

Triple Interface Passivation Strategy-Enabled Efficient and Stable Inverted Perovskite Solar Cells

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Inverted perovskite solar cells (PSCs) are still suffering low power conversion efficiency because of hole accumulation and trap-assisted non-radiative recombination at the interface originating from the large energy offset, interface defects, and rough contact. Here, a triple passivation of the two in-between surfaces of the hole transport layer (HTL) and perovskite is proposed. The inorganic salt of potassium thiocyanate (KSCN) is introduced to simultaneously cross-link NiO_x , HTL, and methylammonium lead iodide (MAPbI_3), which can significantly improve both device performances and stability. In addition to potassium passivation, the thiocyanate shows two good passivation effects on perovskite and NiO_x to achieve the triple passivation. The strong Ni–N bonding exhibits strong polar covalent bond properties to make the electron deviate from the Ni side. Meanwhile, the strong electrostatic force between S and Pb in MAPbI_3 makes the Pb atomic layer closer to perovskite to restrain the I atom. Meanwhile, the KSCN modification leads to better valence band alignment. Eventually, the KSCN mediated PSCs exhibit both high efficiency of 21.23% with open-circuit voltage of 1.14 V and improved operational stability. The demonstration of triple interface passivation contributes to establishing promising multiple passivation strategies for improving the demanding PSC performances and stability.

Organometallic halide perovskites have become a revolutionary semiconductor because of the amazing photoelectric properties including high light absorption, high charge carrier mobility, long charge carrier distance, and diffusion length.^[1–3] Among various optoelectronic applications, perovskite solar cells (PSCs) have shown unprecedented photovoltaic (PV) performance; the power conversion efficiency (PCE) has been raised from unstable 3.8% to a certified 25.2%.^[4,5] In the progress, various strategies including composition optimization, crystallization and phase control, carrier transport layers' (CTLs) regulation and defect passivation have been successfully developed to improve the PV performance of PSCs.^[6–10] In particular, the interface modification between CTLs and the perovskite light absorber layer always plays a pivotal role to improve the performance of PSCs.

The interfacial trap state, energy level alignment, and carrier extraction not only affected the PV performance of PSCs, but also resulted in poor device stability.^[11–14]

The sundry organic and inorganic materials have been used as interface modification for the electron transport layer (ETL) in conventional n-i-p formal architecture to improve the interfacial energy level alignment, reduce the interface trap-state and promote the interface carrier extraction.^[15–23] The p-i-n inverted architecture devices, especially NiO_x -based inverted PSCs, have exhibited many advantages, such as low-temperature solution processing and negligible hysteresis.^[24] However, inverted architecture devices are still suffering low PCE because of the large energy offset and undesirable charge carrier extraction at the interface.^[25,26] Moreover, the interface defects and rough contact with perovskite layer for nonstoichiometric NiO_x thin film will cause the hole accumulation and trap-assisted non-radiative recombination losses.^[27,28] There

are few works focusing on the modification of NiO_x hole transport layer. Limited alkali halides have been reported to provide an interface passivation effect for NiO_x -based inverted PSCs and only focused on one in-between surface to the perovskite side.^[29] It is of great significance to find efficient interface mediation to improve the NiO_x /perovskite interface.^[26,27,29–31]

The alkali metal cation has proved to be an important role for PSCs, both as the additives in the perovskite films or as passivation layers between CTLs.^[13,32] The thiocyanate has been used as the passivation anion due to the strong interaction with Pb^{2+} ions of perovskite.^[32,33] In this work, we introduce the inorganic salt of potassium thiocyanate (KSCN) as a promising interface to offer its superiority for triple passivation including the potassium-induced passivation, the double passivation of thiocyanate in the in-between surface of perovskite and NiO_x hole transport layer (HTL) as compared with other inorganic potassium salts, such as KCl and KAc (CH_3COOK). The theoretical and experimental results indicate that there is statistic interaction with perovskite and a strong covalent band with NiO_x . The KSCN interfacial modification can not only reduce the defects on the surface of both NiO_x and perovskite effectively, but also result in improved energy level alignment between NiO_x HTL and perovskite. Benefiting from these improvements, the charge carrier extraction and transport are

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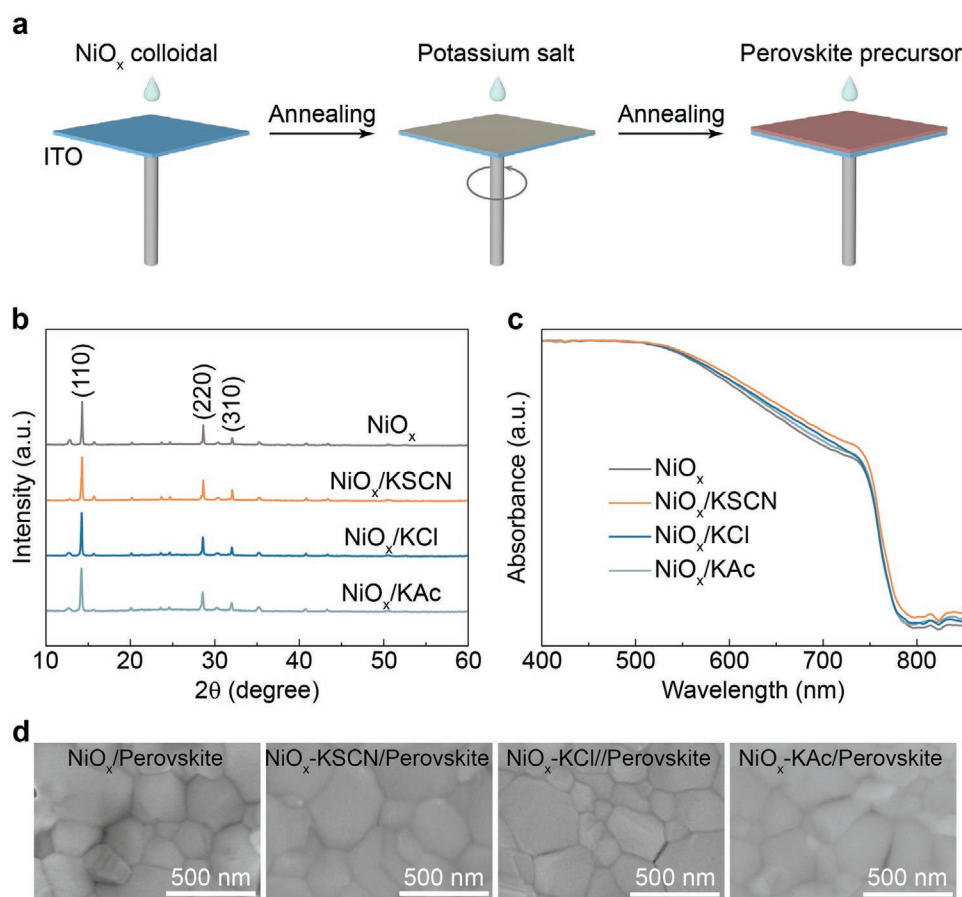


Figure 1. a) Schematic diagram of the surface mediation and perovskite deposition. b) XRD patterns, c) UV-Vis absorption spectra and d) SEM images of the perovskite deposited on the pristine and potassium salt modified- NiO_x films.

significantly promoted. Finally, with KSCN interface mediation, the champion PSCs based on the NiO_x -based inverted PSCs achieve a PCE of 21.23% with high open-circuit voltage (V_{oc}) of 1.14 V and fill factor (FF) of 0.8, which is superior to that of the device based on pristine NiO_x (18.69%), KAc modified NiO_x (19.02%) and KCl modified NiO_x (19.81%).

The preparation of NiO_x film can be referred to from our previous work^[34] and the subsequent NiO_x surface mediation process with different potassium salts is presented in the schematic diagram (Figure 1a). Considering the effect of potassium ions on perovskite,^[35] we choose three different potassium salts, that is, KSCN, KCl, and KAc, to investigate the role of anion at the interface. As shown in Figure S1, Supporting Information, both pristine and potassium salt-modified NiO_x films showed well-coverage for indium doped tin oxide (ITO) glass substrate without notable pinhole. Atomic force microscopy (AFM) was utilized to investigate the roughness of NiO_x films with and without potassium salt-mediation, as shown in Figure S2, Supporting Information. All the pristine and modified NiO_x films have nearly the same nanometer-scale smooth surface. However, the potassium salt-mediation reduces the surface roughness of the NiO_x substrate to some extent.

The MAPbI_3 perovskite absorber layer was deposited on NiO_x -based films using the one-step anti-solvent method.^[36] As shown in Figure 1b, X-ray diffraction (XRD) was first used

to compare the crystal structure of the as-achieved perovskite layers on pure NiO_x and modified- NiO_x layers, respectively. Both of the thin films show strong diffraction peaks with similar intensity at 14.1°, 28.4° and 31.8°, which are respectively assigned to 110, 220 and 310 reflections in the typical tetragonal phase of MAPbI_3 perovskite. Figure 1c reveals that the incorporation of potassium salt has a negligible effect on the UV-Vis spectra of the perovskite thin films. The absorbance edges of all thin films are located at ≈ 780 nm, which is consistent with previous results. Furthermore, the MAPbI_3 deposited on all NiO_x -based HTLs exhibits similar grain size, suggesting that the anions on the modified NiO_x cannot impact the nucleation and growth of MAPbI_3 perovskite (Figure 1d).

We further fabricated the PSCs with a configuration of glass/ITO/ NiO_x -based HTLs/Perovskite/PCBM:C60+ZrAcac/Ag to investigate the effect of potassium salt interface layer on the PV performance, as shown in Figure S3, Supporting Information. Figure 2a compares the champion devices J - V curves based on NiO_x without and with potassium salt mediation. The NiO_x/KSCN -based yields a PCE of 21.23% with J_{sc} of 23.28 mA cm^{-2} , V_{oc} of 1.14 V and 0.80 of fill factor (FF), which performed the best compared with control device (18.69%) and NiO_x/KCl - (19.81%) and NiO_x/KAc - (19.02%) based devices. The external quantum efficiency (EQE) measurement was employed to explore the photon-to-current

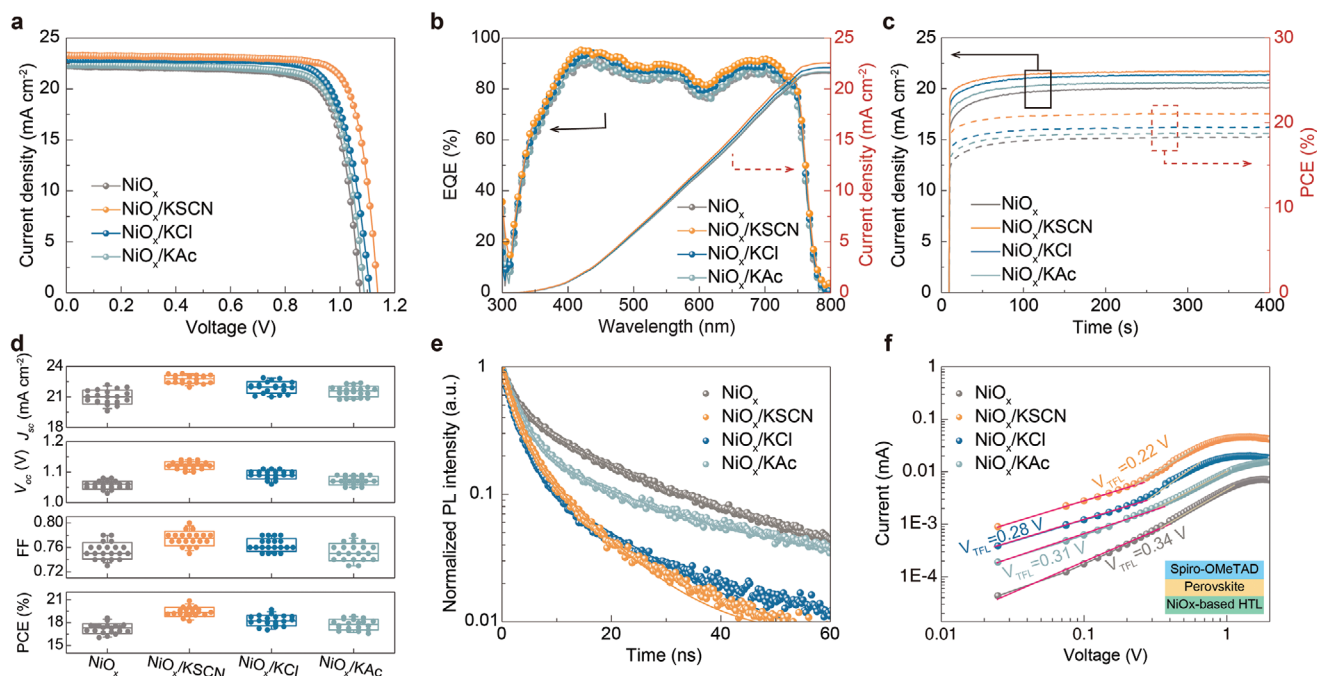


Figure 2. a) Stabilized $J-V$ curves of the best-performing devices with different modification layers compared with control devices. b) EQE spectra and the corresponding integrated J_{sc} . c) Stabilized current density and efficiency of the respective devices at the maximum power point. d) PV parameter statistics for the investigated PSCs extracted by the $J-V$ characteristics were measured on 20 PSCs for each architecture. e) TRPL decay curves for MAPbI₃ deposited on the NiO_x without and with potassium salt mediation. f) Dark $I-V$ curves of hole-only devices with different NiO_x -based films.

conversion efficiency, as shown in Figure 2b. The integrated J_{sc} is within the reasonable error range and well-matched with the $J-V$ data. Moreover, the NiO_x/KSCN -based device also exhibits negligible hysteresis (Figure S4, Supporting Information), and shows very stable 21.07% PCE output (Figure 2c). The statistical distribution of device performances with different NiO_x -based HTLs is shown in Figure 2d and listed in Table 1. After potassium salt treatment, all the PV's parameters are improved. Especially, the NiO_x/KSCN based PSCs exhibit the most prominent improvement in V_{oc} and FF. Besides, the NiO_x/KSCN -based PSCs show good photostability. After 432h continuous illumination, the unencapsulated NiO_x/KSCN -based device has only 11% PCE's decay, while the NiO_x -based has decayed to 67% of initial efficiency (Figure S6, Supporting Information). The improved stability may be attributed to the buffer layer of inorganic salt which can protect the metal oxide from MAI.

To explore the origin of PV performance improvement in NiO_x/KSCN -based devices, we carried out the steady-state photoluminescent (PL) and time-resolved photoluminescent (TRPL) spectroscopy to investigate the charge transfer dynamics of the interface between perovskite and NiO_x -based HTLs. All samples were tested with the laser incident from the glass side. Compared with the pristine NiO_x , NiO_x/KCl , and NiO_x/KAc samples, the NiO_x/KSCN sample exhibited the lowest PL intensity (Figure S7, Supporting Information), indicating the more efficient charge transfer from the perovskite to the NiO_x HTL. The carrier lifetimes are estimated by fitting the TRPL curves with a bi-exponential decay model (details in Experimental Section) and the fitting parameters are listed in Table S1, Supporting Information (Figure 2e). The charge carrier lifetime decreases sharply upon introducing KSCN to NiO_x HTL, which indicates that the addition of KSCN is beneficial to the charge carrier extraction.^[35,37]

Table 1. Summary of photovoltaic parameters for the inverted PSCs with pristine and potassium salt modified NiO_x HTLs.

HTLs	Devices	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
NiO_x	Statistics	20.90 ± 1.29	1.055 ± 0.025	0.755 ± 0.025	17.32 ± 1.29
	Champion	22.19	1.08	0.78	18.69
NiO_x/KSCN	Statistics	22.62 ± 0.66	1.120 ± 0.020	0.775 ± 0.025	19.55 ± 1.32
	Champion	23.28	1.14	0.8	21.23
NiO_x/KCl	Statistics	21.95 ± 0.93	1.085 ± 0.025	0.760 ± 0.020	18.32 ± 1.31
	Champion	22.88	1.11	0.78	19.81
NiO_x/KAc	Statistics	21.56 ± 0.81	1.070 ± 0.020	0.755 ± 0.025	17.71 ± 1.14
	Champion	22.37	1.09	0.78	19.02

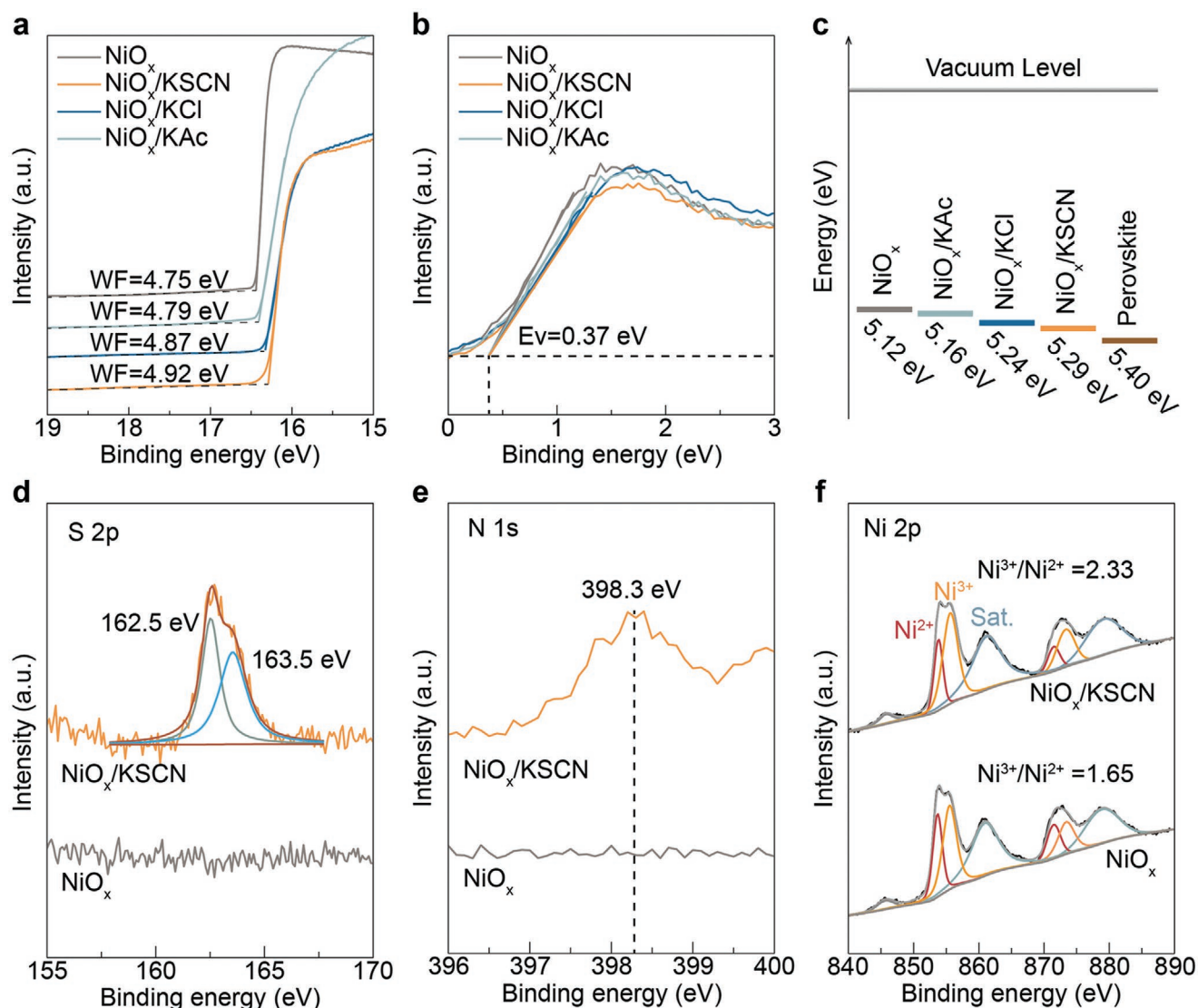


Figure 3. a) UPS spectra of different NiO_x -based films around the secondary electron cut-off. b) Valence band spectra of different NiO_x -based films. c) Energy diagram for different NiO_x -based HTLs compared with the perovskite. d) High-resolution S 2p XPS spectra of pristine NiO_x and KSCN-modified NiO_x films. e) High-resolution N 1s XPS spectra of pristine NiO_x and KSCN-modified NiO_x films. f) High-resolution Ni 2p XPS spectra of pristine NiO_x and KSCN modified NiO_x films.

In order to further probe the impact of these potassium salts, we constructed the hole-only devices of a glass/ITO/ NiO_x -based HTLs/perovskite/Spiro-OMeTAD/Ag for precisely assessing the defect density. The dark J - V curves of different devices are shown in Figure 2f. According to the space-charge-limited-current (SCLC) methods,^[32] (details in Experimental Section), the defect densities which are directly proportional to the trap-filled limit voltage (V_{TFL}) show a reduction trend when introducing the potassium salt interface layers and become the lowest for the device with KSCN-modified NiO_x . Further, the Mott-Schottky plots of C - V measurements show the highest built-in field (V_{bi}) of NiO_x /KSCN HTL-based PSC, which reveals less charge recombination (Figure S8, Supporting Information). Both of these results indicate that the KSCN at the interface has a remarkable inhibitory effect for the formation of interface defects.

The electronic properties of the modified NiO_x films were featured by the measurement of ultraviolet photoelectron spectroscopy (UPS). The work functions (WF) determined from the secondary electron onset, shift to a high level after the addition of the potassium salt, especially for NiO_x /KSCN (Figure 3a). However, the valence band spectrum measured on the modified NiO_x film showed the nearly identical value compared with pristine NiO_x (Figure 3b). The increase in WF of the potassium salt-treated samples can produce a better energy level alignment between MAPbI₃ perovskite absorber and HTLs (Figure 3c), which is beneficial for the extraction of carriers and suppression of voltage losses. Therefore, the NiO_x /KSCN-based devices show significantly improved FF and V_{oc} .

Further, X-ray photoelectron spectroscopy (XPS) was carried out on the NiO_x film without and with different potassium salts to identify the interaction between potassium salt and NiO_x thin

film. The XPS spectra of K_{2p} orbital indicate the beneficiation of potassium on the surface of NiO_x film (Figure S9, Supporting Information). Meanwhile, the survey spectra confirm the existence of the other elements of potassium salts (Figure S10, Supporting Information). Furthermore, the high-resolution XPS spectrum was used to determine the impact of the KSCN for NiO_x . The S 2p and N 1s core-level spectra identify the existence of SCN^- (Figure 3d,e) and the Ni 2p core-level spectra identify the Ni^{2+} (853.7 eV) and Ni^{3+} (855.6 eV) species from the deconvolution of Ni 2p_{3/2} peak (Figure 3f). Interestingly, the relative content of Ni^{3+} species increases significantly by introducing the KSCN modification on the NiO_x film whereas there is a slight change when KCl and KAc treated the NiO_x films (Figure 3f and S11, Supporting Information). Obviously, the KSCN surface modification has more potential to change the electronic property of the NiO_x surface than other potassium salts.

The density functional theory (DFT) was further used to gain insight into the unique impact of KSCN at the interface. For the interface of $NiO/MAPI_3$, the surface structure of $MAPI_3$ perovskite appears changed because of the strong attraction caused by the opposite charge (Figure 4a and Table S2, Supporting Information). The electrons are enriched at the interface of $MAPI_3$ and NiO (Figure 4b). From the results of the 2D slices of charge density distribution, the main interactions at interface come from the Ni-Pb and Ni-I (Figure 4c). Because

of the rearrangement at interface, the I atoms close to the interface show more positive charge compared with the inner, which tend to come out to form the iodine vacancy V_I and form deep level defect without the constraint of the Pb (Figure S14, Supporting Information). However, the undesired significant reconstruction of perovskite crystal structure happening at the interface is alleviated when there is a KSCN buffer layer (Figure 4d). Figure 4e shows a strong interaction at the interface between SCN^- and NiO_x with the formation of bonding of Ni–N and Ni–S (Figure 4f). Especially for Ni–N bonding, it exhibits the strong polar covalent bond property which makes the electron cloud deviate from the Ni side. Hence, it can effectively passivate incomplete coordination of Ni atoms on the surface. This is consistent with the result of XPS that the content of Ni^{3+} species increase (Figure 3f). The strong covalent bonding can passivate the surface of NiO_x effectively. On the other hand, there is an electrostatic force between S and Pb, which makes the Pb atomic layer closer to the perovskite side to restrain the I atom. Meanwhile, the I atoms show the charge close to that of the inner layer. The DOS of I shows that the highest occupied states close to the Fermi level shift to the lower energy state, which closes to the inner layer (Figure S14, Supporting Information). This means that the iodine atoms at the interface are more stable with a KSCN interface passivation layer. Consequently, the SCN^- offers double-sided passivation effect as an

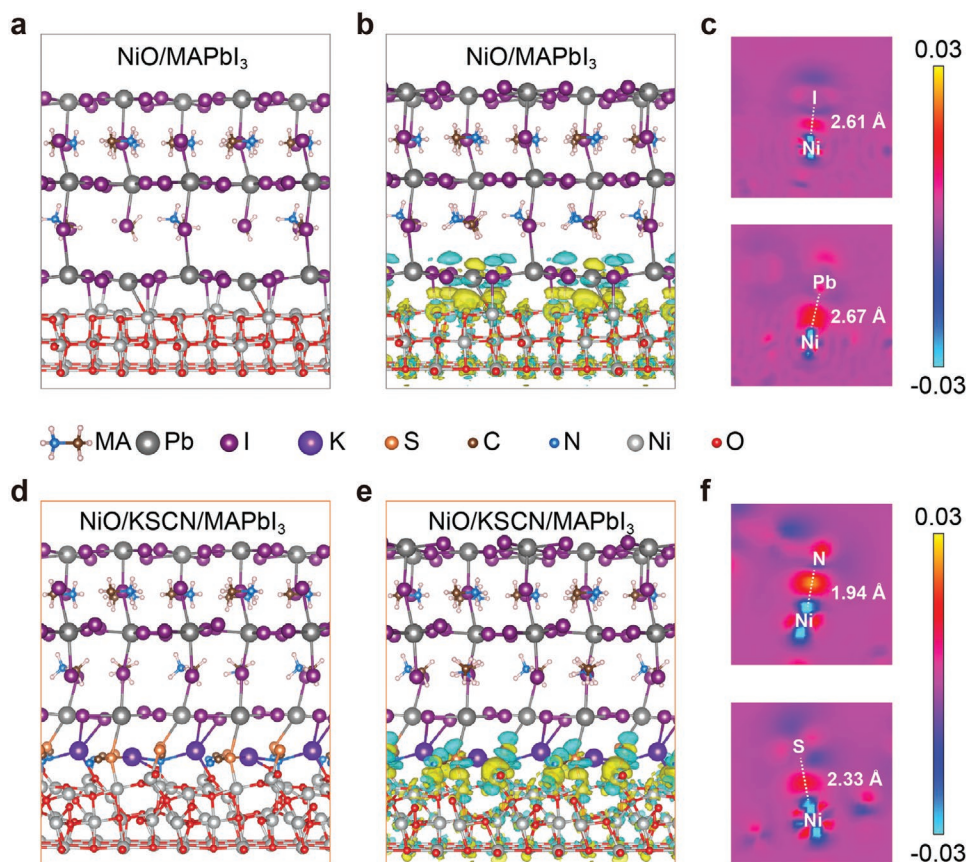


Figure 4. a) Geometries obtained after first principle molecular dynamics with a time length of 3 ps. b) Calculated charge density difference, and c) Slices along Ni-I (top) and Ni-Pb (bottom) planes at interface. d) Geometries obtained after first principle molecular dynamics with time length of 3 ps. e) Calculated charge density difference; and f) Slices along Ni–N (top) and Ni–S (bottom) planes at interface.

interface modification layer between NiO_x and MAPbI_3 , which can promote the transport of carriers through the interface and inhibit the formation of interfacial defects. Combined with the potassium ion passivation, a triple interface passivation effect could be realized at the interface of NiO_x and perovskite with a KSCN modification.

In conclusion, we demonstrate an effective method to modify the NiO_x HTL and passivate the interface with perovskite through novel triple passivation of KSCN. Apart from the potassium-induced passivation, the thiocyanate offers double passivation effects via the electrostatic interaction with perovskite and strong covalent bonding with NiO_x . As a result, interface defects are suppressed and carrier transfer is enhanced significantly. Moreover, a better valence band alignment is obtained by potassium salt modification, which will help to expedite carrier extraction. Photovoltaic devices based on KSCN modified NO_x HTL can generate a PCE over 21% with good stability and negligible hysteresis. This work contributes to shedding a new direction on the interface passivation by simple and effective inorganic salt and enlightening new insights into the interface modification to improve PSC performance and stability.

Experimental Section

Chemicals: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98.5\%$ in purity), NaOH ($\geq 98\%$ in purity), lead (II) iodide (PbI_2 , 99%), and zirconium (IV) acetylacetonate (ZrAcac , 98%) were purchased from Sigma-Aldrich. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$, MAI, 99%) and Methylammonium chloride ($\text{CH}_3\text{NH}_3\text{Cl}$, MACl, 99%) were purchased from Dyesol. Dimethylformamide (extra dry, 99%), chlorobenzene (extra dry, 99.8%), 1,2-dichlorobenzene (extra dry, 98+%), isopropanol (99.8%) were purchased from Acros Organics. PC_{61}BM and C60 were purchased from Solarmer Energy, Inc. All chemicals with analytical reagent grade were used as received unless otherwise noted.

Synthesis of NiO_x Nanocrystals: NiO_x nanocrystals (NCs) were prepared based on our previous report.^[34] Briefly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 M) was dissolved in 100 mL of deionized water. Then, by adding an NaOH solution (10 mol L^{-1}), the pH of the solution was adjusted to ≈ 10 . The result of colloidal precipitation was washed with deionized water twice and dried at 60 °C. Then, the obtained green powder was calcined at 270 °C for 2 h to obtain a dark-black powder. The NiO_x NC's ink was prepared by dispersing the obtained NiO_x NCs in deionized water with a concentration of 25 mg mL^{-1} .

Device Fabrication: Indium-tin-oxide (ITO) glass was sequentially cleaned with liquid detergent, deionized (DI) water, acetone and ethanol, followed by exposure to UV-ozone for 30 min before use. The NiO_x HTL was prepared on the ITO substrate by spin-coating freshly prepared NiO_x NC's inks and annealed on a hot plate at the temperature of 120 °C for 30 min in ambient air. Then, the potassium salts of 10 mM (KCl, KSCN and KAc in absolute ethanol) were dynamic spin-coated on NiO_x HTLs (5000 rpm, 30 s). The films were annealed at 100 °C for 10 min in air. After cooling down, the substrates were transferred to the N_2 glove box for the deposition of perovskite films. The MAPbI_3 precursor solution (1.4 M) with MACl (0.25 M) was prepared in a mixed solvent of DMF and DMSO with a volume ratio of 4:1. The perovskite films were deposited onto the substrates with a spin coating at 5000 rpm for 20 s. Chlorobenzene was dropped on the spinning substrate at 10 s before the end of the procedure. Then, the substrate was immediately transferred on a hotplate and heated at 100 °C for 20 min. A total concentration of 20 mg mL^{-1} mix solution of $\text{PC}_{61}\text{BM}/\text{C60}$ (weight ratio, 2:3) in dichlorobenzene was spin-coated at 900 rpm for 60 s and then 4000 rpm for 40 s over the perovskite layer, followed by spin-coating ZrAcac (2 mg mL^{-1} in isopropanol) at 4000 rpm. Finally, the Ag electrode with a thickness of 100 nm was thermally evaporated on top of the device with

an area of 0.08 cm^2 . The device structure was ITO/NiO_x -based HTLs/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PC}_{61}\text{BM}:\text{C60}/\text{ZrAcac}/\text{Ag}$.

Measurement and Characterization: The morphology and roughness of NiO_x and perovskite films were tested by SEM (HitachiS-4800, and LEO 1530 FEG) and tapping mode AFM (NT-MDTNTEGRA), respectively. The crystal phase of perovskite was identified by X-ray powder diffraction with $\text{Cu K}\alpha$ radiation under λ of 1.54056 Å (XRD, Bruker D2 PHASER). The chemical composition of NiO_x films was verified by XPS (Physical Electronics PHI 5802 with a monochromatic Al $\text{K}\alpha$ X-ray source). The UPS was characterized by using a He discharged lamp (He I 21.22 eV, Kratos Analytical). The current density-voltage (J - V) curves of PSCs were tested by using a Newport AM 1.5 G solar simulator under a light intensity of 100 mW cm^{-2} , calibrated with a standard silicon reference cell. The steady-state PCE was measured at a maximum power point and then tracing the current density. The EQE measurement was performed by a system combining xenon lamp monochromatic chopper, and a lock-in amplifier with a calibrated silicon photodetector (Hamamatsu mono-Si cell). The steady-state photoluminescence (PL) and time-resolved PL spectra were measured on a PicoQuant FluoroTime 300 instrument. A picosecond 375 nm pulse laser (LDH-P-C-75) with a pulse width of <40 ps was used to excite the samples.

The Bi-Exponential Decay Model:

$$I(t) = A_1 \exp\left(-\frac{t-t_0}{\tau_1}\right) + A_2 \exp\left(-\frac{t-t_0}{\tau_2}\right) \quad (1)$$

where t_0 is the start time of the decay process, τ_1 and τ_2 represent the first- and second-order decay times, A_1 and A_2 are weighting coefficients of each decay channel.

The space-charge-limited-current (SCLC) method:

$$N_d = \frac{2\varepsilon_0 \varepsilon V_{\text{TFL}}}{eL^2} \quad (2)$$

where ε_0 is the vacuum permittivity, ε of 46.9 for the perovskite is adopted, e is the electron charge, and L is the thickness of the film.

Theoretical Calculations: The spin-polarized first-principles calculations based on the Density Functional Theory (DFT) were performed using the CASTEP.^[38,39] The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional^[40] within the generalized gradient approximation (GGA) was utilized to describe the exchange-correlation energy. The projector-augmented-wave (PAW)^[41] method was adopted for the pseudopotentials. The kinetic energy cutoff for the plane wave basis expansion was set to 450 eV. The force on each atom was set as 0.03 eV Å⁻¹ for convergence criterion. First principle molecular dynamics were performed with a time step of 1.0 fs, with an overall length of 3.0 ps. After the simulation, four images with lower potential than average values were used for geometry optimization before electronic calculations. The slab model was constructed with a vacuum layer of 10 Å in the z-direction to avoid the interaction between layers. The sampling in the Brillouin zone was set with Gamma point for molecular dynamics simulations and $3 \times 3 \times 1$ grid by the Monkhorst-Pack method^[42] for electronic calculations. The van der Waals interaction has been considered using the DFT-D3 scheme.^[43]

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.

Keywords

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