

Quenching Detrimental Reactions and Boosting Hole Extraction via Multifunctional NiO_x/Perovskite Interface Passivation for Efficient and Stable Inverted Solar Cells

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Nickel oxide (NiO_x) is one of the most promising hole transport materials for inverted perovskite solar cells (PSCs). However, its application is severely restrained due to unfavorable interfacial reactions and insufficient charge carrier extraction. Herein, a multifunctional modification at the NiO_x/perovskite interface is developed via introducing fluorinated ammonium salt ligand to synthetically solve the obstacles. Specifically, the interface modification can chemically convert detrimental Ni^{≥3+} to lower oxidation state, resulting in the elimination of interfacial redox reactions. Meanwhile, interfacial dipole is incorporated simultaneously to tune the work function of NiO_x and optimize energy level alignment, which effectively promotes the charge carrier extraction. Therefore, the modified NiO_x-based inverted PSCs achieve a remarkable power conversion efficiency (PCE) of 22.93%. Moreover, the unencapsulated devices obtain a significantly enhanced long-term stability, maintaining over 85% and 80% of the initial PCEs after storage in ambient air with a high relative humidity of 50–60% for 1000 h and continuous operation at maximum power point under one-sun illumination for 700 h, respectively.

1. Introduction

Organic-inorganic halide perovskite solar cells (PSCs) have been considered as one of the most promising candidates for the next generation photovoltaic technologies, due to their remarkable photoelectric properties including high light absorption, long

charge carrier diffusion length, superior charge carrier mobility, and tunable energy bandgap.^[1–4] In the past years, PSCs have shown extraordinary growth with the power conversion efficiency (PCE) raised from the initial 3.8% to a certified 25.7%.^[5,6] During this progress, various strategies are developed to acquire high-performance PSCs such as defect passivation, composition optimization as well as charge transport layer (CTL) engineering.^[7–11] Especially, the selection and regulation of CTLs involving interfacial defects, carrier extraction, energy level alignment, and interaction between perovskite light-absorber,^[12–15] have proved to markedly influence both the performance and stability of PSCs.

Numerous charge transport materials have been investigated such as organic molecules or polymers,^[16,17] self-assembled monolayers,^[18] and metal oxide semiconductors;^[19,20] among all of

them, nickel oxide nanoparticles (NiO_x NPs) exhibit distinctive advantages in the excellent intrinsic stability,^[21] low cost,^[22] and great compatibility with tandem and flexible architecture,^[23] which make it a promising hole transport layer (HTL) for p-i-n inverted PSCs. Some of the best-reported performances based on NiO_x HTL have been delivered, however, the PCE of NiO_x-based PSCs still lags behind their most advanced organic counterparts.^[24–26] Some studies attribute the backwardness to the detrimental interfacial redox reactions at perovskite/NiO_x interfaces,^[27] while others emphasize the diverse interface defects or mismatched work functions.^[13,28] Sundry strategies are developed to treat NiO_x using surface modification or elemental doping,^[29,30] however, most of them can only aim at a single issue. It is still urgent to develop the synthetical solution for the multiple obstacles toward high-performance NiO_x-based inverted PSCs.

The ammonium halides have been widely used in the field of PSCs with conventional n-i-p architecture, which are reported to passivate surface defects, optimize energy level alignment and construct 2D/3D heterostructures.^[31–33] However, the utilization of these ligands in p-i-n inverted PSCs sometimes leads to negative effects.^[34,35] Recently, Azmi et al. successfully introduced oleylammonium iodide to inverted PSCs by

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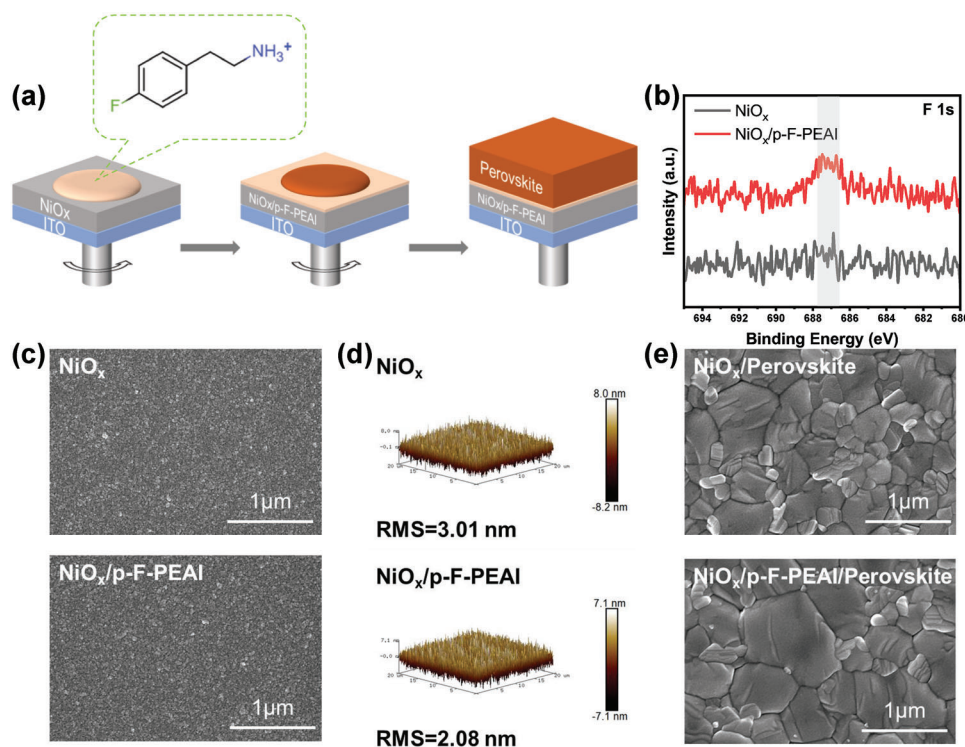


Figure 1. a) Schematic diagram of the surface modification and perovskite deposition. b) XPS spectra of F 1s for NiO_x and NiO_x/p-F-PEAI. c) SEM and d) AFM images of NiO_x and NiO_x/p-F-PEAI. e) SEM images of perovskite films deposited on NiO_x and NiO_x/p-F-PEAI.

regulating the 2D perovskite layer width,^[36] while Chen et al. fabricated record high efficiency inverted devices by using various phenethylammonium-based ligands.^[25] Meanwhile, the utilization of ammonium halides at the buried interfaces of inverted PSCs has also been explored to avoid the detrimental electron-blocking at the top surfaces of the perovskite layer.^[37] Besides, the ammonium-based ligands can interact with metallic oxide through abundant hydrogen bonds and acid-base reactions.^[38,39] These studies reveal the potential of introducing ammonium halide ligands as a synthetical solution to modify the NiO_x/perovskite interface and improve the device performance.

In this study, we employ representative 4-fluorophenethylammonium iodide (p-F-PEAI) to systemically explore the effects of ammonium salt-based interfacial modification at the NiO_x/perovskite interface. Specifically, p-F-PEAI modification is shown to be a multifunctional strategy: first, it effectively suppresses the high oxidation state Ni³⁺ in NiO_x HTL, quenching the detrimental redox reactions that occurred between pristine NiO_x and perovskite. Meanwhile, the terminal fluorine atom with high electronegativity produces strong molecule dipoles, which adjust the energy level alignment and promote the interfacial hole extraction. Besides, the ligands are shown to induce 2D/3D heterostructures at the buried interface, which further helps passivating interface defects. With the synthetically favorable effects, the p-F-PEAI treated NiO_x-based inverted PSCs obtain the champion PCE of 22.93%, which is superior to that of the control devices with a PCE of 21.10%. Moreover, the NiO_x/p-F-PEAI-based devices maintain $\approx 90\%$ and 85% of initial PCE after storing in ambient air for 1000 h and tracking at max power point (MPP) under continuous one-sun illumination for

700 h, respectively, showing a significantly improved long-term stability and remarkable operational stability.

2. Results and Discussion

The NiO_x substrates are prepared referring to our previous report,^[13] while the subsequent processes of NiO_x surface modification and perovskite deposition are presented in the schematic diagram. (Figure 1a). To explore the synthetical effects of modification on the NiO_x/perovskite interface, a representative ammonium salt 4-Fluoro-phenethylammonium iodide (p-F-PEAI) is selected considering its wide application on the low-dimensional perovskite and surface passivation.^[33] The X-ray photoelectron spectroscopy (XPS) spectra of F 1s are displayed in Figure 1b, which identify that p-F-PEAI is successfully introduced to the NiO_x surface. The uniformity of substrates is a critical factor affecting the subsequent deposition of perovskite film. The top-view scanning electron microscope (SEM) images (Figure 1c) reveal that both NiO_x and NiO_x/p-F-PEAI films show well coverage on indium doped tin oxide (ITO) glass substrate without any notable pinhole or crack, implying the high homogeneity and good dispersibility of our prepared NiO_x NPs. To further explore the effect of modification on the NiO_x substrate morphology, atomic force microscopy (AFM) is carried out and the surface roughness is calculated (Figure 1d). Notably, the roughness of NiO_x film with p-F-PEAI treatment is significantly reduced from 3.01 to 2.08 nm, demonstrating the role of p-F-PEAI in filling the nanopores and reacting with the active composition on the NiO_x films, which will be discussed in the later section. Meanwhile, morphologies of subsequently deposited perovskite

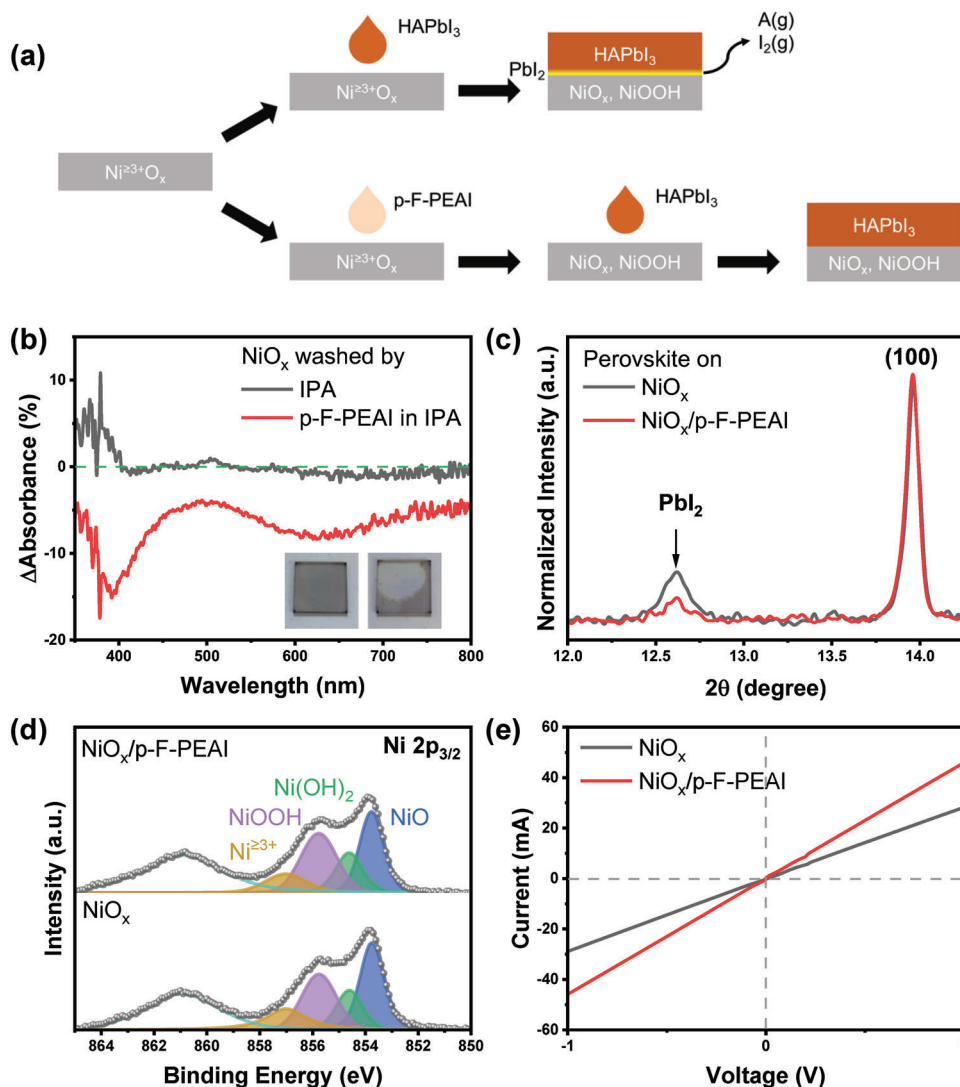


Figure 2. a) Schematic diagram of detrimental reactions during the perovskite deposition on NiO_x and the mechanism of p-F-PEAI modification. The HA here refers to the protonated organic cations (e.g., FA^+ , MA^+) at A-site. b) Change in absorbance of IPA or p-F-PEAI solution washed NiO_x films obtained via UV-vis absorption spectra. c) XRD patterns of perovskite deposited on NiO_x and $\text{NiO}_x/\text{p-F-PEAI}$. d) Ni 2p XPS spectra of NiO_x and $\text{NiO}_x/\text{p-F-PEAI}$. e) I-V curves of the devices with the structure of ITO/NiO_x or $\text{NiO}_x/\text{p-F-PEAI}/\text{Cu}$ for evaluating the conductivity.

films are also evaluated accordingly, as shown in Figure 1e. Compared with perovskite deposited on pristine NiO_x , enlarged grain size for perovskite can be observed after p-F-PEAI modification, indicating the improved crystallization quality. This enhancement can be attributed to the more uniform NiO_x substrate mentioned above, as well as higher surface hydrophobicity derived from the introduction of p-F-PEAI (Figure S1, Supporting Information), which helps modulate the growth of perovskite film.

Based on confirming the treatment for NiO_x film, we further explored the comprehensive effects of p-F-PEAI modification. For NiO_x -based PSCs, a critical problem is the detrimental redox reaction between NiO_x and perovskite that severely affect the performance and long-term stability of devices. A prevailing view indicates that the reactive compositions with a high oxidation state (named Ni^{2+3+} , which refers to the under-coordinated

metal cation sites in NiO_x) in NiO_x thin films tend to deprotonate A-site cationic amines, e.g., FA^+ , MA^+ (FA is formamidinium and MA is methylammonium), and oxidize iodide anions in perovskite precursor, leading to vacancy defects and PbI_2 barrier at NiO_x /perovskite interface (Figure 2a). To add excessive A-site cation salts (formamidinium iodide, FAI ; methylammonium iodide, MAI) in perovskite precursor can partially solve the issue. Nevertheless, the strategy demands precise optimization for the concentration and is unsuitable for other photovoltaic devices with different compositions (e.g., CsPbI_3 -based PSCs or organic photovoltaics).^[38] Therefore, it is highly valuable to explore the positive effect of our strategy on the inhibition of the interfacial reactions. Based on the previous discussion, a central issue throughout the whole process is to suppress the highly reactive composition in NiO_x films. We hypothesize that due to the ammonium-nature of p-F-PEAI, the ligands can interact with

Ni^{2+3+} and convert them to a lower oxidation state prior to the deposition of perovskite, as illustrated in Figure 2a. Qualitative assessments were firstly performed to give a preliminary verification for the process. As shown in Figure 2b, the absorbance of NiO_x film exhibits a significant decline after the treatment of p-F-PEAI, which can be also identified by the inserted photographs showing the more transparent NiO_x film. It should be noted that the sample washed with pure solvent (IPA here, IPA is isopropanol) was also tested, which exhibits a negligible change in absorbance, to exclude the influence of solvent washing on the absorption change. The lower absorbance of NiO_x film can be attributed to the effective suppression of Ni^{2+3+} , considering Ni^{2+3+} can induce extra sub-bandgap absorption and reduce the transmittance of NiO_x film.^[40] In addition, according to the X-ray diffraction (XRD) patterns (Figure 2c), the peak at 12.6° corresponding to the diffraction peak of PbI_2 significantly decreases after p-F-PEAI modification. The lower content of PbI_2 demonstrates the suppressed interfacial redox reactions that can produce excess PbI_2 , as illustrated in Figure 2a. Besides, it is worth noting that although moderate PbI_2 is regarded as a passivator in perovskites, the suppression of overmuch PbI_2 deriving from interfacial redox reactions is still valuable due to the obvious double-edged sword effect of PbI_2 .

To further verify the composition changes quantitatively, XPS spectra for Ni core level were obtained that can provide a deep insight into the composition change for NiO_x films. According to previously reported XPS results, at least four distinct species can be identified to gain a fitting of the Ni 2p spectral envelope, including NiO, Ni(OH)_2 , NiOOH and Ni^{2+3+} (see details in Supplement Information).^[38,41] The Ni $2p_{3/2}$ spectra and corresponding relative content are shown in Figure 2d and Table S1 (Supporting Information). Interestingly, after introducing p-F-PEAI, the relative content of Ni^{2+3+} species significantly decreases from 18.2 to 13.3, whereas some other species, such as Ni(OH)_2 and NiOOH obtain a higher relative content. The results demonstrate that due to the p-F-PEAI modification, Ni^{2+3+} in NiO_x films can be suppressed and converted to some other compositions with lower oxidation states, which correspond well with our hypothesis in Figure 2a. Considering the detrimental effects of Ni^{2+3+} in the interaction with perovskite, this modification provides a potential strategy for improving the performance and long-term stability of PSCs. Besides the reduction of Ni^{2+3+} , it is also worth noting the increase in the content of NiOOH, which is traditionally classified as so-called Ni^{3+} and increase the conductivity for NiO_x films,^[40,42] corresponding to the current-voltage (*I*-*V*) curves of devices with the structure of ITO/ NiO_x or NiO_x /p-F-PEAI/Cu (Figure 2e), which show improved conductivity after modification. The improvement in conductivity can be attributed to the self-doping mechanism due to the Ni vacancy deriving from the increase of NiOOH.

Besides detrimental reactions, the large energy offset and numerous interface defects are critical factors that significantly affect the carrier transport at the NiO_x /perovskite interface and lead to limited device performance. The density functional theory (DFT) calculation was first employed to examine the electrostatic surface potential (ESP) and corresponding dipole moments of p-F-PEAI (Figure 3a). The calculation result of p-F-PEAI reveals the uneven distribution of ESP, inducing a dipole mo-

ment of 16.7 D between the electronegative fluorine atom and electropositive ammonium group, as indicated by the arrow. It has been reported that the energy level alignment can be adjusted by introducing ligands with dipole moments in a particular direction.^[43] Therefore, we further probed the electronic properties of the p-F-PEAI modified NiO_x films by ultraviolet photoelectron spectroscopy (UPS). After p-F-PEAI modification, the secondary electron cut-off of NiO_x shifts to lower binding energy, resulting in a larger effective work function (WF) from an initial 4.38 to 4.54 eV (Figure 3b). In addition, the energy gap between valence band maximum (VBM) remains nearly unchanged, thus, the increase in WF of NiO_x /p-F-PEAI also leads to a downward shift of 0.15 eV for VBM. The results are supposed to be due to the dipole moment of p-F-PEAI while the dipoles produce the corresponding electrical field, leading to a downshift of the vacuum level, as illustrated in the band diagram (Figure 3c; Figures S2 and S3, Supporting Information). For comparison, the same DFT calculation and UPS measurement were carried out for another commonly used ammonium halide, phenethylammonium iodide (PEAI), which owns the identical structure of p-F-PEAI except for the fluorine atom, and the smaller increase in WF corresponds well to the weaker dipole moments (Figures S4 and S5, Supporting Information). Through the p-F-PEAI modification, an optimized energy level alignment between the NiO_x and perovskite absorber layer is obtained, which is beneficial to the carrier extraction and suppression of V_{oc} losses.^[44] The optimization can also be identified through the measurement of time-resolved photoluminescence (TRPL). It should be noted that all samples were excited from the glass side to focus on the properties of the buried interface. As shown in Figure 3d, the PL intensity of perovskite based on NiO_x /p-F-PEAI decays faster than that based on pristine NiO_x , with the carrier lifetimes of 78.49 and 99.63 ns calculated by a bi-exponential fitting, respectively. This decrease in carrier lifetime indicates the improved charge carrier extraction at the NiO_x /perovskite interface due to the introduction of p-F-PEAI, corresponding to the optimization of energy level alignment.

Interestingly, if we remove the NiO_x HTLs and deposit the perovskite absorber on insulating glass substrates immediately, the carrier lifetime after introducing p-F-PEAI will significantly increase on the contrary, from 172.78 to 776.69 ns (Figure 3e). Because the effect of interfacial carrier extraction has been excluded, the improvement of carrier lifetime should be attributed to the suppressed non-radiative recombination, revealing the effective passivation of interfacial defects due to the p-F-PEAI modification. We further carried out the steady-state photoluminescence (PL) spectroscopy of the NiO_x /p-F-PEAI/perovskite sample to explore the origin of the passivation effects. As shown in Figure 3f, the PL spectra excited from the back side (i.e., glass side) and front side (i.e., perovskite side) share a main emission signal at ≈ 795 nm indicating the 3D perovskite, however, a new emerged peak at 555 nm can be found for the back side excitation, which should be identified as the 2D perovskite formed due to the introduction of p-F-PEAI as reported.^[45] Meanwhile, the 2D composition cannot be inspected for the front side-excited spectrum, indicating that the 2D composition is mainly concentrated at the buried interface between NiO_x and perovskite instead of uniform distribution across the bulky perovskite. These results demonstrate that the p-F-PEAI modification can produce

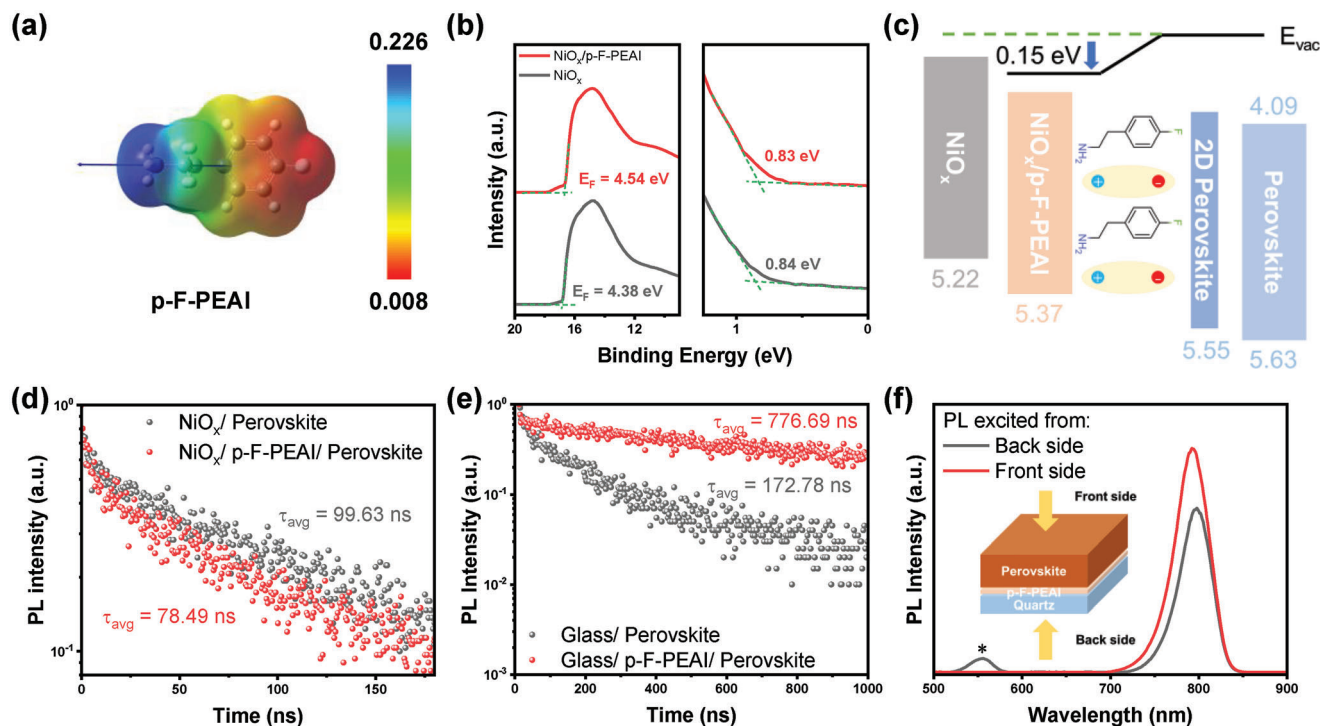


Figure 3. a) Electrostatic surface potential (ESP) and the direction of molecular dipole moments as indicated by the arrow for p-F-PEAI. b) UPS spectra of secondary electron cut-off and valence bands for NiO_x and $\text{NiO}_x/\text{p-F-PEAI}$. c) Schematic of adjustment of energy level alignment for $\text{NiO}_x/\text{p-F-PEAI}$ compared with perovskite due to the dipoles. TRPL spectra of perovskite film d) with or e) without NiO_x HTL. f) PL spectra of perovskite excited from front and back direction as shown in the inserted diagram.

a 2D/3D heterostructure at the buried interface, which is beneficial for passivating interface defects and improving the film-formation quality.^[37]

To investigate the effect of p-F-PEAI modification on the photovoltaic performance, p-n planar PSCs were fabricated with the architecture of $\text{ITO}/\text{NiO}_x/\text{HTLs}/\text{Cs}_{0.05}\text{FA}_{0.85}\text{MA}_{0.1}\text{PbI}_3/\text{C60}/\text{BCP}/\text{Cu}$ (Figure 4a). As displayed in Figure 4b, the $\text{NiO}_x/\text{p-F-PEAI}$ -based PSCs exhibit a champion PCE of 22.93%, with a short-circuit current density (J_{sc}) of 24.01 mA cm^{-2} , open-circuit voltage (V_{oc}) of 1.124 V, and fill factor (FF) of 84.98%, which presents an overall superiority compared with the device based on pristine NiO_x (PCE of 21.10%, J_{sc} of 23.56 mA cm^{-2} , V_{oc} of 1.072 V, and FF of 83.55%). Meanwhile, the treated device shows a very stable PCE output of 22.23% (Figure S6, Supporting Information) and displays negligible hysteresis (Figure S7, Supporting Information). Moreover, the distribution of PCE shows higher reproducibility for $\text{NiO}_x/\text{p-F-PEAI}$ -based PSCs (Figure S8, Supporting Information). The improvements can be attributed to the above-mentioned suppression of interfacial defects and optimized energy level alignment. Additionally, the photon-to-current conversion efficiency (EQE) measurement. As shown in Figure 4c, the integrated J_{sc} values correspond to the J_{sc} values of devices within a reasonable range of error.

To further understand the performance enhancement in p-F-PEAI treated devices, we first measured the V_{oc} as a function of the illumination intensity, which has been reported to indicate

the dominant recombination mechanism within an operating device. The ideality factor (n) can be calculated by fitting V_{oc} according to

$$V_{\text{oc}} = \frac{nkT}{q} \ln \varphi \quad (1)$$

where k is the Boltzmann constant, q is the elementary charge, and φ is light intensity. As shown in Figure 4d, the ideality factor of the device based on $\text{NiO}_x/\text{p-F-PEAI}$ is calculated to be 1.11, which is much closer to 1 compared with 1.43 of the control device, indicating that trap-assisted nonradiative recombination has effectively been reduced due to the modification by p-F-PEAI. Meanwhile, the electrical impedance spectroscopy (EIS) was also performed to investigate the carrier dynamics in devices. As can be seen in the Nyquist plots tested under dark conditions (Figure 4e), the device based on $\text{NiO}_x/\text{p-F-PEAI}$ exhibits a higher R_{rec} value compared with that of the control device, which indicates that the p-F-PEAI modification effectively decreases the recombination paths within devices, leading to a lower V_{oc} losses. Moreover, the space-charge-limited-current (SCLC) method was used to probe the passivation effect of p-F-PEAI modification by constructing hole-only devices with the architecture of $\text{ITO}/\text{NiO}_x/\text{HTLs}/\text{perovskite}/\text{Spiro-OMeTAD}/\text{Cu}$. The current-voltage curves under dark condition are displayed in Figure 4f. In the SCLC method, the trap-filled limit voltage (V_{TFL}) is directly proportional to the defect density. Therefore, the obviously lower V_{TFL} from 0.30 to 0.24 V gives a reduced defect

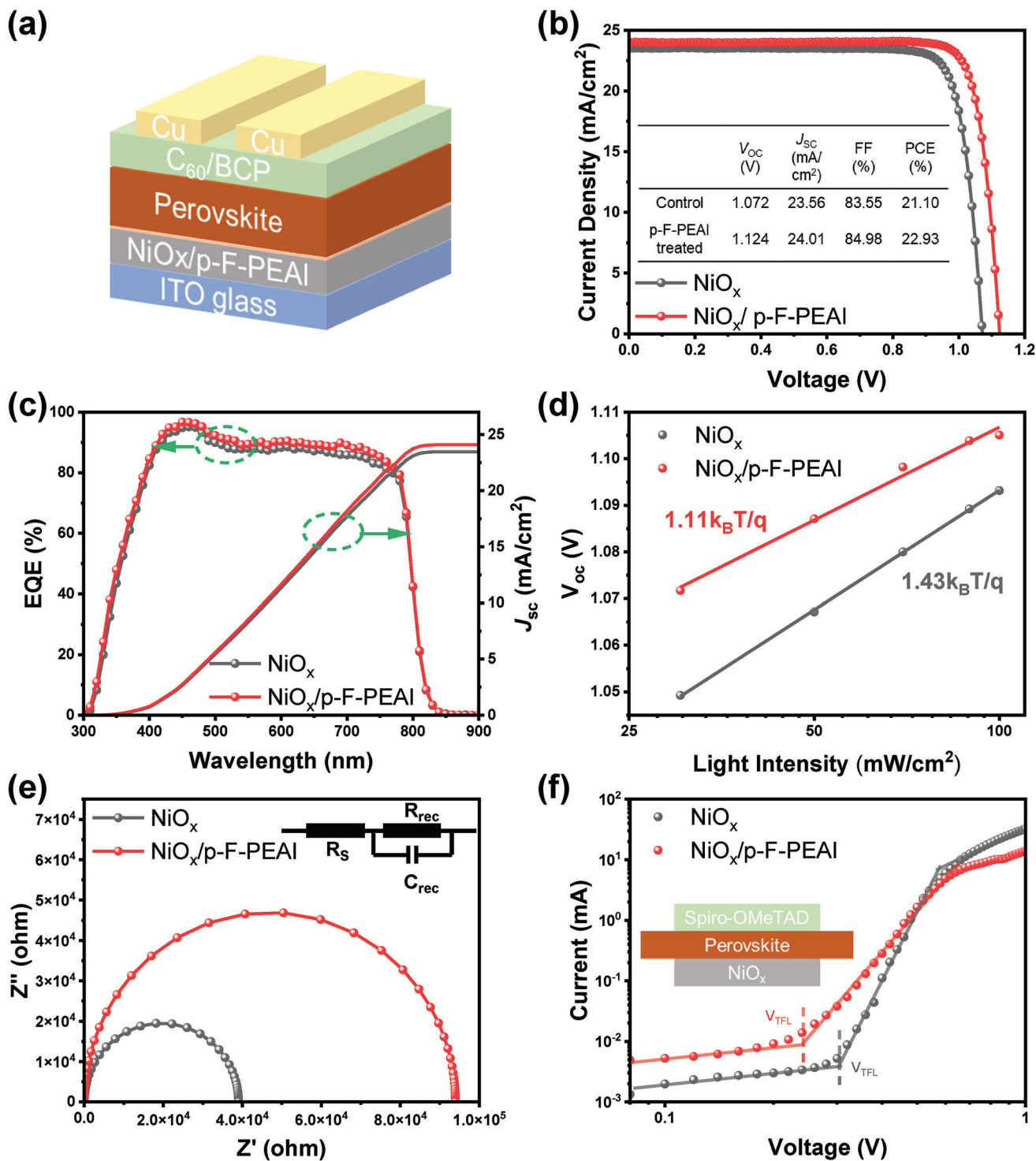


Figure 4. a) Schematic of the structure of p-i-n perovskite solar cells fabricated in this study. b) Current density-voltage (J - V) curves measured under AM 1.5 G illumination (100 mW cm^{-2}), c) EQE spectra, d) V_{OC} versus light intensity, and e) Nyquist plots of PSCs based on NiO_x and $\text{NiO}_x/\text{p-F-PEAI}$, respectively. f) J - V curves measured under the dark condition with the SCLC model based on the device structure of ITO/ NiO_x HTLs/perovskite/Spiro-OMeTAD/Cu.

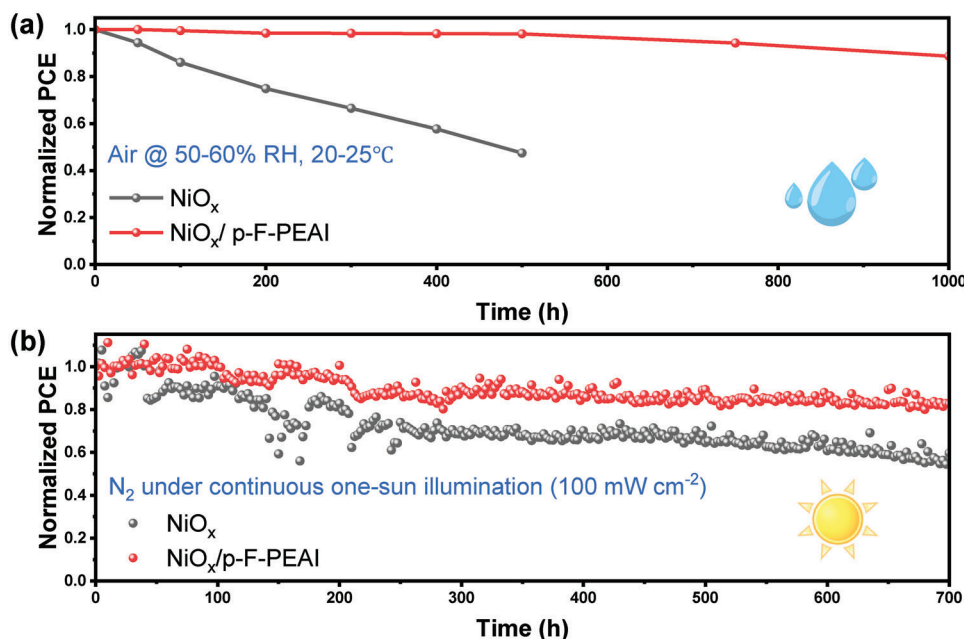


Figure 5. a) Normalized PCE of the corresponding devices kept in ambient air at 25 °C for 1000 h. b) Max power point (MPP) tracking of NiO_x/p-F-PEAI based device in nitrogen under continuous illumination with a power of 100 mW cm⁻² for 700 h.

density for devices based on NiO_x/p-F-PEAI, which further confirms the inhibitory effect of p-F-PEAI modification on interface defects.

The insurmountable instability has been the main obstacle to the practical application of PSCs. Especially, the redox reactions that occurred at the NiO_x/perovskite interface come with the potential risk of accelerated degradation, as discussed above. Therefore, it is of great significance to explore the positive effect of p-F-PEAI modification on the long-term stability of PSC devices. First, the evolution of PCE for p-i-n PSCs based on pristine or p-F-PEAI treated NiO_x was monitored in ambient air with a high relative humidity (RH) of 50–60%. As shown in Figure 5a, the PSCs based on NiO_x/p-F-PEAI exhibit dramatically improved long-term stability which can maintain above 85% of the initial PCE after storing for 1000 h. As a contrast, the devices based on NiO_x with the same structure are rapidly degraded while the PCE drops to <50% after only 500 h storage. To further affirm the potential of p-F-PEAI in improving long-term operational stability, we also performed maximum power point (MPP) tracking for unencapsulated devices at 1 sun illumination (Figure 5b). PSCs with the p-F-PEAI modification maintain above 80% of the initial PCE after 700 h of continuous illumination, exhibiting remarkable photostability and long-term operational stability. The significant enhancement in stability may derive from at least two aspects: 1) during initial film formation, the p-F-PEAI interacts with Ni²⁺ and reduces its content in NiO_x film, which immediately quenches the interfacial redox reactions that lead to excessive PbI₂ and A-site vacancy defects; 2) during the subsequent operation period of devices, the ligands remaining between NiO_x and perovskite play a role of buffer layer which continuously protect perovskite from detrimental reactions with NiO_x.

3. Conclusion

In conclusion, we have demonstrated a novel multifunctional modification using p-F-PEAI to treat NiO_x HTL, which provides several positive effects simultaneously. Through the modification, the Ni²⁺ composition leading to detrimental redox reactions between perovskite is suppressed, meanwhile, the energy level alignment is optimized due to the adjustment of dipoles and the interface of NiO_x/perovskite is effectively passivated. As a result, the p-i-n PSCs with p-F-PEAI treatment showed a champion efficiency of up to 22.93%, which has been an impressive value for the NiO_x-based inverted PSCs. Besides, the device based on NiO_x/p-F-PEAI exhibited a significantly improved long-term stability, which maintained above 85% of the initial PCE for 1000 h in ambient air with a high RH of 50–60%. Meanwhile, excellent operational stability was also obtained while above 80% of the initial PCE was maintained after MPP tracking under one-sun irradiation over 700 h. More importantly, the simple and novel strategy provides an insight into the degradation mechanism and a new perspective to solve the issues of interfacial detrimental reactions for highly efficient and stable metal oxide-based PSCs.

4. Experimental Section

Materials: All the materials were purchased and used as received unless otherwise stated. Formamidinium iodide (FAI), methylammonium iodide (MAI), cesium iodide (CsI), methylammonium chloride (MACl), bathocuproine (BCP), C60 and lead iodide (PbI₂, 99.99%) were purchased from Xi'an Polymer Light Technology Corp. Phenethylammonium iodide (PEAI) and 2-(4-fluorophenyl)ethylammonium iodide (p-F-PEAI) were purchased from Aladdin. All the anhydrous solvents including dimethylformamide (DMF), dimethyl sulfoxide (DMSO), isopropanol (IPA), and

chlorobenzene (CB) were obtained from Sigma-Aldrich. NiO_x nanoparticles (NPs) were prepared based on the previous reports.^[46,47]

Device Fabrication: ITO-coated glass was washed successively by ultrasonic cleaning with detergent, deionized water, acetone, and isopropyl alcohol for 20 min, then ultraviolet-ozone treated for 15 min before used. To fabricate the NiO_x HTLs, freshly prepared NiO_x NPs ink (10 mg mL^{-1} dispersed in deionized water) was spin-coated onto the cleaned ITO glass at 3000 rpm for 40 s, following with annealing at 120 °C for 10 min in ambient air. After cooling down, the NiO_x HTLs were transferred to glovebox with nitrogen atmosphere. For the modified samples, the NiO_x HTLs were treated by dripping 50 μL of ammonium salt solution (p-F-PEAI or PEA1, 15 mM in IPA) at 4000 rpm, the heated at 100 °C for 5 min to remove the solvent. The $\text{Cs}_{0.05}\text{FA}_{0.85}\text{MA}_{0.1}\text{PbI}_3$ precursor solution (1.65 M) with MACl (0.2 M) was prepared in a mixed solvent of DMF:DMSO (4:1 v/v) and stirred for 2 h at room temperature. To deposit the perovskite layer, 50 μL of the precursor solution was first dropped on the NiO_x HTLs, and spin-coated at 1000 rpm for 10 s, and 5000 rpm for 30 s. At 12 s before the end of the whole program, 150 μL of chlorobenzene was quickly dripped onto the film as anti-solvent, and then annealed at 100 °C for 30 min. Finally, 40 nm C60, 8 nm BCP, and 100 nm copper electrode was evaporated under high vacuum ($<5 \times 10^{-6}$ Torr) in sequence.

Measurements and Characterizations: The morphology and roughness of films were characterized by a scanning electron microscope (SEM) (TESCAN MIRA3) and an atomic force microscope (AFM) (Bruker, Dimension Edge). The UV–vis absorption spectra were obtained by an Ultraviolet-visible near-infrared spectrophotometer (Lambda 950). The X-ray diffraction (XRD) pattern was measured by a Bruker D8 Advance X-ray diffractometer (Cu $\text{K}\alpha$ 1, $\lambda = 0.154$ nm, 40 kV, 40 mA). The ultraviolet photoelectron spectroscopy (UPS) was performed by Escalab Xi+ Ultra-violet electron. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were tested using a time-correlated single photon counting setup (Edinburgh FLS 1000), and the TRPL data was fitted using the bi-exponential decay model. The current density-voltage (J – V) curves of devices were measured using a Keithley 2400 source meter and a solar simulator (Newport, model 91 192) with a simulated AM 1.5 G illumination (100 mW cm^{-2}). The range of reverse scan is from 1.2 to -0.2 V, with 10 mV for each step. X-ray photoelectron spectroscopy (XPS) spectra was measured by Axis Ultra D1d (Al $\text{K}\alpha$ radiation as an X-ray source). The external quantum efficiency (EQE) was measured by a SM-250 hyper mono-light system (Bunkoukeiki, Japan). The electrical impedance spectroscopy (EIS) was performed on the Zahner IM6 system.

Lift-off Method: The lift-off process was in the same way as previous report.^[48] Briefly, the PTAA (30 mg mL^{-1} , in toluene) solution was spin-coated onto the as-prepared NiO_x substrate at 4000 rpm for 40 s then annealed at 100 °C for 15 min in a nitrogen glovebox as a sacrificial layer. Then the p-F-PEAI modification and perovskite were deposited onto the PTAA coated substrate with the same procedures. After that, Cu capping layer with a thickness of ≈ 200 nm was evaporated on the perovskite. The resulting samples were immersed in CB solvent for 30 min, while the PTAA was gradually dissolved by CB and the integrated perovskite/metal film naturally detached from the substrate and floated in CB. Finally, the lift-off perovskite/metal film was transferred to another clean glass substrate to expose the bottom side of perovskite. The bottom side was further washed twice by CB to remove any residual PTAA.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

carrier extraction, defect passivation, interfacial reaction, inverted perovskite solar cells, nickel oxide

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