation from kT/q is closely associated with the trap-assisted recombination within the PSCs [64]. In addition, by investigating the charge carrier recombination dynamics of Shockley-Read-Hall (SRH), we can conclude that the concentration of trap states within the devices increases with the slope when the slope exceeds 1. As a result, trap-assisted recombination within PEACl-SnO₂-NPB based PSCs was effectively suppressed since its slope (1.35 kT/q) is smaller than that of the pristine (1.73 kT/q) and PEACl-SnO₂ (1.49 kT/



Fig. 4. (a) Dark I-V characteristics of the pristine and PEACI-SnO₂ based electron-only devices with structure of ITO/SnO₂(PEACI-SnO₂)/perovskite/PCBM/Ag (b) Dark I-V characteristics of pristine and perovskite-NPB based hole-only devices with structure of ITO/PEDOT:PSS/perovskite(perovskite-NPB)/SpiroOMeTAD/Ag. (c) PL and (d) TRPL spectra of perovskite films deposited on ITO/SnO₂ and ITO/PEACI-SnO₂ substrates, and pristine and NPB post-treated perovskite films deposited on the quartz glass substrates. (e) Nyquist plot of pristine, PEACI-SnO₂ and PEACI-SnO₂-NPB based PSCs with fitting model inset. (f) Light-intensity dependent V_{OC} characteristics of the above PSCs. (g) Dark J-V curves of the corresponding PSCs.

q) based ones, which is consistent with the above characterization results related to the defect states [65]. The dark J-V characteristic curves of corresponding PSCs are presented in Fig. 4g to further investigate the charge recombination process and the variation of V_{OC}. By using the equation $ln(J_{SC}/J_0) = qV_{OC}/nkT$, we can obtain the ideality factor (n) and the saturation current density (J₀) of the devices from the linear part of the curves, where the elemental charge q, Boltzmann constant k and temperature T are fixed values [66,67]. After calculations, the n and J₀ of PEACl-SnO₂-NPB based device is 1.68 and a of 1.87×10^{-10} mA/cm², respectively. But the n and J₀ for the pristine and PEACl-SnO₂ based devices is 1.77 and 1.73, 8.91×10^{-9} mA/cm² and 9.41×10^{-9} mA/cm², respectively. All these results further proved that we can achieve both the reduction in charge recombination and the increase in V_{OC} due to the full range passivation of defect states within the PEACl-SnO₂-NPB

based devices.

Since the energy band alignment is another key factor in determining the charge transport behaviors, we further adopt UPS measurements to characterize the energy level change of perovskite films before and after NPB post-treatment, and corresponding UPS spectra are shown in Fig. 5a-e. We calculate the E_F , VBE and CBE of the corresponding perovskite films and obtained the band gap values of the films from the UV–vis absorption curves provided in Fig. 5f. Where, the VBE of the NPB post-treated perovskite film (-5.58 eV) lies between that of the pristine film (-5.78 eV) and the highest occupied molecular orbital (HOMO) of the SpiroOMeTAD layer (-5.20 eV), indicating that the cross-linked ptype NPB can provide a more favorable transport pathway for the migration of hole carriers and further improve the extraction efficiency at the interface by forming GHJ between the upper perovskite layer and



Fig. 5. UPS spectra of pristine perovskite film in (a) valence band edge region and (b) secondary electron cut-off edge.(c) Full UPS spectra of pristine and NPB post-treated perovskite film. UPS spectra of NPB post-treated perovskite film in (d) valence band edge region and (e) secondary electron cut-off edge. (f) Tauc plots derived from the UV–vis spectra of pristine and NPB post-treated perovskite films. Energy level schematic diagrams of (g) pristine and (h) PEACl-SnO₂-NPB based PSCs. (i) Mott-Schottky curves of the above PSCs. (j) Light-intensity dependent V_{OC} characteristics of the above PSCs.

SpiroOMeTAD due to the penetration of NPB, which is also the main reason for the enhanced V_{OC} of PSCs [68]. Combining the UPS results in Fig. 1 and Fig. 5, the advantages of bilateral interface modulation are more visually demonstrated in Fig. 5g and h by comparing the energy band alignment of PSCs before and after PEACl and NPB modulation. Therefore, the full range defect passivation, the precise alignment of energy levels induced by the bilateral modulation via PEACl and NPB greatly reduce the interfacial non-radiative recombination of the charge carriers within the PSCs and improve the transport dynamic properties of charge carriers.

In order to further investigate the regulatory mechanisms of the above optimization on the interfacial charge transport properties as well as the regulation on boosting V_{OC} of the devices, we further investigate the variations of the interfacial charge defects as well as the built-in potential (Vbi) of the PSCs by capacitance-voltage (C-V) measurements with a fixed frequency of 1 k HZ and a bias potential range of 0 V to 1.2 V. The corresponding Mott-Schottky curves for all the above PSCs are presented in Fig. 5i. We can see that both PEACl-SnO₂ and PEACl-SnO₂-NPB based devices exhibit relatively larger slopes than that obtained in the pristine one, demonstrating that an effective reduction in the interfacial charge density can be achieved after co-modification, which in turn suppresses the charge accumulation at the ETL/perovskite and perovskite/HTL interfaces to reduce the hysteresis of PSCs [69]. In addition, we can also obtain V_{bi} from the intersection of the linear part of the C-V curves with the X-axis. The PEACl-SnO₂-NPB based device shows a V_{bi} of 1.06 V, slightly higher than that of 1.04 V and 1.02 V of the PEACI-SnO₂ and pristine based ones, which facilitates the device to achieve a higher V_{OC} [70]. Transient photovoltage (TPV) decay curves are further shown in Fig. 5j. The PEACl-SnO₂-NPB based PSCs exhibits a longer lifetime of 3.24 μs than that of 2.33 μs and 2.67 μs for the pristine and PEACl-SnO2 based counterparts, which further demonstrates that the charge carrier recombination within PEACl-SnO₂-NPB based devices is effectively suppressed due to the realization of full range of defect passivation and the more matched energy level structure within the devices.

To further verify the repeatability of co-modulation effect on PSCs, 20 individual devices for each PSCs are fabricated. The distribution of corresponding PV parameters is summarized in Figure S9a-d. The PV parameters in the PEACl-SnO₂-NPB based devices exhibit higher mean values and narrower distributions compared with those in the pristine and PEACl-SnO₂ based ones, indicating that the improved PV performance through the above bilateral interface regulation strategies is repeatable.

The presence of a large number of NPB molecules at the grain boundaries and on the upper surfaces of the perovskite films would greatly enhance the moisture resistance of polycrystalline perovskite films due to the inherent good hydrophobic properties of the NPB molecules. To further verify this assumption, we then perform the water contact angle measurements on these perovskite films. As presented in Figure S10a-c, it can be seen that the contact angle of the PEACl-SnO₂-NPB based perovskite film of 86.7° is higher than that of 56.3° and 64.8° of the pristine and PEACl-SnO₂ based ones, which is beneficial to inhibit water vapor penetration into the perovskite films to improve the stability of PSCs. In addition, the steady-state PCE output curves of the PSCs are also obtained at the maximum power point voltage (Vmpp), which have been shown in Figure S11a. Apparently, the PEACl-SnO₂-NPB and PEACl-SnO₂ based champion devices can still respectively achieve higher steady-state PCEs of 21.37% and 19.94% than 18.51% for the pristine one after the continuous illumination of 200 s. Meanwhile, the saturation times of co-modified PSCs is relatively short, which is consistent with the negligible hysteresis behavior obtained in the J-V curves [71].

In addition, we store the unencapsulated PSCs at ambient conditions of 40% relative humidity (RH) and 25 °C for 30 days to further examine the variations in the humidity stability of these PSCs. As shown in Figure S11b, it can be found that the PEACI-SnO₂-NPB based PSC maintained 88.21% of the initial PCE, which is higher than that of pristine (64.32%) and PEACI-SnO₂ (78.51%) based counterparts. Furthermore, the thermal stability of the unencapsulated PSCs is also examined on a hot plat at 85 °C in a glove box. As shown in Figure S11c, the PCE of the PEACI-SnO₂-NPB based device decreases to 81.56% of the initial PCE after 200 h of aging time, while the pristine and PEACI-SnO₂ based ones can only maintain 71.93% and 59.61% of the initial PCE, respectively. The improved stability of PEACI-SnO₂-NPB based device can be attributed to the full range defect passivation, the inherent good hydrophobic properties of NPB, as well as the higher thermal stability of both additives, which is undoubtedly crucial for the overall improvement of photovoltaic performances of PSCs.

3. Conclusion

In summary, we have designed a full range of defect passivation strategy via bilateral interface modulation by PEACl and NPB to realize synergistic regulation of PV performance as well as long-term stability of PSCs. Such full range of defect passivation strategy has been proved to successfully work as the following functions in the PSCs. Firstly, the adding of PEACl in the SnO₂ aqueous colloidal dispersion can improve the crystal quality of the SnO₂ ETL and modulate its energy level structure, which not only enhances the extraction ability of electron carriers at the interface, but also improves the crystalline quality of perovskite films with the help of Cl⁻ diffusion. Secondly, the introduction of NPB via anti-solvent procedure can form a cross-linked distribution on the surface and at grain boundaries of the perovskite films, which further suppresses the non-radiative recombination within perovskite films. Moreover, its good p-type conductivity also allows the formation of a GHJ structure between the upper perovskite film and SpiroOMeTAD HTL, which also provides a convenient channel for the effective migration and transport of hole carriers. As a result, a high PCE of 21.88% with a large V_{OC} of 1.163 V can be achieved for PEACl-SnO₂-NPB based PSCs. Finally, given the excellent hydrophobic properties of the NPB molecules, the high decomposition point, and the full range of passivation of defects within the devices, PEACl-SnO2-NPB based device exhibits improved moisture and heat tolerance, which improves the long-term operational stability of the devices. Our research highlights the guiding role of full range of defect passivation strategies to improve the PV performance and long-term stability of PSCs, which will pave the way for the commercialization of PV devices, especially for flexible and large-scale manufactured devices.

4. Supporting Information.

Details of experimental methods for PSCs fabrication along with characterizations including TG and DSC curves of PEACl and NPB powders; Physical diagrams of pristine and PEACl modified SnO₂ precursor solutions; Hall-effect measurements, SEM, mapping and EDS images of pristine and PEACl modified SnO2 films; KPFM images of pristine and 0.6 mg/ml NPB post-treated perovskite films, XPS spectra of pristine and PEACl modified SnO2 films; Statistical graph of grain size distribution of pristine, $\ensuremath{\text{PEACl-SnO}}_2$ and $\ensuremath{\text{PEACl-SnO}}_2\ensuremath{\text{-NPB}}$ based perovskite films; XRD and UV-vis spectra of pristine, PEACl-SnO2 and PEACI-SnO₂-NPB based perovskite films; J-V characteristic curves modified with different concentrations of NPB; Statistics box plot of PV parameters of pristine, PEACI-SnO2 and PEACI-SnO2-NPB based PSCs; Water contact angle measurements on pristine, PEACI-SnO2 and PEACI-SnO₂-NPB based perovskite films; Steady-state PCE, long-term and thermal stability of pristine, PEACl-SnO2 and PEACl-SnO2-NPB based PSCs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

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