High crystallization and conductivity are always required for inorganic carrier transport materials for cheap and high-performance inverted perovskite solar cells (PSCs). High temperature and external doping are inevitably introduced and thus greatly hamper the applications of inorganic materials for mass production of flexible and tandem devices. Here, an amorphous and dopant-free inorganic material, Ni$_{3+}$-rich NiO$_x$, is reported to be fabricated by a novel UV irradiation strategy, which is facile, easily scaled-up, and energy-saving because all the processing temperatures are below 82 °C. The as-prepared NiO$_x$ film shows highly improved conductivity and hole extraction ability. The rigid and flexible PSCs present the champion efficiencies of 22.45% and 19.7%, respectively. This work fills the gap of preparing metal oxide films at the temperature below 150 °C for inverted PSCs with the high efficiency of >22%. More importantly, this work upgrades the substantial understanding about inorganic materials to function well as efficient carrier transport layers without external doping and high crystallization.

1. Introduction

Despite rapid lab-on-the-chip breakthroughs in hybrid organic–inorganic, there are serious challenges appearing against the commercialization and mass production of halide perovskite solar cells (PSCs), including the lack of facile and low-temperature protocols. Inverted planar devices, compared to the regular ones, have received specific attentions for their simple architecture and fabrication process; they are useful for large-area flexible devices, and excellently compatible with tandem devices. In inverted PSCs, inorganic hole transport materials demonstrate admiring advantages such as higher carrier mobility, superior stability, and low-cost, and thus have been intensively investigated. Among them, NiO$_x$ has recently been emerged because of its adapted valence band to that of perovskite, ensuring a great potential for high-performance inverted PSCs.

The reported NiO$_x$ hole transport layers (HTLs) are always a mixture of nickel oxides with dominant NiO composition. However, stoichiometric NiO is a wide-bandgap semiconductor with poor conductivity, that severely inhibits hole transport. To address this problem, various strategies have been developed such as inorganic elements and small molecules doping and post-treatments including sulphuration, annealing, etc. Upon these efforts, the highest power conversion efficiency (PCE) of NiO$_x$ nanocrystal-based PSCs has reached 22.74% [9]. These achievements suggest the superior potential of NiO$_x$ film for efficient inverted PSCs. Currently, two mainstream approaches, nanocrystals ink and sol–gel method, are under development for the preparation of crystalline NiO$_x$ films. High-temperature processes (>200 °C) are always needed to improve the crystallization of NiO$_x$ and doping effect for enhanced hole extraction and transport ability of NiO$_x$ as well as boosted PCE of PSCs. Additionally, the preparation of NiO$_x$ nanocrystals ink has a complex procedure (centrifugation, vacuum drying, redispersing, etc.). These obstacles hamper the mass fabrication and promising applications of NiO$_x$ film for flexible devices. Therefore, it is yet a crucial challenge to facilely prepare effective NiO$_x$ HTLs at temperatures <150 °C.

Here, we report a strategy that simultaneously addresses conductivity, high temperature, complex process, and uniformity issues that are facing current NiO$_x$-based efficient PSCs embodiments. We found the amorphous, Ni$_{3+}$-rich, and uniform NiO$_x$ film with a large area by using UV irradiation method at 82 °C. The remarkable increase in the conductivity enabled the doping-free NiO$_x$ film to be used for effective hole extraction. This led to a great improvement in fill factor and boosted PCE (22.45% and 19.70% for rigid and flexible devices, respectively) for the...
NiO$_x$-based inverted PSCs. Our work fills the gap of preparing metal oxide film at the temperature under 150 °C for efficient PSCs, with the great potential for the mass production of PSCs.

### 2. Results and Discussion

#### 2.1. Fabrication and Characterization of UV-NiO$_x$ Film

The preparation procedure of NiO$_x$ films by UV irradiation (UV-NiO$_x$) is shown in Figure 1a. In brief, a batch of ITO substrates was soaked in Ni$^{2+}$ solution for tens of seconds, then transferred to the commercial UV box after drying. UV-NiO$_x$ film was obtained after the UV irradiation in ambient conditions for several minutes. Notably, the surface temperature of ITO substrate increased upon UV irradiation and stabilized quickly at 82 °C. For comparison, the control HT-NiO$_x$ film was prepared by the conventional high-temperature annealing of sol–gel Ni(acac)$_2$ (see details in Experimental Section).

X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) were used to investigate the crystallinity of NiO$_x$ samples. We identified the HT-NiO$_x$ film with a mixture of crystalline NiO, Ni$_2$O$_3$, and NiOOH while UV-NiO$_x$ film possessed an amorphous structure (Figure 1b). Further STEM and selected area electron diffraction (SAED) results confirmed the amorphous features of UV-NiO$_x$ film with irregular morphology and diffuse halo (Figure 1c,d). In contrast, HT-NiO$_x$ possessed a nanoparticle morphology and poly-crystalline structure (Figure S1, Supporting Information). The low process temperature (≈82 °C) and short time irradiation (several minutes) during the film preparation were the rationale for the formation of amorphous structure of UV-NiO$_x$ film; this can provide uniformly physical and chemical properties for large scale geometries.

We probe the compositions of NiO$_x$ films by using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. From Figure 2a, HT-NiO$_x$ film is identified as a mixture of Ni$^{2+}$ and Ni$^{3+}$ composites, including NiO, Ni$_2$O$_3$, and NiOOH (64.9%:16.5%:18.6% in molar ratio), where Ni$^{2+}$ is rich with the molar ratio of Ni$^{2+}$:Ni$^{3+}$ as 64.9%:35.1%. Notably, UV-NiO$_x$ film consists of almost 100% Ni$^{3+}$ composition; the molar ratio of Ni$^{3+}$ for Ni$_2$O$_3$ and Ni$^{3+}$ for NiOOH is 69.3%:30.7% (Figure 2a). This indicates that UV irradiation can effectively convert Ni$^{2+}$ to Ni$^{3+}$ at a relatively low temperature within a short period of time. Further, the Raman spectroscopy is used to distinguish Ni-O bands as shown in Figure 2b. We observe the peak for A$_{1g}$ stretching bands.
Figure 2. NiOx film components, optical and electrical characterizations, and the uniformity. a) High-resolution Ni2p3/2 XPS spectrum. XPS peaks of Ni2+ and Ni3+ composites are observed in HT-NiOx, while no Ni3+ peak is observed in UV-NiOx. b) Raman spectra and c) transmittance spectra of HT and UV-NiOx film. d) Dark current–voltage curves of hole-only devices. UV-NiOx film exhibits higher current density at the same forward bias than HT-NiOx film, which indicates better hole extraction capability.

mode ($\nu$(Ni$^{\text{III}}$-O)) of dehydrated form of nickel hydroxide in HT-NiOx film, and the peaks for $E_g$ bending vibration ($6$(Ni$^{\text{III}}$-O)) and A1$g$ stretching vibration ($\nu$(Ni$^{\text{III}}$-O)) modes of Ni$^{\text{III}}$-O in dehydrated form of nickel oxyhydroxide (NiOOH) in UV-NiOx. The peaks attributed to NiOO- are also observed in both HT- and UV-NiOx. More details of Raman results are provided in Discussion S1 and Figure S2 (Supporting Information). All the above compositional characterizations show that UV-NiOx film is Ni$^{\text{3+}}$-dominated while HT-NiOx film is rich in Ni$^{\text{2+}}$ components.

The optical transmittance of NiOx films is further studied through UV–vis spectra. Both HT and UV-NiOx films exhibit high transmittance in the visible spectrum with an average transmittance >90% (Figure 2c). Specifically, UV-NiOx film has a higher transmittance than HT-NiOx film at the wavelength between 300 and 400 nm. The high transparency of UV-NiOx film minimizes optical losses of PSCs, ensuring the higher photocurrent of PSCs. We further study and confirm the uniformity of UV-NiOx film on the compositions and low sheet resistance (Figure S2e, Supporting Information). The excellent conductivity of UV-NiOx film can be well understood by knowing that Ni$^{\text{3+}}$ donates more vacancies that improve the electrical conductivity. To study the hole extraction ability of NiOx films, the dark current–voltage curves of hole-only devices of ITO/NiOx/Cu are obtained (Figure 2d). UV-NiOx film exhibits higher current density at the same forward bias than HT-NiOx film, which indicates its better hole extraction capability. Consequently, the conductive UV-NiOx film boosts the hole transport from perovskite to HTL layers, and thus the NiOx-based PSCs have a potential to achieve higher PCE by replacing HT-NiOx with UV-NiOx. From the above comprehensive characterizations, it is concluded that the as-prepared UV-NiOx film is a promising HTL with high optical transmittance, enhanced conductivity, and hole extract ability, very uniform composition, and electrical properties; these characteristics endow UV-NiOx film with a great potential for mass manufacturing of effective PSCs.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to probe the surface morphology and height difference properties of NiOx films. SEM images show a smooth surface for HT-NiOx film (Figure 3a) and a relatively rough surface for UV-NiOx film with many spread white particles (Figure 3b). These dots are attributed to slightly self-aggregated amorphous UV-NiOx. Further, AFM images in Figure S3a,b (Supporting Information) reveal that $R_{\text{q}}$ of HT and UV-NiOx films are as low as 1.84 and 3.21 nm, respectively. Based on the SEM and AFM results, it is concluded that UV-NiOx film has a slightly rougher surface than that of HT-NiOx film that may suggest the better wetting property of UV-NiOx film. This is proved by the results from contact angle measurement (Figure S3c,d,
Supporting Information), where HT-NiO\textsubscript{x} film has a reduced contact angle of 24.7°, smaller than that of UV-NiO\textsubscript{x} film (33.1°).

Ultraviolet photoelectron spectroscopy (UPS) was carried out to identify the energy levels of NiO\textsubscript{x} films. From Figure 3c, the valence band maximum (VBM) of HT-/UV-NiO\textsubscript{x} films were calculated as −5.11 and −5.37 eV, respectively. The scheme of energy-level alignment for NiO\textsubscript{x} and perovskite films was consequently constructed (Figure 3d). It is known that a better band alignment with the perovskite layer can reduce the deficiency of carrier transport between perovskite layer and NiO\textsubscript{x} layer\textsuperscript{[7a,b]} Here, the VBM difference between NiO\textsubscript{x} film and perovskite shrinks to only 0.03 from 0.29 eV upon replacing HT-NiO\textsubscript{x} with UV-NiO\textsubscript{x}; this setup can promote the extraction of holes from perovskite to NiO\textsubscript{x} layer, while reducing the energy loss during the hole transfer\textsuperscript{[5a]}

In this way, the efficient holes extraction from perovskite to UV-NiO\textsubscript{x} film can be greatly promoted, and nonradiative recombination can be suppressed at the interface of UV-NiO\textsubscript{x}/perovskite.

Kelvin probe force microscopy (KPFM) is used to measure the surface potential/work function of thin films by which the fluctuation can reveal the local distribution of surface traps\textsuperscript{[5a]} Surface traps can bring self-doping and thus induce local variation in the band bending and surface potential; these always cause negative impacts on the overall carrier transport. Figure 3e,f provides the KPFM results of NiO\textsubscript{x} films; UV-NiO\textsubscript{x} film exhibits lower mag-
nitudes for surface potential (Maximum: ~74.3 mV, Minimum: ~95.2 mV, and Mean: ~80.1 mV) than those for HT-NiO sub>film (Maximum: 98.2 mV, Minimum: 66.9 mV, and Mean: 82.2 mV); this result suggests that the work function of UV-NiO sub>film is substantially reduced. The difference of mean values gives the change of work functions of these two films (162.3 mV), which is quite consistent with the result from UPS tests (220 mV). From the difference of maximum and minimum values, it is found that the surface potential of UV-NiO sub>film is even more across the surface than that of HT-NiO sub>film; this property is beneficial for carrier transport. This observation further confirms the fact that UV-NiO sub>film has much more uniform properties than HT-NiO sub>film, as revealed in Figure S2 (Supporting Information).

2.2. Proposed Reaction Mechanisms of NiO sub>Films

In order to understand the reaction mechanism, comprehensive characterizations were carried out on the samples of UV-NiO sub>film prepared at different UV irradiation time. It was found that the morphology (SEM and TEM), crystal structure (XRD), and surface properties (Contact Angle measurement) of UV-NiO sub>films did not undergo evident changes. However, Raman data clearly showed a significant composition change of UV-NiO sub>film with the illumination time (Figure S4) that reveals the reaction process of NiO sub>. According to the reaction conditions and characterization results of the preparation of HT- and UV-NiO sub>films, the relevant reactions are proposed as follow:

\[
\text{Ni(acac)}_2 (s) + \text{O}_2 (g) \xrightarrow{\text{HT} = 400 \degree \text{C}} \text{nNiO bNi}_2\text{O}_3 c\text{NiOOH} (s) + \text{H}_2\text{O (g)} + \text{CO}_2 (g) \quad (1)
\]

\[
\text{Ni(OH)}_2 (s) + \text{O}_2 (g) \xrightarrow{\text{UV}} \text{nNi}_2\text{O}_3 b\text{NiOOH} (s) + \text{H}_2\text{O (g)} \quad (2)
\]

As clearly stated before, for the preparation of HT-NiO sub>, Ni(acac)_2 sub>converts to Ni^{4+} sub>rich oxides by the pyrolysis and oxidation reaction of (1). For the preparation of UV-NiO sub>, the photon energy of 185 nm that is dominant in the spectrum of UV lamp emission (Figure S4a, Supporting Information), is calculated as 646.63 kJ mol^{-1}; this is high enough to decompose Ni(OH) sub> by breaking Ni-O and O-H bonds to form free radicals of Ni: and O- and H- (Table S1, Supporting Information). O_3 sub> generated by the UV irradiation of O_2 in air (Equation S4, Supporting Information) has an extremely high oxidizing activity and thus it reacts with these free radicals to form Ni^{4+} sub> compositions of NiOOH and Ni_2O sub> (Figure 2a,b) at a relatively low temperature of ~82 °C (Figure S4b, Supporting Information). The low temperature also inhibits the crystallization of the precursor, forming an amorphous structure of UV-NiO sub> (Figure 1b–d) (Reaction (2), more details on the reaction mechanism are shown in Discussion S2 and Figure S4, Supporting Information).

2.3. Characterizations of Perovskite/NiO sub> Films and Their Interfaces

Perovskite films were prepared over NiO sub> layers to study the impacts of different NiO sub> films on the morphology and photoelectric property of perovskite as well as their interface structure and properties. The top view SEM images of perovskite films on HT and UV-NiO sub> layers reveal that both perovskite films are well-crystallized and pinhole-free with the grain size of 400–800 nm (Figure S5a,b, Supporting Information) and similar XRD patterns (Figure S5c, Supporting Information). This suggests their identical morphology and structure, although the underneath NiO sub> films have distinct component and properties (Figures 2.3). This result is consistent with the cross-section HAADF-STEM images of NiO sub>-based PSCs, where NiO sub> and perovskite layers are almost identical in morphology and component distribution with the compact and smooth interfaces (Figure S6, Supporting Information).

Figure 4a shows the UV-vis absorption spectra of three perovskite films on quartz, HT- or UV-NiO sub>quartz. All the perovskite films on different surfaces possess a similar bandgap of ~1.57 eV, but with slightly different absorbance. The perovskite film on UV-NiO sub>quartz has a similar absorbance to the one on quartz but slightly larger than the one on HT-NiO sub>quartz, so UV-NiO sub> has a negligible parasitic light absorption when combined with the perovskite film. Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) were also taken to probe the charge transfer kinetics between perovskite and NiO sub> layers in the above three samples. PL quenching is regarded as an indicator to monitor the charge transfer between heterostructures. Figure 4a shows the PL spectra of the above three samples. Significant PL quenching is observed on both perovskite/NiO sub>/quartz samples while a much more PL quenching is found on perovskite/UV-NiO sub>/quartz, which means a better charge transfer through the perovskite/UV-NiO sub> interface. To verify this point, TRPL spectra were attained as shown in Figure 4b. The carrier lifetime of perovskite layer reduces from 1566.69 to 985.43 and 797.86 ns in the presence of HT and UV-NiO sub>, respectively. The details of TRPL value are shown in Table S2 (Supporting Information) for reference. These data support the fact that the charge carriers within perovskite layer can be extracted more effectively by UV-NiO sub> film than HT-NiO sub> film. The excellent hole extraction ability contributes to the enhancement of open-circuit voltage and fill factor in PSCs. The hole-only device was also prepared with a configuration of glass/ITO/HT or UV-NiO sub>/perovskite/Cu to evaluate the interfacial trap density N_{trap}. As shown in Figure 4c,d, V_{FF} is set at 0.82 and 0.54 V for the perovskite on HT and UV-NiO sub>, respectively. The perovskite films on UV-NiO sub> exhibit lower N_{trap} (5.94 × 10^{11}) than that on HT-NiO sub> (9.02 × 10^{15}). This result indicates that UV-NiO sub> film can effectively suppress the trap sites of perovskite films.

From the above comprehensive characterizations, it is concluded that UV-NiO sub> film has a better hole extraction ability when compared with HT-NiO sub> film. This can reduce the trap density in the perovskite/NiO sub> interface without any observable negative impacts on the morphology of as-formed perovskite layer and interface physical contact. This conclusion is consistent with the characterization results of NiO sub> films in Figure 3.

2.4. HT and UV-NiO sub>-Based PSCs

Inverted PSCs with ITO/NiO sub>/CsFAMA/C60/BCP/Cu structure (Figure 5a) were fabricated to highlight the merits of UV-NiO sub> for
Figure 4. Structure and interface carrier transport properties of perovskite and NiOₓ layers. a) Light absorption and PL emission of perovskite films on quartz, HT, and UV-NiOₓ films, and b) TRPL of perovskite films on quartz, HT, and UV-NiOₓ films. To understand the optoelectronic properties at the interfaces of NiOₓ/perovskite, the perovskite layer was excited from quartz/NiOₓ side. Dark J–V characteristics of trap density and carrier mobility of the perovskite films are obtained for c) HT-NiOₓ/ITO and d) UV-NiOₓ/ITO with the device structure of ITO/HT- or UV-NiOₓ/perovskite/Cu.

photovoltaic applications. We studied the structure and component of devices through STEM (Figure S6, Supporting Information). Functional layers were clearly distinguished from the cross-section images with EDX mapping. The monolithic perovskite layers were observed in both HT and UV-NiOₓ-based devices, representing the well-preparation of devices. The optimized conditions of 0.03 M NiOₓ precursor and UV irradiation time of 10 min were applied in the whole work, if not specifically mentioned (Figure S7, Supporting Information).

The performances of triple cation perovskite PSCs with HT-NiOₓ (HTNi-PSCs) or UV-NiOₓ (UVNi-PSCs) HTLs are comprehensively investigated and analyzed. The detailed comparison of device parameters is summarized in the inserted table in Figure 5b. The champion UVNi-PSCs has a PCE of 22.45%, which is significantly boosted compared to the champion HTNi-PSCs (19.79%). For comparison, the results of sol–gel-based NiOₓ PSCs in recent years are summarized in Table S3 and Figure S8 (Supporting Information). By comparing these pioneering works, the PCE of 22.45% of our champion device is achieved by an integral contribution from admiring Voc (1.126 V), large current density (24.25 mA cm⁻²), and a record of 82.19% for FF. Figure 5c shows the trend that the higher the annealing temperature is, the higher the PCE is obtained. Recently, Zhang et al. reported the sol–gel NiOₓ-based inverted PSCs with a champion PCE of 21.79% while a process temperature as high as 500 °C was needed; this was quite close to the softening temperature of the glass. Our work is currently the only one to fill the gap in the upper left area of Figure 5c (PCE > 22% and T_process < 150 °C), which has been long desired in the field of sol–gel NiOₓ-based inverted PSCs. It also proves that the crystallization and intentional doping are not necessary for high-performance inorganic carrier transport materials and thus the high temperature and tedious doping process can be ruled out. Also, to verify the application of UV-NiOₓ film preparation method in flexible devices fabrication, we prepared flexible devices; the flexible device PCE reached 19.70% (Figure S9, Supporting Information) which is listed as one of the top efficiencies of flexible inverted PSCs.[19]

To investigate the reproducibility of these devices, 60 pieces of HTNi and UVNi-PSCs were fabricated, and their performances were statistically shown in Figure 5d and summarized in Table S4 (Supporting Information). The standard deviation of PCE of UVNi-PSCs (0.3%) was smaller than that of HTNi-PSCs (0.68%), indicating a better reproducibility. It is noted that the FF of UVNi-PSCs has a superior average value of 80.89%, which is 7.39% higher than that of HTNi-PSCs (73.32%). In addition to high efficiency, the use of UV-NiOₓ HTL led to a suppressed hysteresis (Figure S10a, Supporting Information), providing more reliable PCE data derived from J–V curves. Further, the steady-state output of unencapsulated HTNi and UVNi-PSCs were examined...
Figure 5. Perovskite device architecture and performance characterization. a) Schematic diagram of inverted PSCs, b) J-V curves of the champion devices, c) Summary of efficient solgel NiOx-based inverted PSCs reported in recent years versus annealing temperature, d) statistics of PCE from 60 devices, e) SPO and f) EQE spectra of UV-Ni-PSCs and HTNi-PSCs. *Represents maximum processing temperature of flexible substrate (150 °C), #Represents glass transition temperature (500 °C). The resistance of transparent conductive oxides, especially ITO, increases significantly at 500 °C.
in air ($T = 25 \degree C$, 60% relative humidity) at their maximum power points (MPPs) for 600 s (Figure 5e). UV-Ni-PSCs delivered a stabilized $V_{oc}$ of 0.96 V, $J_{sc}$ of 22.3 mA cm$^{-2}$, and a corresponding PCE of 21.41%, higher than those of HTNi-PSCs (0.86 V, 21.3 mA cm$^{-2}$, and 18.3%). This result also indicates excellent illumination stability for UVNi-PSCs. To verify the $J_{sc}$ values from $J$–$V$ curves, the external quantum efficiency (EQE) was conducted (Figure 5f). It was found that UVNi-PSCs device had a higher EQE than HTNi-PSCs device at the wavelength of 300 to 450 nm; this was consistent with the UV–vis spectrum of NiO$_x$ films (Figure 2d) where the UV-NiO$_x$ film had a higher transmittance at the wavelength between 300 and 400 nm. A high transmittance donated high photocurrent generation and resulted in a high current density.\[56\] Finally, the stability test of UVNi and HTNi-PSCs was conducted on all devices that were stored in ambient air ($T = 25 \degree C$, 60% relative humidity) as revealed in Figure S11 (Supporting Information). UVNi-PSCs maintained 85% of initial PCE after 960 h (40 days) storage, while the HTNi-PSCs were reduced to 81% of initial PCE. From Figure 5e and Figure S11 (Supporting Information), it was concluded that UV-NiO$_x$ film endowed PSCs excellent light and moisture stability.

To rationalize the superior performance of UVNi-PSCs, further investigations were carried out on the interfacial traps and recombination in PSCs devices, by $I$–$V$ measurement under various light illuminations and in the dark. The dependence of $V_{oc}$ on the light intensity is thus provided in Figure S12a–c (Supporting Information). A slower photovoltaic decay is observed in UVNi-PSCs device compared to HTNi-PSCs device; this indicates reduced recombination losses at UV-NiO$_x$/perovskite interfaces as revealed in Figure 4. Electrochemical impedance spectroscopy (EIS) in the dark with frequencies ranging from 1 MHz to 1 Hz was measured to understand the charge transfer and recombination dynamics in the devices. The fitted Nyquist plots of the EIS curves of UVNi and HTNi-PSCs are shown in Figure S12d (Supporting Information). $R_s$ is referring to series resistance and $R_{rec}$ is the recombination resistance of PSCs devices. HTNi-PSCs device has $R_s$ of 185.7 $\Omega$ and $R_{rec}$ of 4366 $\Omega$, whereas $R_s$ of UVNi-PSCs device is reduced to 59.5 $\Omega$ with the promoted $R_{rec}$ to 7677 $\Omega$. This result agrees well with the conclusion that UV-NiO$_x$ layer is in favor of improving charge transfer and suppressing the charge recombination in PSC device (Figure 2–4).\[20\] Therefore, it is concluded that the significantly enhanced performance of UVNi-PSCs derives is routed in the effective role of UV-NiO$_x$ film.

Further, we analyze the merits of UV irradiation method from the aspects of energy, cost, and environment. Compared to conventional annealing treatment, UV irradiation is more uniform, efficient, and thus energy-saving.\[11,21\] In Table S5 (Supporting Information), we compare the cost of raw materials for the preparation of HTLs by UV, HT-NiO$_x$, and PTAA (a known organic HTL, efficient and cheap). It is found that for the preparation of UV-NiO$_x$ HTL, the cost can be reduced by a factor of $\approx$9000 (compared to PTAA) or $\approx$58 (compared to HT-NiO$_x$). This is in addition to the fact that the film preparation process is free of toxic organic or alcoholic solvents, and greenhouse gases. All in all, to the best of the authors’ knowledge, the proposed method in this work is the most economic and eco-friendly method to produce doping-free NiO$_x$ HTLs for efficient inverted PSCs.

3. Conclusion

In this study, we present a simple, economic, eco-friendly, and commercially applicable metal oxide synthesis method that greatly enhances the PCE of doping-free NiO$_x$ sol-gel-based inverted PSCs to 22.45%. Due to the merits of UV irradiation-induced synthesis NiO$_x$ method, high-temperature annealing ($>150 \degree C$) is not required, which is a promising HTL preparation technique compatible to other existing protocols for the fabrication of flexible and tandem PSCs. Also, our method greatly reduces the cost of materials and process and is free of toxic or organic solvents and greenhouse gases, and thus represents a highly competitive strategy to prepare high-quality inorganic hole transport layers based on the photochemical reaction kinetics. The protocol provided here is anticipated to be useful for other optoelectronic applications and commercialization.

4. Experimental Section

Materials: Formamidinium iodide (FAI, 99.9%), methylammonium chloride (MACI, 99.9%), cesium iodide (CsI, 99.999%), methylammonium bromide (MABr, 99.9%), and lead iodide (PbI$_2$, 99.99%) were purchased from Advanced Election Technology Co. Ltd. (P. R. China). Cs$_2$ (99.99%) and bathocuproine (BCP, 99%) were purchased from Xi’an Polymer Light Technology Corp. (P. R. China). Nickel(II) acetylacetonate (Ni(acac)$_2$, 95%), hydrochloric acid (ACS reagent, 37%), ammonium hydroxide (NH$_4$OH, 28.0-30.0% NH$_3$ basis), nickel hydroxide, nickel(II) nitrate hydrate (Ni(NO$_3$)$_2$·6H$_2$O, 99.99% trace metals basis), Ni,N-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), 2-propanol (IPA, anhydrous, 99.5%), and ethanol (anhydrous) were obtained from Sigma–Aldrich (P. R. China). All materials were used as received.

UV-NiO$_x$ Film Preparation: The NiO$_x$ precursor solution was prepared by dissolving $0.01-0.1$ m Ni(OH)$_2$ or Ni(NO$_3$)$_2$·6H$_2$O in ammonium hydroxide to form a light blue solution, then the solution was filtered by a 0.22 mm PTFE filter. The precursor solution concentration of 0.03 m spun on a cleaned ITO substrate at 2000 rpm for 30–60 s, or the substrates were soaked in a diluted solution (0.005 m, pH of 14) 20–30 s and dried by N$_2$ gun or spinning. Then, the substrates were transferred to a commercial UV box (250 W, Shenzhen HWO Technology Co. Ltd) for irradiation at varied time of several to tens of minutes. The film thickness was $\approx$13–17 nm at the concentration of 0.02 m L$^{-1}$, 35–40 nm at the concentration of 0.05 m L$^{-1}$, and 70–85 nm at the concentration of 0.1 m L$^{-1}$. After the irradiation, the films were immediately transferred into the glovebox for the perovskite deposition.

HT-NiO$_x$ Film Preparation: The HT-NiO$_x$ layer was prepared according to the previously reported method.\[21\] In brief, 0.1 m of Ni(acac)$_2$ was dissolved in ethanol with 1% v/v HCl. The solution was filtered via 0.22 m PTFE filter and spread on a cleaned ITO/glass substrate, then the substrate was spun at 4000 rpm for 40 s. The substrates were transferred into a N$_2$ glovebox after annealing at 180 $\degree$C for 10 min and 400 $\degree$C for 45 min.

Device Fabrication: Patterned ITO glass was cleaned by sonication in 2% Helmanex solution, acetone, EtOH, IPA, and deionized water. NiO$_x$ films were prepared as described above. The C$_{0.95}$FA$_{0.05}$MA$_{1.1}$Pb$_{1.2}$I$_{3.8}$Br$_{0.9}$ perovskite precursor was prepared by mixing 1.5 m A-site salt with a molar ratio of Cs$_2$:FAI:MABr = 0.05:0.85:0.1 and 1.6 m PbI$_2$ in 1 mL DMF and DMSO (8:2, v/v); an extra 0.3 m MACI was added to the precursor. The perovskite precursor solution was spread on the NiO$_x$ coated substrate and spun at 1000 rpm at a ramp rate of 200 rpm s$^{-1}$ for 10 s and 4000 rpm at the ramp rate of 1000 rpm s$^{-1}$ for 30 s; then 130 $\mu$L of ethyl acetate was quickly dripped onto the substrate in the last 5 to 10 s. The perovskite layer was then annealed at 65 $\degree$C for 5 min and 150 $\degree$C for 10 min. Devices were completed by the thermal evaporation of 40 nm Ca, 8 nm BCP, and 100 nm Cu. The active area of the devices was 0.12 cm$^2$. 

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Device Performance Characterizations: Current density–voltage character- 
ization was conducted using a Keithley 2400 source meter under AM
1.5G irradiation. Sunlight was generated using an Enlitech SS-F7A solar
simulator with 300 W Xenon lamp in ambient air (humidity ≈60%). To
correctly estimate the equivalent AM 1.5G irradiance level and the mis-
match factor for the tested cell, the light intensity was calibrated by Na-
tional Renewable Energy Laboratories (NREL)-calibrated Si solar cell. The
J–V curves were extracted in a range of 1.2–0.2 V with 0.2 V stepwise.
The cells were measured multiple times (typically five to eight scans in 1—
2 min) until reaching the performance peak. The 0.09 cm² metal mask
was used for J–V measurement. The external quantum efficiency (EQE)
measurements were performed using Enlitech QE-R3011 EQE system in
ambient temperature. A 300 W Xenon lamp was used as the light source,
and the light intensity was calibrated with NREL-calibrated reference Si
photodiode.

Film Characterizations: The morphologies of both NiOx-coated ITO
films and perovskite films were characterized using a Zeiss Merlin SEM
at an accelerating voltage of 3 kV. The Raman spectra of products and the
pulse laser were obtained by using a HORIBA Raman spectrometer (LaBram HR Evolution) with an excitation wavelength of 532 nm. The
data related to the surface potential and roughness were collected using a
Dimension FastScan Atomic Force Microscope (Bruker Fastscan) in the
KPFM tapping mode. The SCM-PIT-V2 probe coated with PtIr was used
for KPFM and AFM image acquisitions. The diffraction patterns were ob-
tained using a Bruker ECO D8 diffractometer with Cu Kα (λ = 1.5418 Å)
radiation. UPS and XPS measurements were carried out using an ES-
CALAB 250Xi (Thermo Fisher Scientific) in an ultrahigh vacuum with a
base pressure of 1 × 10⁻¹⁰ mbar. A monochromatic aluminum (Kα) X-
ray source providing photons with the energy of 1486.7 eV for XPS, and a
standard helium-discharge lamp with He λ photons at 21.22 V for UPS.
The total energy-resolutions of XPS and UPS were 0.30 eV and 50 meV, re-
spectively. The XPS data was analyzed and calculated using the Advantage
software; the ratio of nickel components was obtained from the ratio of
peaks area. The work function of the film was extracted from the edge of
the secondary electron cut-off of the UPS spectra by applying a bias volt-
age of ~5 V to the sample. The steady-state and time-resolve photolu-
minescence spectra were collected from Edinburgh Instruments FLS 1000.
Samples were prepared on a quartz for all photoluminescence measure-
ments. The 470 nm wavelength was used for the excitation light for the
steady-state photoluminescence measurement, and a pulsed laser with
405 nm light-emitting diode was utilized for the time-resolve photolu-
minescence measurement. To understand the performance of carrier trans-
port and hole extraction at the interface, the incident beam was emitted
from the quartz side passed through the hole transport layer to excite the
perovskite layer. The absorbance spectra for all films were collected using a
PerkinElmer lambda 950 UV–vis–NIR spectrometer. The electrochemical
impedance spectroscopy (EIS) measurements were performed on a Zah-
erner PP211 electrochemical workstation with max-power-point voltage
for each device. The NiOx particle STEM-DF2 images and the selected area
electron diffraction patterns were obtained from FEI Talos F200X with X-
FEG gun operated at 200 kV. The preparation of particle samples was
different from the film preparation. For the STEM-DF2 images, solutions
were distributed on the glass substrate without spin-coating, then the sub-
strate was transferred on a hot plate for high-temperature annealing in the
commercial UV box for photon-induced synthesis. So, the particles
had a variety of sizes for the solar cells’ fabrication with a relatively sim-
ilar crystallinity. Device cross-section TEM lamellae was prepared using
Thermofisher Scientific Helios 5 UX DualBeam. Tungsten was coated on
the top of the sample for protecting sample damaging from the ion beam;
Ga⁺ ion beam was used for TEM lamellae preparation; the lamellae under-
went a final thinning to 50–60 nm with 2 kV 43 pA to ensure a comparable
gesture for STEM image and spectrum analysis. The STEM-HAADF im-
age with EDX mapping was obtained from FEI Titan Cubed Themis G2
doubl CS-corrected TEM with X-FEG gun operated at 300 kV in the STEM
mode. The electron beam current was reduced using Monochromator to
minimize the damage in perovskite cells during the characterization. De-
vice cross-section EDX mapping was obtained from four Si SuperX EDX
detectors.

Supporting Information
Supporting Information is available from the Wiley Online Library or from
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Conflict of Interest
C.C. and Q.L. are the inventors on a patent application related to this
work filed by Southern University of Science and Technology (CN
202110220543.4). The other authors declare no competing interests.

Data Availability Statement
The data that support the findings of this study are available from the cor-
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green synthesis, inverted perovskite solar cells, NiOx, photochemistry syn-
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