Optoelectronic Modulation of Undoped NiO_x Films for Inverted Perovskite Solar Cells via Intrinsic Defect Regulation

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ABSTRACT: Ni vacancy (V_{Ni}) as an intrinsic defect plays an important role in the optical and electronic properties of NiO_x films for inverted planar perovskite solar cell (PSC) applications. This work presents a facile method to fabricate highly dense and continuous NiO_x films with excellent optical transmittance and electronic conductivity by pulsed laser deposition. By simply adjusting the preparation parameters, including oxygen partial pressure, postannealing temperature, and duration time, the well-regulated V_{Ni} defects contribute to the modified conductivity and optical transmittance of the NiO_x films. The conductivity and optical transmittance of NiO_x films are all dramatically enhanced with the increasing oxygen partial pressure. Specifically, the valence band level of NiO_x is adjusted by the V_{Ni} defect densities to better match or align with that of the perovskite layer for faster hole extraction with lower energy losses. Density functional theory calculation displays that the Fermi energy level is shifted to a lower energy level due to the



enhanced hole carrier concentration generated from the increased V_{Ni} . Benefiting from the excellent optical transmittance, electronic conductivity, and well-matched energy alignment, the inverted PSC with NiO_x hole transport layer (HTL) exhibits the highest power conversion efficiency of 16.85% with high open-circuit voltage (1.14 V), short-circuit current density (20.49 mA/cm²), fill factor (0.72), and negligible current–voltage hysteresis effect. This work reveals that modulating the intrinsic defects of NiO_x HTLs is an efficient way to achieve high performance of NiO_x-based inverted PSCs.

KEYWORDS: perovskite solar cell, NiO₃, hole transport layer, oxygen partial pressure, postannealing treatment

1. INTRODUCTION

Nowadays, hybrid organic—inorganic halide perovskite materials have attracted increasing attention and achieved exceptional progress in perovskite solar cell (PSC) areas, owing to their unique advantages such as direct and tunable band gap, broad range of light absorption with high absorption coefficient $(10^5/cm)$, low cost, and simple fabrication process.^{1–5} The first PSCs using MAPbI₃ as a light absorber layer were reported by Miyasaka et al. in 2009,⁶ and till date, the reported highest power conversion efficiency (PCE) of PSCs has reached 25.2%.⁷ Among all device configurations used for PSCs, compared to the normal n–i–p configuration, the inverted p–i–n planar PSCs have shown extensive merits such as low-cost fabrication, low-temperature processing, and reduced hysteresis, which are of fundamental importance to the commercial application.^{8–10}

In the inverted planar PSCs, hole transport layers (HTLs) are particularly important for transmitting light and extracting/ transporting hole carriers, as well as improving the crystal qualities of perovskite layers. Many organic materials such as poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT:PSS), 2,2',7,7'-tetrakis(N,N-pdimethoxyphenylamino)-9,9-spirobifluorene (spiro-OMeTAD), poly[bis(4-

phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), and poly(3hexylthiophene-2,5-diyl) (P3HT) were widely used as HTLs for PSCs.^{11–14} Unfortunately, these organic hole transport materials suffered from the drawbacks of the high price and poor environmental stability, resulting in poor device stability. To address this dilemma, inorganic p-type semiconductor materials such as NiO_x, CuI, CuSCN, and Cu₂O have emerged as stable HTLs for PSCs.^{15–19} These inorganic HTLs exhibit the inherent material advantages including superior environmental stability, lower cost, and higher hole mobility than organic HTLs.

Nickel oxide (NiO_x) stands out from all inorganic materials as a stable alternative to the HTL due to its p-type conductivity characteristics and high optical transmittance as well as good chemical stability. NiO_x has a cubic rock salt structure with a wide band gap of about 3.8 eV,²⁰ while its deep valence band

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Figure 1. (a) XRD patterns and (b) optical transmittance spectra of NiO_x (11.0 Pa) films annealed at different temperatures (RT to 300 °C) in air.

maximum can match well with that (-5.4 eV) of halide perovskite.²¹ Meanwhile, the high conduction band bottom of NiO_x can effectively block the electron transport from the perovskite layer, minimizing the photocurrent losses and voltage losses of NiO_x-based inverted PSCs. Indeed, NiO_x has already been intensively studied as a potential stable HTL candidate for PSCs. The first reported NiO_x thin film as the HTL achieved the PCE of 7.8% in 2014.²² Recently, Chen et al. reported NiO_x-based inverted PSCs with high PCE of 20.96%.²³

Some techniques, including sol–gel process, electrochemical deposition, atomic layer deposition, pulsed laser deposition (PLD), electron-beam-evaporated, and magnetron sputtering, have been employed to fabricate NiO_x films as HTLs for inverted PSCs.^{24–29} Among all methods, PLD is a feasible and versatile film growth technique, where the films deposited by PLD exhibited better crystallinity and smooth and uniform surface with fewer defects.^{30,31}

With the aim of improving the optical transmittance and electronic conductivities of NiO_x films, doping with foreign ions and interfacial engineering have been widely used and significant improvements have been made.^{32,33} However, doping foreign ions created unexpected defective states in the crystal structure which would lead to the deterioration of carrier mobility. In this regard, fabricating undoped NiO_x films with good optical transmittance and electronic conductivities via intrinsic defect regulation is fundamentally interesting for inverted PSC applications.

It is well believed that the p-type conductivity of NiO_x is originated from the nonstoichiometric $NiO_{1+\delta}$ due to low formation energy of Ni vacancy (V_{Ni}). Actually, in an oxygenrich atmosphere, V_{Ni} is easily formed³⁴

$$2Ni^{2+} + 1/2O_2(g) \to O^{2-} + V_{Ni} + 2Ni^{3+}$$
(1)

Specifically, during the deposition process, the oxygen partial pressure can be well adjusted at ultralow base pressure by PLD, which is crucial for the optical transmittance and conductivity of NiO_x films. The high optical transmittance of undoped NiO_x is attributed to the wide band gap (3.0–4.0 eV), while the p-type conductivity of undoped nonstoichiometric NiO_x is originated from Ni vacancies.^{35,36} The optical transmittance and p-type conductivity of NiO_x films are particularly affected by the intrinsic V_{Ni} defects. Accordingly, it is of great importance to develop a facile method to regulate the V_{Ni} defects of NiO_x to realize the optical transmittance and conductivities improvements.

In this work, we systematically investigated the influence of oxygen partial pressure and postannealing treatment on the conductivity and optical transmittance of NiO_x films, which were prepared under different oxygen partial pressures (3 \times

 10^{-4} to 30.0 Pa) by PLD. In this way, the intrinsic defects of NiO_r films were controlled by adjusting the oxygen partial pressure. Meanwhile, the prepared NiO_x films were annealed at different temperatures (RT to 300 °C) and duration time (15 to 120 min) to balance the optical transmittance and conductivity. The optimal NiO_x-based inverted planar PSCs exhibited a higher open-circuit voltage (V_{oc}) of 1.14 V, shortcircuit current (I_{sc}) of 20.49 mA/cm², fill factor (FF) of 0.72, and PCE of 16.85%. The optimal inverted PSCs with the structure of Ag/LiF/RhB101/PCBM/MAPbI3-xClx/NiOx/ ITO/glass were obtained when the NiO_x HTLs were deposited under 11.0 Pa and annealed at 200 °C for 60 min. For the undoped NiO_x films as HTLs, the obtained V_{oc} and PCE in this work were relatively high compared with other NiO_x-based inverted PSCs. The experiment results revealed that controlling intrinsic defects of NiO_x by regulating the oxygen partial pressures and postannealing treatment was an efficient method to adjust the physical and chemical properties of NiO_x films and dramatically boost the photovoltaic performance of NiO_xbased inverted PSCs.

2. RESULTS AND DISCUSSION

2.1. Fundamental Characteristics of NiO, Films. First, we investigated the effect of postannealing treatment on the crystal qualities of NiO_x films. As shown in Figure 1a, the amorphous film deposited at room temperature (RT) was converted to the crystalline cubic NiO_x phase after annealing treatment.³⁷ The crystallinity of NiO_x films was improved, and diffraction peak of (111) was slightly shifted to a higher angle with the increasing annealing temperature, which was attributed to the decrease of intrinsic V_{Ni} defects.^{38,39} When the annealing temperature was increased, some Ni³⁺ ions were reduced to Ni2+ ions, resulting in the decreased defects and improved crystallinity of NiO_x. As a result, the conductivity of NiO_x was decreased as the V_{Ni} decreased with the elevated annealing temperature, which is depicted in Table 1. Meanwhile, the optical transmittance of NiO_x films was significantly improved after annealing treatments (Figure 1b) due to the improved crystallinity.40,41 However, the high annealing temperature above 200 °C is harmful to the underlying indium tin oxide (ITO) front electrode (Figure

Table 1. Electrical Properties of NiO_x Films Treated at Different Annealing Temperatures, and the NiO_x Films Were Deposited on Glass Substrates

annealing temperature	carrier concentration (cm^{-3})	mobility (cm ² /V·s)	conductivity (S/cm)
RT	1.69×10^{19}	3.07	8.31
200 °C	7.55×10^{17}	8.27	1.00

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Figure 2. (a) XRD patterns of NiO_x films deposited on the glass substrate, (b) Raman, (c) optical transmittance spectra of NiO_x films deposited on ITO substrates, and (d) Tauc plots of NiO_x films deposited on quartz substrates under different oxygen partial pressures with annealing at 200 °C.

S2). For achieving high performance of inverted PSCs, it was imperative to find the optimal balance between conductivity and transparency of NiO_x films by controlling the intrinsic V_{Ni} defects. The J-V curves of inverted planar PSC-based NiO_x HTLs annealed at different temperatures, and duration time are shown in Figure S3, which indicated that the optimal annealing temperature and duration time were 200 °C and 60 min, respectively.

The crystal structures of NiO_x films prepared at different oxygen partial pressures were studied by X-ray diffraction (XRD). As shown in Figure 2a, all NiO, films exhibited poor crystallinity, where the two weak diffraction peaks are at 37.2° from the (111) plane and 43.1° from the (200) plane of cubic $NiO_x^{27,42}$ due to the thickness of the NiO_x film being only about 20 nm (Table S1). It was found that the (200) diffraction peak slightly shifted to a lower angle at higher oxygen partial pressure, which implied the increased lattice constant due to the increase of V_{Ni} .⁴³⁻⁴⁵ When the V_{Ni} existed in the crystal lattice structure of NiO_{xy} the six nearest oxygen atoms moved away from the center of V_{Ni}, thus increasing the distance between the oxygen atom and V_{Ni}.^{45,46} Figure 2b presents that there were two obvious Raman peaks located at about 495 and 1090 cm⁻¹, corresponding to the LO and 2LO mode of NiO₂₁ which represented the vibrations of Ni-O.⁴⁷ Furthermore, the peak at 495 cm⁻¹ was related to the defect of V_{Ni} existing in the NiO_x crystal structure.⁴⁸ The intensity of the LO peak gradually increased with the increased oxygen partial pressure, indicating the increased V_{Ni} defects.

The optical transmittance in the range of 300-800 nm regarding the NiO_x films with different oxygen partial pressures is displayed in Figure 2c. The optical transmittance dramatically enhanced with increased oxygen partial pressure. Since the thickness of NiO_x films under all oxygen partial pressure conditions was barely changed (Table S1), the oxygen partial pressure was the main factor that affected the film transmittance. Figure 2d depicts the Tauc plots of the asprepared NiO_x films deposited on quartz substrates, where the band gaps (E_g) were increased from 3.25 to 3.50 eV with the

increased oxygen partial pressure during the deposition process. The enlarged $E_{\rm g}$ was attributed to the increase of $V_{\rm Ni}$, which produced more Ni₂O₃ with a wider band gap in the films.^{44,49,50} The incorporation of Ni₂O₃ resulted in an improved optical transmittance and a reduced parasitic absorption in the short wavelength range.⁴²

The surface morphologies recorded by scanning electron microscopy (SEM) of the NiO_x films deposited on ITO substrates are displayed in Figure 3. The ITO substrate surface is composed of stripe-like shape particles with the size of dozens of nanometers (Figure 3a). As the oxygen partial pressure increased, highly dense and continuous films were successfully deposited on the ITO substrates (Figure 3b–d), which would facilitate the hole transport. Meanwhile, the root-



Figure 3. Top-view SEM surface images of (a) bare ITO substrate and NiO_x films under the oxygen partial pressures of (b) 3×10^{-4} , (c) 11.0, and (d) 30.0 Pa, respectively.

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Figure 4. XPS spectra of Ni 2p orbit of NiO_x films deposited under the different oxygen partial pressures of (a) 3×10^{-4} , (b) 0.5, (c) 11.0, and (d) 30.0 Pa, respectively.



Figure 5. (a) XRD patterns and (b) absorbance spectra, (c) steady-state, and (d) TRPL spectra of $MAPbI_{3-x}Cl_x/NiO_x$ (3 × 10⁻⁴ to 30.0 Pa)/ITO/glass films.

mean-square roughness of NiO_x films were 2.79, 3.12, 2.12, and 2.09 nm corresponding to the oxygen partial pressures of 3×10^{-4} , 0.5, 11.0, and 30.0 Pa, respectively (Figure S4). The smooth and uniform morphology of HTLs are beneficial to the formation of the upper perovskite films and modulate the interfacial contacts between HTL and perovskite layers.^{51,52} In addition, chemical element analysis revealed that O and Ni were uniformly distributed in the NiO_x films (Figure S5).

2.2. Role of V_{Ni} in NiO_x Films. X-ray photoelectron spectroscopy (XPS) was performed to elucidate the chemical compositions and states of NiO_x films under different oxygen partial pressures. The peaks centered at 854.4 and 856.1 eV were ascribed to Ni²⁺ 2p_{3/2} orbits in Ni–O octahedral bonding

and V_{Ni} -induced Ni³⁺ $2p_{3/2}$ orbits of Ni₂O₃, respectively. Besides, the positions of Ni²⁺ and Ni³⁺ corresponding shake-up satellite peaks were assigned as 861.2 and 863.9 eV, respectively.⁵³⁻⁵⁵ No remarkable change happened to the Ni 2p peak positions for the different NiO_x films. Therefore, the prepared films were nonstoichiometric noted as NiO_x rather than NiO or Ni₂O₃. Table S2 lists the Ni 2p analysis results for NiO_x films prepared under different oxygen partial pressures. The Ni³⁺/Ni²⁺ ratio, estimated from the curve area of Ni³⁺ and Ni²⁺ 2p_{3/2} peaks, was increased with the increased oxygen partial pressure (Figure 4a–d). The Ni³⁺/Ni²⁺ ratios were 1.94, 2.67, 3.33, and 3.47 for 3 × 10⁻⁴, 0.5, 11.0, and 30.0 Pa, respectively, which indicated that more Ni³⁺ ions were formed

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with the increase of oxygen partial pressure. Furthermore, apparent increased Ni³⁺–O 1s (531.4 eV) peak intensity compared with Ni²⁺–O1s (529.3 eV) further confirmed the octahedral bonding of Ni–O and the incorporation of Ni₂O₃ with an increase of oxygen partial pressure (Figure S6 and Table S3).¹⁵ More Ni³⁺ ions indicated that more V_{Ni} exist in the NiO_x film, resulting in a higher hole concentration and higher electrical conductivity. Conductive atomic force microscopy measurements confirmed the enhanced conductivity of NiO_x films with the increased oxygen partial pressure (Figure S7).

2.3. Hole Transport and Extract Ability from Perovskite to NiO_x HTLs. The crystal qualities of perovskite films coated on NiO_x films were measured by XRD (Figure 5a). The asterisk indicated the diffraction peaks of the ITO substrate, and the peak positions of 14.2, 28.5, and 32.0° were corresponding to the characteristic peaks of (110), (220), and (310) planes of the MAPbI_{3-x}Cl_x films, 9,56,57 respectively. The peak located at 12.5° was from the PbI₂ phase, which was beneficial to passivate the grain boundary defects of perovskite films.^{58,59} However, an excess amount of PbI₂ may form the $PbI_{2-x}Br_x$ phase to act as the hole extraction barriers at the perovskite-NiO, interface, which deliver lower open-circuit voltage of PSCs.⁶⁰ It was found that perovskite films exhibited the best crystallinity [the highest XRD intensity and smallest full width at half-maximum of preference (110) peak] when it was deposited on the NiO_r (11.0 Pa) substrate. The space charge limited current shows the lowest trap density of perovskite coated on NiO_x (11.0 Pa) HTLs and the reduced trap-assisted nonradiative bulk recombination process (Figure S8). The surface morphologies of perovskite layers growing on different NiO_x films exhibited similar continuous and uniform properties (Figure S9). The water contact angles of the NiO_x films under different oxygen partial pressures are shown in Figure S10, where an appropriate contact angle was advantageous for the growth of perovskite films. The corresponding absorbance spectra of perovskite films are shown in Figure 5b; the absorbance curve grown on NiO_x (11.0 Pa) was significantly higher than others, which was attributed to the better crystallinity of perovskite films.

Efficient charge transport and extraction between the perovskite layer and HTL are critical to the photovoltaic performance of PSCs. The increased conductivity of NiO_x HTL was beneficial for the transfer of hole carriers and suppressing the nonradiative interface recombination.^{61,62} Steady-state photoluminescence (PL) measurements were implemented to investigate the effect of charge transfer and extract efficiency from perovskite layers to NiO, HTLs under different oxygen partial pressures (Figure 5c). It was well known that the lower PL intensity meant a higher PL quenching effect, indicating better charge transport and extract efficiency. The prepared perovskite films exhibited strong emission at about 764 nm.63 As the oxygen partial pressure increased, the PL intensity dramatically decreased and increased again at 30.0 Pa. As shown in Figure S10, the higher contact angle of NiO_x films (30.0 Pa) indicates the poor interface contact between perovskites and NiO_x HTLs. The weak hole transport and extract abilities result from the poor interface contact.^{64–66} The films grown on NiO_x (11.0 Pa) showed the lowest PL emission intensity which indicated a high charge transport and extraction efficiency. Furthermore, the time-resolved PL (TRPL) spectra (Figure 5d) were also used to investigate the interfacial charge transport and extract

properties. The PL decay data were fitted by a biexponential function $^{\rm 32,34,63}$

$$I(t) = I_0 + A_1 \exp\left(-\frac{t - t_0}{\tau_1}\right) + A_2 \exp\left(-\frac{t - t_0}{\tau_2}\right)$$
(2)

$$\tau_{\rm avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \tag{3}$$

where A_1 and A_2 are the relative weighting coefficients, τ_1 and τ_2 are the fast and slow recombination lifetime, and τ_{avg} is the average PL lifetime. Table 2 presents the fitting results for the

Table 2. Biexponential Fitting Results of PL Decay Measurements for $MAPbI_{3-x}Cl_x/NiO_x$ (3 × 10⁻⁴ to 30.0 Pa)/ITO/Glass Films

samples	A_1 (%)	$ au_1$ (ns)	$^{A_2}_{(\%)}$	τ_2 (ns)	$ au_{\mathrm{avg}} \ (\mathrm{ns})$
$\frac{\text{ITO/NiO}_x}{(3 \times 10^{-4} \text{ Pa})/\text{PVK}}$	28.0	50.59	72.0	121.61	111.71
ITO/NiO _x (0.5 Pa)/PVK	21.9	37.11	78.1	78.1	76.31
ITO/NiO _x (11.0 Pa)/PVK	32.8	19.27	67.2	67.2	49.10
ITO/NiO _x (30.0 Pa)/PVK	61.4	44.10	38.6	38.6	65.41

TRPL decay measurements. The average PL lifetimes of different NiO_x-based perovskite films were 182.83, 76.16, 50.05, and 61.50 ns corresponding to the oxygen partial pressures of 3×10^{-4} , 0.5, 11.0, and 30.0 Pa, respectively. The low lifetime of NiO_x indicated a more efficient hole extraction, which contributed to the enhancement in the V_{oc} and FF of the PSCs. The lowest τ_{avg} from perovskite/NiO_x (11.0 Pa) suggested the best hole collection and transport efficiency, which was attributed to the increased electrical conductivity of HTLs. Meanwhile, the increased conductivity of NiO_x HTLs was also beneficial for suppressing the interfacial recombination and charge trapping at the interface between the NiO_x HTL and perovskite layer.

2.4. Work Function and Valence Band Level of NiO_x **HTLs.** For the PSC architecture, the energy band alignment between HTLs and perovskite layers played an important role in improving the V_{oc} and hole extraction ability. Ultraviolet photoelectron spectroscopy (UPS) was carried out to check the work function (WF) and valence band energy (E_{VB}) of NiO_x films. The WF and E_{VB} were obtained as the following formulas^{24,34,67}

$$WF = 21.2 - E_{cutoff} \tag{4}$$

$$E_{\rm VB} = 21.2 - (E_{\rm cutoff} - E_{\rm onset}) \tag{5}$$

where 21.2 was the energy of a He I light source, $E_{\rm cutoff}$ was the energy of secondary electron cutoff, and $E_{\rm onset}$ was the energy difference between the Fermi energy ($E_{\rm F}$) and $E_{\rm VB}$ ($E_{\rm VB} - E_{\rm F}$). With the oxygen partial pressure increased from 3 × 10⁻⁴ to 11.0 Pa, the WF increased from 4.75 to 4.98 eV and decreased to 4.8 eV at 30.0 Pa, as shown in Figure 6a–d. The increased Fermi level further confirmed the improved hole carrier concentration produced from the V_{Ni} with the increased oxygen partial pressure. Furthermore, density functional theory (DFT) calculations indicated that the V_{Ni} in a nonstoichiometric Ni₃₁O₃₂ supercell shifted $E_{\rm F}$ to a lower energy level,⁶⁸ which was contributed to the enhanced hole carrier concentration (Figure S11). Meanwhile, the measured $E_{\rm VB}$ of NiO_x films under the oxygen partial pressures of 3 × 10⁻⁴, 0.5,



Figure 6. UPS spectra of NiO_x films deposited on ITO substrates under different oxygen partial pressures of (a) 3×10^{-4} , (b) 0.5, (c) 11.0, and (d) 30.0 Pa, respectively.

11.0, and 30.0 Pa was -5.10, -5.21, -5.23, and -5.22 eV, respectively. The deep E_{VB} of NiO_x is closer to that of perovskite (-5.4 eV), which boosted the high V_{oc} . The additional oxygen partial pressure hugely decreased the E_{VB} of NiO_x by about 0.1 eV. Meanwhile, the synergistic effect of decreased E_{VB} and increased WF of NiO_x (11.0 Pa) films formed a better-matched energy alignment with the perovskite layer for faster hole extraction with lower energy losses.

2.5. Performance of Inverted PSCs. The device architecture of inverted planar PSCs based on NiO_x HTL is shown in Figure S12 in which the NiO_x and PCBM layer were

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selected as the HTL and electron transport layer, respectively, and MAPbI_{3-r}Cl_r was used as a light-absorbing layer. Figure 7a displays the cross-section SEM image of PSCs, where the thickness of the NiO_x film was about 20 nm. Based on the measured values, the corresponding energy level structure of the inverted planar PSCs is presented in Figure 7b. The energy levels of perovskite and PCBM were obtained from the reported literature.^{32,69} The higher WF and deeper $E_{\rm VB}$ promoted the better energy alignment between the NiO_x and perovskite layer, indicating better hole transport and extraction ability. The J-V curves of NiO_x (3 × 10⁻⁴ to 30.0 Pa)-based inverted planar PSCs are shown in Figure 7c. The photovoltaic parameters of inverted planar PSCs based on NiO_r (11.0 Pa) films with different deposition times are summarized in Figure S13 and Table S4, indicating that the optimal deposition time was 60 s. Table 3 presents that the best solar cell performance was obtained for NiO_r (11.0 Pa) HTL-based PSCs. The performance of the champion device exhibited the PCE of 16.85%, J_{sc} of 20.49 mA/cm², FF of 72.2%, and $V_{\rm oc}$ of 1.14 V, which are relatively high for the NiO. HTL-based PSCs. Meanwhile, the average V_{oc} of 1.12 V, J_{sc} of 19.62 mA/cm², FF of 74%, and PCE of 16.23% for the NiO_x (11.0 Pa)-based PSCs are revealed from Figure S14. The enhanced J_{sc} and FF were ascribed to the increased optical transmittance and conductivity. When the oxygen partial pressure increased to 30.0 Pa, the crystallinity of perovskite films deposited on NiO_x was slightly inferior. Thus, the I_{sc} and PCE of NiO_x (30.0 Pa)-based PSCs were lower than those of NiO_{x} (11.0 Pa)-based PSCs. Meanwhile, under higher oxygen partial pressure (30.0 Pa), the significant decrease in shunt resistance mainly is resulted from the poorer interface contact between 30.0 Pa-NiO_x HTLs and perovskites. The corresponding incident photon-to-current density efficiency (IPCE) spectra of the devices based on NiO_x HTLs with different oxygen partial pressure are shown in Figure 7d, which suggested that the highest IPCE in the visible range (400-750 nm) was NiO_x (11.0 Pa) HTL-based PSCs. The improved IPCE was mainly dependent on the enhanced optical



Figure 7. (a) Cross-sectional SEM image of a NiO_x-based inverted planar PSC and (b) corresponding energy band alignment diagram. (c) J-V curves and (d) IPCE spectra based on NiO_x-based PSCs as a function of oxygen partial pressure. (e) J-V curves of the champion device under forward and reverse scan. (f) Steady photocurrent output as a function of applied time (500 s) at the MPP.

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oxygen partial pressure (Pa)	$J_{\rm sc}~({\rm mA/cm^2})$	$J_{\rm sc}$ by IPCE (mA/cm ²)	$V_{\rm oc}~({\rm V})$	FF (%)	PCE (%)	$R_{\rm s}(\Omega)$	$R_{\rm sh}~({\rm k}\Omega)$
3×10^{-4}	11.66	11.74	1.10	43.4	5.56	482	9.4
0.5	14.10	13.99	1.12	59.1	9.35	91	3.8
11.0	20.49	19.53	1.14	72.2	16.85	44	18.4
30.0	18.90	18.74	1.12	68.9	14.57	99	6.3



Figure 8. Normalized photovoltaic parameters stability with (a) $V_{o\sigma}$ (b) $J_{s\sigma}$ (c) FF, and (d) PCE of the optimal NiO_x (11.0 Pa) and PEDOT:PSSbased inverted planar PSCs without encapsulation in the ambient environment (50% humidity at 25 °C).

transmittance and conductivity. The high optical transmittance of HTLs allowed more incident light to be absorbed by the perovskite layer for generating more hole–electron pairs, while the high conductivity of HTLs promoted more efficient hole transport and extraction. The integrated $J_{\rm sc}$ values from IPCE spectra were comparable with the obtained $J_{\rm sc}$ from J-V measurement. The hysteresis characteristics of the optimal device are presented in Figure 7e, which showed that the PCE of reverse scan direction was only increased by 0.47% compared to that of forward scan direction. There was a negligible hysteresis effect existing in the NiO_x-based inverted planar PSCs. Figure 7f displays the steady photocurrent output for 500 s under the maximum power point (MPP), where the fixed bias was set as 0.87 V, and steady photocurrent output was 18.4 mA/cm² contributing to a PCE of 16.0%.

2.6. Environmental Stability of PSC Devices. The environmental stability of PSCs is highly desirable for future commercial applications. The environmental stability of inorganic HTL (NiO_x) and organic HTL (PEDOT:PSS)-based PSCs were compared and analyzed. As shown in Figure 8a–c, the V_{oc} and J_{sc} almost remained unchanged and FF degraded to 92% for NiO_x-based PSCs after 20 days in dark storage, which indicated a commendable long-term stability. On the contrary, the V_{oc} J_{sc} and FF of PEDOT:PSS-based PSCs were degraded dramatically after only 10 days in dark storage due to their notorious hydrophilic and acidic nature.⁷⁰ The PCE of NiO_x-based and PEDOT:PSS-based PSCs degraded to 93 and 62%, respectively (Figure 8d). Therefore, the stable p-type metal oxide NiO_x HTLs can improve the device stability of PSCs.

3. CONCLUSIONS

In summary, NiO_x films were deposited under different oxygen partial pressures by PLD and annealed at different temperatures and duration times, showing a simple and efficient way to adjust the intrinsic defects (V_{Ni}) of NiO_x films. The optical transparency at higher oxygen partial pressure was increased due to more Ni_2O_3 formed in the NiO_x film. Meanwhile, the electrical conductivity originated from on the amounts of $V_{Ni\prime}$ which could be easily adjusted by oxygen partial pressure. The presence of increasing oxygen partial pressure was favorable for lowering Fermi level and increasing the $V_{\rm oc}$ of the devices. Meanwhile, the crystallinity of NiO_x films was increased by annealing treatment for reducing V_{Ni} defects. As a result, the short-circuit current density of PSC devices was significantly boosted from 11.66 to 20.49 mA/cm². Furthermore, the champion devices with the best PCE of 16.85%, Jsc of 20.49 mA/cm², FF of 72.2%, and V_{oc} of 1.14 V were obtained, which were very high for the undoped NiO_x-based PSCs. More importantly, the NiOx-based PSC devices had negligible hysteresis effect and superior long-term environmental stability. The study reveals that controlling the intrinsic defects of NiO_x HTLs is an efficient way to achieve high performance of NiO_x-based PSCs.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c01330.

Film deposition, device fabrication, device characterization, and DFT calculation (PDF)

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Notes

The authors declare no competing financial interest.

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