Interface modification of sputtered NiO\textsubscript{x} as the hole-transporting layer for efficient inverted planar perovskite solar cells$^\dagger$

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Nickel oxide (NiO\textsubscript{x}) as a hole-transporting layer (HTL) in perovskite solar cells (PSCs) has been studied extensively in recent years. However, unlike the solution-processed NiO\textsubscript{x} films, magnetron sputtered NiO\textsubscript{x} exhibits relatively low conductivity and imperfect band alignment with perovskites, severely limiting the device performance of PSCs. In this study, a synergistically combined strategy consisting of triple interface treatments— including post-annealing, O\textsubscript{2}-plasma, and potassium chloride treatments— is employed to modulate the optoelectronic properties of the sputtered NiO\textsubscript{x} films. Through this approach, we successfully obtained NiO\textsubscript{x} films with increased carrier density and conductivity, better energy level alignment with the perovskite absorber layer, reduced interface trap density, and improved interfacial charge extraction. PSCs using this modified sputtered NiO\textsubscript{x} as the HTL deliver a highest stabilized efficiency of 18.7\%. Our result offers an alternative method to manipulate sputtered NiO\textsubscript{x} thin film properties and thereby sheds light on a manufacturing pathway to perovskite solar cells featuring sputtered NiO\textsubscript{x} HTL.

Introduction

Perovskite solar cells (PSCs) have attracted tremendous attention due to their excellent photovoltaic properties$^1$–$^3$ and rapidly increasing power conversion efficiencies (PCEs).$^4$ Nickel oxide (NiO\textsubscript{x}) as an intrinsic p-type semiconductor is considered to be a potential low-cost candidate as a stable hole-transporting layer (HTL) in inverted p–i–n structure PSCs owing to its wide band gap, well-aligned valence band edge, and appropriate electrical properties.$^5$–$^8$ Diverse deposition methods have been adopted to fabricate NiO\textsubscript{x} HTLs, including solution-based methods, such as nanoparticle,$^9$–$^{11}$ sol-gel,$^7$ solution-combustion route,$^{12}$ and electrochemical deposition,$^{13}$ and vacuum-based approaches, including magnetron sputtering,$^{6,14,15}$ atomic layer deposition,$^{16}$ pulsed laser deposition,$^{17}$ and electron beam evaporation.$^{18}$ Among these methods, magnetron sputtering is more favorable in the industry due to its high compatibility, low cost, large-scale applicability, and universality for flat and textured substrates. While PSCs with solution-processed NiO\textsubscript{x} HTLs have demonstrated PCEs over 20\%,$^9$,$^{12,19}$ devices with sputtered NiO\textsubscript{x} have typically suffered from less competitive PCEs below 18.5\%.$^6$ The relatively low conductivity and imperfect band alignment with the perovskite absorber layers are considered to be the main hurdles in obtaining good device performances for sputtered NiO\textsubscript{x}-based PSCs.$^{14,20,21}$

Many efforts have been devoted to improving the optoelectronic properties of NiO\textsubscript{x} films. Lattice doping is conventionally adopted to ameliorate the electrical properties of solution-processed NiO\textsubscript{x} films.$^5,22$–$^{24}$ However, this strategy encounters some obstacles when preparing sputtered NiO\textsubscript{x}. For example, co-sputtering deposition is subject to complicated parameter control and limited element selection,$^6,25$ and thus has rarely been explored. Alternatively, interface modification has been employed in both electron-transporting layers (ETLs) and HTLs to achieve better device performance and stability.$^{26}$–$^{29}$ Ratcliff et al.$^{30}$ discovered that O\textsubscript{2}-plasma treatment on the NiO\textsubscript{x} film increased its work function (WF) and decreased the midgap states close to its valence band edge. Chen et al.$^{19}$ demonstrated that the alkali chloride interfacial layer could improve
the ordering of the atop perovskite layer and hence reduced
defect density and interfacial recombination. Although most
interface treatments were done on solution-processed \( \text{NiO} \)
films, these strategies are in fact also suitable for the sputtered
ones due to their good usability and maneuverability.

In this work, we demonstrated that appropriate interface
treatments modify the optoelectronic properties of the sputtered
\( \text{NiO} \) films. Through the synergistic combination of three
interface treatments, namely, post-annealing, \( \text{O}_2 \)-plasma, and
potassium chloride (KCl) passivation, we successfully increased
the carrier density of the sputtered \( \text{NiO} \) films, adjusted the
surface work function, reduced the interfacial trap density, and
improved charge extraction at the interface. As a result, PSCs
with the optimally modified \( \text{NiO} \) HTL delivered a PCE of 19.16%
with the reversed voltage scan and a steady state efficiency (SSE)
of 18.7%, approximately 25% efficiency enhancement compared
to the ones with the as-sputtered \( \text{NiO} \). Our results prove the
feasibility of the interface treatment in enhancing the performance
of PSCs with sputtered \( \text{NiO} \) HTL.

Results and discussion

We first characterized the structural and optoelectronic proper-
ties of \( \text{NiO} \) thin films prepared by radio frequency (RF)
magnetron sputtering with a \( \text{NiO} \) target. The top-view scanning
electron microscopy (SEM) image shown in Fig. 1(a) reveals
the dense and uniform surface of the as-sputtered \( \text{NiO} \) film
with an average crystallite size of \( \sim 10 \text{ nm} \). Grazing incidence
X-ray diffraction (GIXRD) measurement of the \( \text{NiO} \) film deposited
on a glass substrate shows the cubic crystal structure of \( \text{NiO} \) with
characteristic peaks located at \( \sim 37^\circ, 43^\circ \) and \( 63^\circ \), corresponding
to the (111), (200), and (220) planes, respectively (Fig. 1(b)).
The optical band gap \( (E_g) \) of the \( \text{NiO} \) film is determined to be
3.63 eV by the Tauc plot from the UV-vis spectroscopy measure-
ment (Fig. 1(c)), consistent with the values reported in the
literature.\(^{31,32}\) The Fermi energy level \( (E_F) \) and the valence band
maximum \( (E_{\text{VB}}) \) of the as-sputtered \( \text{NiO} \) measured by ultra-
visible photoelectron spectroscopy (UPS) are 4.85 and 5.35 eV,
respectively (Fig. 1(d)). The appropriate energy level matches
indium tin oxide (ITO) and perovskites (Fig. 1(e) and Table S1,
ESI\(^+\)) make the as-sputtered \( \text{NiO} \) an ideal HTL for PSCs in the
inverted (or p–i–n) configuration (Fig. 1(f)).

To test the feasibility of the as-sputtered \( \text{NiO} \) as the HTL
in PSCs, we fabricated inverted PSCs with a structure of ITO/
\( \text{NiO} \)/perovskite/phenyl-C61-butyric acid methyl ester (PCBM)/
bathocuproine (BCP)/Ag (Fig. 1(f)), where the perovskite absor-
ber composition is MA\(_{0.65}\)FA\(_{0.35}\)PbI\(_3\) (MA is methylammonium;
FA is formamidinium). Current density–voltage \( (J-V) \) character-
istics and external quantum efficiency (EQE) spectra of repre-
sentative devices as a function of the as-sputtered \( \text{NiO} \)
thickness (varying from 10 to 40 nm) are shown in Fig. S1
(ESI\(^+\)). The spectral responses, especially in the short wave-
length \( (<500 \text{ nm}) \) range, decrease upon increasing the \( \text{NiO} \)
thickness. In contrast, the open-circuit voltage \( (V_{oc}) \) increases

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** (a) Top-view SEM image of an as-sputtered \( \text{NiO} \) film deposited on a silicon substrate. (b) GIXRD pattern of an as-sputtered \( \text{NiO} \) film deposited on a glass substrate. (c) Transmission spectrum of an as-sputtered \( \text{NiO} \) film with a thickness of 20 nm and its corresponding Tauc plot. (d) UPS spectrum of an as-sputtered \( \text{NiO} \) film deposited on an ITO coated glass substrate. The inset shows the magnified image of the low binding energy onset. (e) Schematic of the energy diagram and (f) cross-sectional SEM image of PSCs with the structure of ITO/\( \text{NiO} \)/perovskite/PCBM/BCP/Ag.
with the film thickness due to the reduced leakage current at the front ITO electrode. Nonetheless, all the devices exhibit moderate performances with PCEs less than 15.3%. The limited performance of these devices is attributed to the relatively low carrier density in the as-sputtered NiOx films. The Hall effect measurement reveals that the carrier density of the as-sputtered NiOx film is $3.84 \times 10^{11}$ cm$^{-3}$, substantially lower than that for the NiOx HTLs used in efficient PSCs (> $10^{14}$ cm$^{-3}$). Such low carrier density undoubtedly indicates a high resistivity of the as-sputtered NiOx film. Fig. S3 (ESI†) presents a linear sweep voltammetry (LSV) measurement of the as-sputtered NiOx film using two-electrode configuration, which shows a resistivity value of $1.95 \times 10^5$ Ω cm.

In general, most of the binary metal oxides exhibit semi-insulating properties in perfect stoichiometry. Even a slight deviation from stoichiometric composition changes the electronic structure of these oxides due to the introduction of native defects within the lattice. NiOx tends to show a p-type semi-conducting behavior as a result of the formation of Ni$^{2+}$ ions. For oxygen-rich stoichiometry, two Ni$^{2+}$ ions each lose an extra electron to maintain charge neutrality near the $V_{Ni}$ site of the NiO lattice, thus contributing a quasi-localized pair of holes to form Ni$^{3+}$ ions. Then, the density of localized states near the valence band increases, and the hopping transport barrier for holes reduces, resulting in increased hole mobility and decreased resistivity. The X-ray photoemission spectrum (XPS) displayed in Fig. 2(a) confirms that the as-sputtered NiOx film has a low concentration of Ni$^{3+}$ species. To introduce extra oxygen into the NiOx film to promote the formation of $V_{Ni}^{O}$, which can effectively increase the carrier density and reduce the film resistivity, a simple approach, i.e., post-annealing, was employed to treat the as-sputtered NiOx films.

The as-sputtered NiOx films were annealed in ambient air at various temperatures. The GIXRD patterns displayed in Fig. 2(b) and Fig. S5(a) (ESI†) show that the (200) peak slightly shifts to a higher diffraction angle upon increasing the annealing temperature. This right-shifted diffraction peak corresponds to a decrease in the interplanar spacing, which indicates the formation of $V_{Ni}^{O}$ and the shrinkage of the NiOx lattice. Fig. S5(b) (ESI†) shows that there is no obvious difference in the optical transmittance of the film after post-annealing. The atomic force microscopy (AFM) images illustrated in Fig. S5(c)-(e) (ESI†) reveal that the post-annealing doesn’t influence the root-mean-squared film roughness ($R_q$), but makes the film denser and smoother, indicated by the decreased arithmetical mean deviation roughness ($R_a$). XPS was then conducted to analyze the surface stoichiometry of the annealed NiOx films. Compared with the as-sputtered one (Fig. 2(a)), the Ni 2p$_{3/2}$ peak of the annealed NiOx film at $250^\circ$C (Fig. 2(c)) displays a higher peak intensity for NiOOH (856.87 eV) and an extra peak located at 858.10 eV that is ascribed to the NiO$_2$ species. Note that the Ni$^{3+}$ usually comes from two species: Ni$_2$O$_3$ and NiOOH. In the as-sputtered NiOx film, we ascribed the third peak (856.87 eV) to the NiOOH component because Ni$_2$O$_3$ is not stable at low temperature in ambient air. However, when annealed above $250^\circ$C, there is enough driving force for the dehydration/dehydroxylation reaction to convert Ni(OH)$_2$/NiOOH to the higher order oxide (Ni$_2$O$_3$). Fig. S6 (ESI†) shows more XPS spectra of the NiOx films annealed at various temperatures. The extracted binding energies and component ratios are summarized in Table S3 (ESI†). Clearly the annealing process introduces more Ni$^{3+}$ species into NiOx films. In particular, Ni$_2$O$_3$ appears when the annealing temperature is higher than $250^\circ$C. The film resistivity and carrier density as a function of the annealing temperature were measured and plotted in Fig. 2(d). Hall effect measurement uncovers a continual increase of the carrier density of the annealed NiOx films upon increasing the annealing temperature, which is consistent with the decreased resistivity determined by the LSV measurement (Fig. S7, ESI†). Note that after annealing at $250^\circ$C, both the carrier density and conductivity of the annealed NiOx film increase rapidly, which is associated with the appearance of Ni$_2$O$_3$. The carrier density of the NiOx film jumps from $3.84 \times 10^{11}$ to $3.79 \times 10^{13}$ cm$^{-3}$, while the film resistivity reduces from $1.95 \times 10^5$ to $4.71 \times 10^2$ Ω cm.

Devices with different NiOx film thicknesses and annealing temperatures were then fabricated to verify the feasibility of post-annealing. Fig. S8 and S9 (ESI†) summarize the optimization processes of the device performances. The optimal thickness and annealing temperature are found to be 20 nm and $250^\circ$C, respectively. The $J_{sc}$ first increases upon the annealing temperature, which is in line with the trend of film carrier density; then it decreases once the temperature further rises to $3^\circ$C, likely due to the degradation of ITO at high temperature. However, although the annealing process improves the device performance, especially the $J_{sc}$, the devices still exhibit restrained PCEs of 16.6% with a moderate $V_{oc}$ of 0.98 V.

Although the annealing process improves the carrier density of the sputtered NiOx film significantly, it remains lower than the expected value (> $10^{14}$ cm$^{-3}$) as we mentioned above, which is partially responsible for the limited PSC performance. And to increase the $V_{oc}$ of the PSCs, one can deepen the $E_f$ of NiOx to reduce the potential energy loss of hole transfer from perovskite to NiOx and suppress the interfacial recombination through band alignment engineering.

Oxygen (O$_2$)-plasma treatment is a widely used method to modify the surface and electrical properties of thin films. It has been demonstrated that the O$_2$-plasma treatment could influence the chemical stoichiometry and surface WF of NiOx thin films, thus adjusting their carrier densities and interfacial energy level alignment. In addition to post-annealing, we applied O$_2$-plasma treatment to further adjust the optoelectronic properties of the sputtered NiOx. Considering the possible damage of O$_2$-plasma to the NiOx film surface as reported in the literature, a relatively low plasma power (30 W) and a short treating time (2 min) were chosen first to explore the potential influences of the O$_2$-plasma treatment on the annealed NiOx films. Fig. 2(e) presents the XPS spectrum of the annealed NiOx film ($250^\circ$C) with the O$_2$-plasma treatment. More NiOOH species are presented, but the Ni$_2$O$_3$ signal changes little after
the O2-plasma treatment, compared to the film which underwent only the annealing process (Fig. 2(c) and Table S3, ESI†). This is consistent with the literature that the energy provided by O2-plasma is insufficient to induce the crystallographic reorganization from the cubic (NiO) or rhombohedral (Ni(OH)2) structure to the hexagonal crystal structure (Ni2O3), while the...
conversion from Ni(OH)$_2$ to NiOOH occurs more easily because NiOOH has the same rhombohedral structure as Ni(OH)$_2$. The increased Ni$^{3+}$ content results in the improvement of carrier density as well as film conductivity. Fig. 2(d) and Fig. S10 (ESI†) show that after the O$_2$-plasma treatment, the carrier density of the NiO$_x$ film further increases from 3.79 × 10$^{13}$ to 4.83 × 10$^{14}$ cm$^{-3}$, and the resistivity decreases from 4.71 × 10$^5$ to 2.99 × 10$^5$ Ω cm.

The increased NiOOH has been reported to form a surface dipole of O–Ni–OH, shifting the NiO$_x$ film surface work function (SWF) and reducing the leakage current and recombination at the interface. Scanning Kelvin Probe (SKP) measurement and UPS were then conducted to investigate the SWF variation of NiO$_x$ films with different post treatments. All the results are summarized in Fig. 2(f), and the original UPS spectra can be found in Fig. S11 (ESI†). The as-sputtered NiO$_x$ film shows a relatively low WF of 4.85 eV, and it slightly shifts deep to 4.92 eV after the annealing process. A low power and short time O$_2$-plasma treatment further moves the WF to 5.25 eV. Increasing the plasma power and time just pushes the WF slightly to 5.29 eV, which is in line with the literature. This higher WF is induced by increasing the hole concentration at the NiO$_x$ film surface, repelling electrons and thus lowering the interfacial recombination. Additionally, a high density of holes is beneficial to form a good ohmic contact with the front electrode and thus reduce the series resistance. Note that the UPS measurement cannot detect the WF change of NiO$_x$ film after the O$_2$-plasma treatment, which is likely due to the surface oxygen escape in a high vacuum. Even in an ambient atmosphere, the resistivity of O$_2$-plasma treated NiO$_x$ film recovered to its initial value after 2 h storage (Fig. S10, ESI†), indicating the loss of NiOOH species. Similar behavior was also observed by Steirer et al. who showed that the WF of solution-processed NiO$_x$ films enhanced by the O$_2$-plasma treatment exhibited a fast decay in an inert atmosphere. Fig. 2(g) illustrates the energy level alignments of different NiO$_x$ films with the perovskite layers. After the post-annealing, the $E_F$ of the NiO$_x$ film becomes deeper, which reduces the valence band offset between NiO$_x$ and perovskites. With further O$_2$-plasma treatment, an oxygen-rich NiO$_x$ surface layer with a deep $E_F$ of −5.25 eV forms, which is too close to the valence band of the perovskite. This layer may act as a good surface passivation for the perovskite absorber layer, though it may also impede the carrier transfer to some extent.

We then investigated the devices based on the annealed NiO$_x$ films treated with different plasma powers of 10–50 W for 2 min. The representative J–V characteristics and EQE spectra are shown in Fig. S12 (ESI†). The devices show significantly improved $V_{oc}$ (1.091 V) and fill factor (FF) (76.6%) even with the lowest power of 10 W. However, the $J_{sc}$ dropped about 1 mA cm$^{-2}$ when compared to the device based on the annealed NiO$_x$ without the O$_2$-plasma treatment (Fig. S9, ESI†). Further increase in the plasma power does not affect the $V_{oc}$ or $J_{sc}$ but decreases the FF gradually. The best-performing device shows a PCE of 18.15%. The enhanced $V_{oc}$ can be explained by the downshifted Fermi level of the NiO$_x$ film with O$_2$-plasma treatment, while the reduced $J_{sc}$ is likely due to the damage on the NiO$_x$ surface caused by the O$_2$-plasma treatment. The AFM image displayed in Fig. S13 (ESI†) reveals a fuzzy surface of the O$_2$-plasma treated NiO$_x$ film, which is consistent with the literature.

To overcome these surface imperfection issues, we adopt potassium passivation on the annealed NiO$_x$ surface before the O$_2$-plasma treatment. Potassium passivation has been reported as a universal strategy to suppress the bulk and interface defects and minimize the device hysteresis. The SEM image (Fig. 3(b)) reveals a discrete distribution of KCl particles on the NiO$_x$ surface. This discontinuous coverage of KCl at the interface was also reported by Liu et al. who deposited KCl atop the SnO$_2$ layer. They discovered that the presence of KCl significantly reduced the interface defects and recombination loss, with little effect on the perovskite crystal structure and electrical properties. The nearly invariable surface morphology and diffraction peaks of perovskite films deposited on NiO$_x$ with and without KCl passivation (Fig. 3(c) and Fig. S15, ESI†) confirm that the KCl treatment does not affect the structural properties of the subsequently deposited perovskite films.

Devices were then fabricated to check the potassium passivation tactics. Note that the KCl treatment can influence the optimal O$_2$-plasma power as shown in Fig. S16 (ESI†). This is understandable because a relatively strong plasma power is helpful to etch the redundant insulative Ni(OH)$_2$ formed during the potassium treatment using the aqueous KCl solution, thus enhancing the charge transport and collection at the perovskite/NiO$_x$ interface. On this basis, we further investigated the effect of KCl concentration on the device performance. Fig. S17 (ESI†) displays the photovoltaic performance of the devices as a function of KCl concentration, including the J–V characteristics, EQE spectra and the corresponding steady state efficiencies. The KCl concentration seems to have very limited effect on the device performance especially for the PSCs with high plasma power (30 W) treatment. One possible reason is that the KCl particles were partially rinsed out during perovskite deposition due to the low solubility of KCl in mixed dimethyl sulfoxide (DMSO)/dimethylformamide (DMF), and the other may be originated from the etching effect of the plasma treatment (Fig. S18, ESI†). They both make the actual content of KCl in the final devices relatively low and have little discrepancy. The optimized device with 20 mg ml$^{-1}$ KCl plus 30 W O$_2$-plasma etch yields a champion PCE of 19.16%, with a $J_{sc}$ of 23.27 mA cm$^{-2}$, $V_{oc}$ of 1.049 V, and FF of 78.8%.

Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) of the perovskites deposited on different NiO$_x$ films were then performed to identify the causes of
performance improvement, and the results are illustrated in Fig. 3(d) and (e), respectively. The measurements were made using excitation/collection through the NiO\textsubscript{x}/perovskite interface to evaluate the behavior of charge carriers nearest to the interface. Three representative NiO\textsubscript{x} films, treated with only thermal annealing (NiO\textsubscript{x}-250 °C), thermal annealing plus O\textsubscript{2}-plasma (NiO\textsubscript{x}-250 °C-10 W), and 3-step treatment with KCl passivation (NiO\textsubscript{x}-250 °C-20–30 W) were selected for comparison. As a contrast, a bare perovskite film that deposited on a clean glass substrate have also been measured and are shown in Fig. S19 (ESI†).

The perovskite layer deposited on the NiO\textsubscript{x}-250 °C-10 W film shows higher PL intensity and longer PL lifetime (\tau\text{ave}) than the one with the NiO\textsubscript{x}-250 °C film. The presence of a high SWF layer atop the NiO\textsubscript{x} surface after the O\textsubscript{2}-plasma treatment should be partially responsible for the increased PL intensity because it retards the charge extraction from the perovskite to NiO\textsubscript{x}. Interestingly, the sample based on NiO\textsubscript{x}-250 °C-K 20–30 W shows a similar PL intensity and lifetime compared to the post-annealed sample (NiO\textsubscript{x}-250 °C), seemingly indicating a higher hole extraction efficiency from the perovskite to NiO\textsubscript{x}. However, besides the charge extraction, the trap density also influences the PL emission and carrier lifetime. A high trap density in the perovskite layer and at the interface would increase the non-radiative recombination, thus decreasing the fluorescence intensity and carrier lifetime.

To further analyze the trap density in the perovskite films deposited on different NiO\textsubscript{x} layers, we conducted the LSV measurement using hole-only devices with the structure of ITO/different NiO\textsubscript{x}/perovskite/spiro-OMeTAD/Au. Fig. 3(f) shows the results plotted in double logarithmic scale. The trap-state density (N\text{d}) can be estimated by the trap-filled limit voltage (\V\text{TFL}), which is determined from the first kink point.\textsuperscript{7,50} The \V\text{TFL} extracted from these devices are 0.198, 0.114, and 0.093 V for the perovskite deposited on NiO\textsubscript{x}-250 °C, NiO\textsubscript{x}-250 °C-10 W, and NiO\textsubscript{x}-250 °C-K 20–30 W, respectively. The corresponding trap densities are thus calculated to be 1.49 \times 10\textsuperscript{15}, 8.60 \times 10\textsuperscript{13}, and 7.02 \times 10\textsuperscript{14} cm\textsuperscript{-3}. The reduced trap density in the O\textsubscript{2}-plasma treated device (NiO\textsubscript{x}-250 °C-10 W) is likely due to the suppressed surface defects at the NiO\textsubscript{x}/perovskite interface, which is believed to originate from the presence of dipoles (NiOOH) on the NiO\textsubscript{x} film surface.\textsuperscript{30} As to the device with the KCl treatment, although the effect of O\textsubscript{2}-plasma is likely weakened due to the introduction of KCl, the incorporation of K\textsuperscript{+} ions helps decrease the defect density in the perovskite owing to the reduced ionode Frenkel defect\textsuperscript{51} and/or the formation of ordered NiO\textsubscript{x}/perovskite interface.\textsuperscript{49} A similar trap density between the NiO\textsubscript{x}-250 °C-10 W and NiO\textsubscript{x}-250 °C-K 20–30 W samples confirms that the faster charge extraction of the latter one is the main reason for the quicker PL quenching and shorter carrier lifetime. The combination of low trap density and fast charge extraction accounts for the excellent device performances in PSCs with NiO\textsubscript{x}-250 °C-K 20–30 W.

The champion device performances and their corresponding device structures with NiO\textsubscript{x}-250 °C, NiO\textsubscript{x}-250 °C-10 W, and NiO\textsubscript{x}-250 °C-K 20–30 W HTLs are displayed in Fig. 4(a)–(c), respectively. Clearly, the O\textsubscript{2}-plasma treatment strikingly improves the device \V\text{oc} but decreases \J\text{sc} with unexpectedly increased hysteresis. Furthermore, KCl passivation leads to the
recovered $J_{sc}$ and reduced hysteresis without sacrificing $V_{oc}$, resulting in the best device performance. The integrated current density ($J_{\text{integrate}}$) calculated from the corresponding EQE spectra (Fig. 4(d)) is consistent with the $J_{sc}$ of the best performing cell in each category. The statistical distributions of more than 15 cells for each category of devices (Fig. 4(e)) reveals similar PCE and hysteresis trends with the best-performing devices. The detailed photovoltaic parameter statistics including the $V_{oc}$, $J_{sc}$, FF, and PCE are presented in Fig. S20 (ESI†). The best and statistic device performance of these three types of PSCs are tabulated in Table 1.

In addition to power conversion efficiency, stability is another important metric for evaluating PSCs. Fig. 4(f) shows the device efficiency evolution with the optimized HTL (NiO$_x$-250 °C-K 20–30 W) under continuous illumination (top panel) and stored in dark and ambient air without encapsulation (bottom panel).

### Table 1: Summary of the photovoltaic parameters of PSCs based on NiO$_x$-250 °C, NiO$_x$-250 °C-10 W, and NiO$_x$-250 °C-K 20–30 W HTLs

<table>
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<tr>
<th>Sweep</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>$J_{\text{integrate}}$ [mA cm$^{-2}$]</th>
<th>MPP [%]</th>
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<tr>
<td>Average</td>
<td>0.944 ± 0.004</td>
<td>22.81 ± 0.18</td>
<td>0.78 ± 0.01</td>
<td>16.83 ± 0.28</td>
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<td>Fwd</td>
<td>0.942 ± 0.004</td>
<td>22.66 ± 0.18</td>
<td>0.74 ± 0.01</td>
<td>15.68 ± 0.30</td>
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<td>Champion</td>
<td>0.953</td>
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<td></td>
<td>Fwd</td>
<td>0.950</td>
<td>22.797</td>
<td>0.744</td>
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<tr>
<td>Average</td>
<td>1.082 ± 0.013</td>
<td>21.59 ± 0.11</td>
<td>0.78 ± 0.01</td>
<td>18.22 ± 0.27</td>
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<tr>
<td>Fwd</td>
<td>1.081 ± 0.014</td>
<td>21.71 ± 0.16</td>
<td>0.71 ± 0.01</td>
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<td>NiO$_x$-250 °C-K 20–30 W</td>
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<tr>
<td>Average</td>
<td>1.049 ± 0.004</td>
<td>23.10 ± 0.07</td>
<td>0.79 ± 0.01</td>
<td>19.12 ± 0.24</td>
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<tr>
<td>Fwd</td>
<td>1.046 ± 0.007</td>
<td>23.16 ± 0.10</td>
<td>0.75 ± 0.01</td>
<td>18.27 ± 0.17</td>
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<tr>
<td>Champion</td>
<td>1.049</td>
<td>23.170</td>
<td>0.788</td>
<td>19.158</td>
<td>22.26</td>
<td>18.7</td>
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</table>
The device maintained 88% of its initial efficiency after 660 min tracking at maximum power point (MPP) under continuous AM1.5 G solar illumination. As to the shelf lifetime test, the device was stored in a dry box and tested periodically in ambient air with a fluctuant relative humidity (RH) varying from 30 to 80%. Fig. S21 (ESI†) gives the detailed J–V curves and their corresponding MPP efficiencies tested at certain times, and the relevant parameters are summarized in Table S10 (ESI†). When RH is less than 50%, the device shows insignificant PCE changes. However, when the ambient RH is higher than 80% and the PCE drops significantly. The device only maintains 75% of its initial efficiency after 600 h aging. More interestingly, the device aging process shows a clear increase and reverse in hysteresis, which means the hysteresis index (PCE_reverse scan–PCE_forward scan) changes from positive to negative during the aging test. We speculated that this phenomenon might be related to the interdiffusion and reaction of iodine and silver ions. As time passes, the I– ions can diffuse through the electron transport layer and accumulate at the Ag inner surface and then react with it. The high humidity that helps to decompose the perovskite undoubtedly accelerates this process.52–54 As a result, the decreased electron extraction and collection caused by the erosion of Ag and the formation of an AgI barrier can significantly degrade the device performance and affect its hysteresis behavior. Meanwhile, the diffused Ag in perovskite that may react with the perovskite and/or form the Ag metal clusters acting as recombination centers should also contribute to the degradation of device efficiency.55 Further evidence is still needed to determine the underlying reasons for this to avoid the device deterioration from the side of the Ag electrode.

Conflicts of interest
There are no conflicts to declare.

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Notes and references