High-performance ITO-free perovskite solar cells enabled by single-walled carbon nanotube films

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Abstract

The unprecedented advancement in power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) have rendered them a promising game-changer in photovoltaics. However, unsatisfactory environmental stability and high manufacturing cost of window electrodes are bottlenecks impeding their commercialization. Here, a strategy is introduced to address these bottlenecks by replacing the costly indium tin oxide (ITO) window electrodes via a simple transfer technique with single-walled carbon nanotubes (SWCNTs) films, which are made of earth-abundant elements with superior chemical and environmental stability. The resultant devices exhibit PCEs of ~19% on rigid substrates, which is the highest value reported to date for ITO-free PSCs. The facile approach for SWCNTs also enables application in flexible PSCs (f-PSCs), delivering a PCE of ~18% with superior mechanical robustness over their ITO-based counterparts due to the excellent mechanical properties of SWCNTs. The SWCNT-based PSCs also deliver satisfactory performances on large-area (1 cm² active area PSCs in this work). Furthermore, these SWCNT-based PSCs can retain over 80% of original PCEs after exposure to air over 700 h while ITO-based devices only sustain ~60% of initial PCEs. This work paves a promising way to accelerate the commercialization of ITO-free PSCs with reduced material cost and prolonged lifetimes.

Keywords: Single-walled carbon nanotubes; high-performance; perovskite solar cells; ITO-free.
Introduction

Exploring clean and sustainable energy resources to meet the ever-increasing energy demand and to reduce CO₂ emission is one of the most pressing global challenges. Direct energy harvesting from the sun using photovoltaic (PV) solar cells represents an ideal solution. To date, perovskite solar cells (PSCs) have achieved unprecedented advancement over the last decade with a certified power conversion efficiency (PCE) up to 25.5%,[1] representing a promising candidate for future PV devices. A series of outstanding features of metal halide perovskites such as tunable bandgap, high absorption coefficient, high charge carrier mobility, and long charge diffusion length, in conjugation with cheap material cost and facile fabrication processes,[2-6] highlights the reasons for the rapid evolution of PSCs. In particular, low-temperature solution processing (typically < 150 °C) enables the fabrication of PSCs on flexible substrates (especially on plastic substrates), delivering the highest certified PCE of 20.7%.[7] Indium tin oxide (ITO), deposited on glass or other flexible substrates (e.g. plastics, mica,[8] willow glass,[9] etc.) via magnetron sputtering or atomic layer deposition, is widely used as the window electrode in both rigid perovskite solar cells (r-PSCs) and flexible perovskite solar cells (f-PSCs). The unique combination of properties of ITO, including high optical transparency, low sheet resistance (< 15 Ω sq⁻¹), and appropriate work function (W_f ~4.7eV), make it an indispensable material to realize high PCEs for PSCs. However, the scarcity of indium and the complicated deposition procedure ultimately hamper its commercial application.[10-12] The estimated cost of the transparent conductive oxide (TCO) in a PSC comprises ~50 - 60% of the total material cost.[13, 14] In addition, the commonly used plastic substrates for f-PSCs including polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyestersulfone (PES), etc. have a much higher water vapor transmission rate (WVTR) than glass,[15] allowing moisture, oxygen, and other hazardous substances to penetrate through and degrade the perovskite layer. Moreover, the brittleness of ITO makes it susceptible to cracking after repeated bending,
twisting, and deforming. All these obstacles will significantly shorten the lifespan of f-PSCs. On the other hand, the considerable novel features and properties enable f-PSCs to be compelling competitors in the current PV market once the remaining challenges are solved. For example, as the power supply for smart and aerial devices (such as flexible smartphones, smartwatches, unmanned aerial vehicles, etc.) where a high power-to-weight ratio and high docility are often required, f-PSCs are proposed to be an ideal candidate to supply continuous powers to ion batteries. Moreover, the high power-to-weight ratio of f-PSCs also leads to cheaper installation costs. Remarkably, the market of building-integrated photovoltaics (BIPV) is expected to reach US$56.2 billion in 2027,[16] and modern buildings have been becoming irregular and non-uniform due to aesthetic needs. Therefore, highly bendable, colorful, and light-weight f-PSCs may occupy a greater share in the future BIPV market. To accelerate the manufacturing process of f-PSCs, novel low-temperature fabrication methods, additives, and passivation engineering approaches have been developed and proven to be effective ways to advance the development of f-PSCs.[17-19] Over the last decade, durable alternatives have been explored to replace ITO, including metal-grids, polymers, graphene, organic materials, etc [20-22]. For example, Ag nanowires (AgNWs) prepared by slot-die coating were used as the transparent conductive electrodes (TCEs), resulting in a PCE of ~11% on f-PSCs.[23] Later, a novel oxide–metal–oxide (OMO) layer prepared via reactive plasma deposition was employed to replace the ITO layer and achieved a PCE of ~14%.[24] However, we note that expensive materials and complex manufacturing procedures are incompatible with cost-effective and scalable production. Despite the high potential of the ITO-free PSCs, unfortunately, either the complex preparation procedures of these ITO substitutes or insufficient PCEs of resulting devices do not meet the strict requirements of fast and scalable productions. Consequently, it is urgent to develop a simple and scalable technique for preparing high-quality transparent electrodes.
Among numerous candidates, carbon materials have attracted tremendous attention due to their high chemical and environmental stability, favorable mechanical robustness, and excellent optoelectrical properties.\textsuperscript{[25, 26]} Therefore, PSCs employing carbon materials have been advancing rapidly.\textsuperscript{[27]} For example, graphene films deposited via chemical vapor deposition (CVD) were used to replace ITO, achieving a PCE of 17.1\% with the configuration of glass/graphene/MoO\textsubscript{3}/PEDOT:PSS/MA\textsubscript{2}PbI\textsubscript{3}/C\textsubscript{60}/BCP/LiF/Al.\textsuperscript{[28]} Recently, double-wall carbon nanotubes (DWCNTs) prepared by solution processing, helped PSCs reach a respectable PCE of 17.2\% on rigid substrates, which is the highest value for ITO-free PSCs to date.\textsuperscript{[29]} Among all types of carbon electrodes, single-wall carbon nanotube (SWCNT) films, prepared from a direct dry-transfer method are an ideal choice because of their superior properties such as high optical transparency (can reach up to \textasciitilde 95\%), the low sheet resistance (can achieve as low as \textasciitilde 35 \Omega \text{ sq}\textsuperscript{-1}), high compatibility with scalable production, and low cost.\textsuperscript{[30, 31]} The cost of SWCNT films is only \textasciitilde \$40 per square meter (\textasciitilde 50 \Omega \text{ sq}\textsuperscript{-1}, \textasciitilde 85\% optical transmittance on glass) (Details of the cost calculation are included in the Method section), much cheaper than that of commercial ITO \textasciitilde \$900 per square meter (\textasciitilde 15 \Omega \text{ sq}\textsuperscript{-1}, \textasciitilde 85\% optical transmittance on glass).

More significantly, the simple transfer procedure enables SWCNT films more favorable to the fabrication of large-area PSCs on both rigid and flexible substrates, which can not realized for graphene. Here, we have successfully replaced the ITO with SWCNT films as window electrodes in PSCs and achieved a high PCE of \textasciitilde 19.0\% on glass substrates and \textasciitilde 18.0\% on flexible substrates via a simple transfer process. In addition, the SWCNT films have illustrated satisfactory performances for large-area PCEs (1 cm\textsuperscript{2} active area in this work), with PCEs of 17.0\% for r-PSCs and 15.8\% for f-PSCs, respectively. We further demonstrate that by incorporating SWCNTs in f-PSCs, both mechanical robustness and environmental stability are considerably enhanced.
Results and discussion

Characterization of SWCNT films. In this work, SWCNT films were prepared by injection floating catalyst chemical vapor deposition (FCCVD). During the process, a carrier gas, high-flux of hydrogen, was introduced to prevent the aggregation of SWCNTs into large bundles and to in situ etch away amorphous carbon. The thickness of SWCNT films was controlled by adjusting the collecting time. The detailed preparation procedure is illustrated in the Method section. To transfer these SWCNT films onto target substrates, a dry transfer process was applied, which is illustrated in Figure 1a. A membrane (here is a filter paper) coated with a SWCNT film was cut into the required size and placed on a target substrate, which was then removed and leaving the SWCNT film on the target substrate. This facile method is applied to the production of both r-PSCs and f-PSCs on a lab-scale and large-area, which will be demonstrated later on. Due to the strong van der Waals force, individual SWCNTs are likely to aggregate with the adjacent SWCNTs to form large bundles. These large bundles not only deteriorate the electrical properties but also affect the optical properties of SWCNT films. Here, the high-flux H₂ gas greatly mitigates the formation of large bundles by decreasing the concentrations of catalyst precursor (ferrocene), growth promoter (thiophene), and carbon source (ethylene and toluene), resulting in few nuclei for SWCNTs in a specific volume. Another factor that leads to the formation of smaller bundles is that the residence time of the gas in the high-temperature zone decreases, which reduces the growth time of SWCNTs. Collectively, the introduction of the high-flux H₂ has decreased the number and length of SWCNTs in the reactor, which vastly suppresses the formation of larger bundles caused by the van der Waals force between adjacent SWCNTs during growth. The transmission electron microscope (TEM) image of SWCNTs is shown in Figure 1b, from which we can estimate the mean diameter of isolated tubes to be ~2.2 nm. The isolated tubes and bundles with sizes less than 10 nm occupy ~60% of the total number of tubes (Figure S1 in supporting information).
A typical scanning electron microscope (SEM) image shown in Figure 1c demonstrates a randomly entangled network of SWCNTs. The interconnected SWCNT network without large bundles endows the film with efficient electron transfer pathways. The Raman spectrum of the SWCNT film illustrates a very high-intensity ratio of G to D bands (IG/ID = 157) (Figure S2 in support information), indicating high crystallinity and low defect density of the resultant SWCNTs. Besides, from the main radial breathing mode (RBM) peak located at 114.3 cm\(^{-1}\), and the reciprocal relationship between the frequency of the RBM (\(\omega_r\)) and the nanotube diameter (\(d_t\)) \[^{35}\] via the relation \(\omega_r = 248/d_t\) \[^{36}\], the mean diameter of the SWCNTs is calculated to be \(~2.2\) nm, which is consistent with TEM result.

For an ideal TCE, low sheet resistance and high transmittance are required. Although we can obtain highly transparent SWCNT films with optical transmittance up to 95\%, in this work we purposely chose SWCNT films with an optical transmittance of \(~85\%) to achieve a good balance between the optical transparency and conductivity (Figure 1d). We note that the transmittance value of the same SWCNT film on flexible substrates (PEN in this work) is slightly lower than that on glass, which can be attributed to the inherent absorption of polymeric materials.\[^{37}\]

Normally, the junction resistance between nanotubes is much higher than the intrinsic resistance of a nanotube. Thus, the electrical conductivity of an SWCNT network is largely determined by the resistance at intertube junctions.\[^{38}\] The sheet resistance of the pristine SWCNT films falls between 70-80 \(\Omega\) sq\(^{-1}\), which is better than other reported undoped SWCNT films (~100 \(\Omega\) sq\(^{-1}\)) with identical transparency.\[^{39, 40}\] However, this value is still higher than that of commercial ITO (typically below 15 \(\Omega\) sq\(^{-1}\)). Bearing this challenge in mind, further reduction in the sheet resistance of SWCNT films is regarded as a key step to minimize the photocurrent loss in our work. Chemical doping of SWCNT films, e.g. by nitric acid (HNO\(_3\)) treatment, is widely used to improve the conductivity.\[^{41}\] Commonly, there are two widely accepted effects brought by the HNO\(_3\) treatment: 1) removing the residual amorphous carbon between carbon nanotubes and 2) chemical doping.\[^{42, 43}\] It is noteworthy that a SWCNT film is generally
composed of 1/3 metallic and 2/3 semiconducting SWCNTs. Consequently, the chemical doping effect can be ascribed to the carrier injection into the individual semiconducting nanotubes from the near metallic nanotubes, and a modification of the intertube barriers.\cite{44} For our SWCNT samples, the portion of amorphous carbon is negligible.\cite{26} The effect of HNO\textsubscript{3} should primarily be the chemical doping, contributing to the decrease in the intertube junction resistance.\cite{45} Indeed, after the nitric acid treatment, the sheet resistance of the SWCNT network is significantly reduced, from \(~81\) to \(~33\ \Omega \text{sq}^{-1}\) (Figure 1d). The sheet resistance of HNO\textsubscript{3}-doped here is much lower than other types of HNO\textsubscript{3}-doped carbon nanotubes (the sheet resistances of double-wall or multiwall carbon nanotubes are over \(130\ \Omega \text{sq}^{-1}\)) with the same optical transparency.\cite{29, 46}

In favor of the HNO\textsubscript{3} doping, not only the sheet resistance was decreased, but the \(W_f\) of the nitric acid-doped SWCNT films also shifted from \(~-4.8\) eV to \(~-4.9\) eV. The Raman spectra of the SWCNT films before and after the HNO\textsubscript{3} doping are compared under 633 nm laser excitation (Figure 1e). The RBM peak (located at \(114.3\ \text{cm}^{-1}\)) could be hardly detected after HNO\textsubscript{3} treatment, owing to the loss of resonance enhancement in the HNO\textsubscript{3}-doped SWCNTs.\cite{47}

The significant decrease in the Raman intensity and the blue shift in the G and G' bands demonstrate the \(p\)-type doping effect of the HNO\textsubscript{3}, which is further confirmed by the Ultraviolet-Visible-near-IR Spectroscopy (UV-vis-NIR) optical absorbance spectroscopy (Figure S3a in supporting information): the HNO\textsubscript{3} treatment quenched the first optical transition of the van Hove singularities (\(E_{11}^S\)) and significantly suppressed the second optical transition of the van Hove singularities (\(E_{22}^S\)).\cite{48} These results collectively indicate that HNO\textsubscript{3} serves as a \(p\)-type dopant and downshifts the Fermi level and \(W_f\) of the SWCNT films.\cite{49} Importantly, HNO\textsubscript{3} has little impact on the transmittance of the SWCNT films in the region of the visible wavelengths (Figure S3b in supporting information). The change of the \(W_f\) also enables a better energy level alignment between the SWCNT and triple-cation halide perovskite used in this
work (with valence band maximum (VBM) ~ -5.4 eV), which may reduce the energy barrier between the SWCNT and perovskite and thus reduce the interface energy loss.

**Figure 1** a) Dry transfer procedure of a SWCNT film and transferred SWCNT on glass (left) and PEN substrates (right) partly covering the logo of the University of Surrey. b) TEM image of SWCNTs (*scale bar = 20 nm*). c) SEM image of the SWCNT film (*scale bar = 500 nm*). d) The sheet resistances of SWCNT films with different optical transmittance values before and after HNO₃ treatment. e) Raman spectra of SWCNT before and after HNO₃ treatment.
Fabrication and characterization of PSCs. To efficiently separate and transport the photogenerated electron-hole pairs, a suitable hole transport layer (HTL) is required. Many HTLs have been used in PSCs including inorganic materials like NiOx, CuO, and CuSCN, etc.,[50-52] or organic materials like poly (3,4-ethylenedioxythiphene):poly(styrenesulfonate) (PEDOT:PSS), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobiﬂuorene (Spiro-OMeTAD), poly [bis (4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA), poly (N,N'-bis-4-butylphenyl-N,N'-bisphenyl) benzidine (Poly-TPD), etc.[29, 53-55] Among these HTLs, organic polymer or small molecule materials have shortcomings of high cost, low conductivity without doping, instability in a long run, limiting the manufacturing process of PSCs. For instance, the acidity of PEDOT:PSS corrodes the perovskite layer which signiﬁcantly limits the lifetimes of PSCs.[56] As for the spiro-OMeTAD, the need for hygroscopic dopants triggers degradation of the perovskite layer.[57] In this work, we chose copper-doped nickel oxide (Cu: NiOx) as the HTL due to its low cost and easy preparation protocols. The lightly Cu-doped NiOx has illustrated a signiﬁcant enhancement in the electrical conductivity and device performance as compared with the undoped NiOx.[58] We also note that HNO3 treatment not only shifts the Wf of SWCNT film from -4.8 to -4.9 eV as demonstrated earlier but also improves the film wettability due to the introduction of carboxyl groups,[59] enabling better deposition of Cu: NiOx on the SWCNT film via a simple spin-coating process. Consequently, Cu: NiOx with deeper conduction band minimum (CBM, ~ -5.3 eV) and higher hole mobility (~1.09 × 10^-2 cm^2 V^-1 s^-1) as compared with undoped NiOx (~3.05 × 10^-3 cm^2 V^-1 s^-1),[60] is chosen as a suitable HTL in this work to prepare high-performance and low-cost PSCs.

Subsequently, a triple-cation perovskite layer (CsMAFAPbI_xBr_3-x) was fabricated on top of the HNO3-doped SWCNT/Cu:NiOx film via a one-step solution processing method. Here, it is noteworthy that the pristine perovskite layer contains grain boundaries, electronic defects, and interfacial impurities, all of these have hugely limited the perovskite material to fully illustrate its’ potential.[61, 62] In this work, potassium iodide and choline chloride were both employed to
passivate the perovskite layer from the bottom and topsides, which can suppress the non-radiative losses and photoinduced ion migration.\textsuperscript{[61, 63]} The SEM images (Figure S4 in support information) show that the passivated perovskite layer (KI/perovskite/choline chloride) deposited on HNO\textsubscript{3}-doped SWCNT/Cu:NiO\textsubscript{x} has larger grain sizes than those deposited on the pristine SWCNT film. The X-ray diffraction (XRD) performed to study the phases and crystallinity of perovskite films, from which the high-intensity characteristic peaks at \(\sim 14^\circ\) for the perovskite films deposited on both ITO-based and SWCNT-based substrates are clearly shown, while the photoinactive peaks at 11.6\(^{\circ}\) (\(\delta\)-phase FAPbI\textsubscript{3}) and 12.7\(^{\circ}\) (cubic PbI\textsubscript{2}) disappeared on both samples, confirming the formation of high-quality perovskite layer (Figure S5 in supporting information). Having obtained the high-quality triple-cation perovskite thin film, we studied the behavior of photogenerated charges at the interface between SWCNT film and perovskite by steady-state photoluminescence (PL) measurements. The PL emission spectra (Figure 2a) suggest that the photo-quenching of the passivated perovskite layer on HNO\textsubscript{3}-doped SWCNT/Cu:NiO\textsubscript{x} film is more pronounced than that deposited on pristine SWCNT film. A possible reason could be less charge accumulation at the interface. To confirm our hypothesis, time-resolved photoluminescence (TRPL) was used to explore the carrier recombination behavior at the interface (Figure 2b). The average decay time (\(\tau_{\text{AVG}}\)) dropped from \(\sim 8\) to \(\sim 3\) ns (Table S1), implying that the electron-hole pairs were separated more efficiently for the passivated perovskite layer deposited on the HNO\textsubscript{3}-doped SWCNT/Cu:NiO\textsubscript{x} film than that deposited on the pristine SWCNT film.\textsuperscript{[64]} It is known that non-radiative recombination results from impurities, defects, and mobile species.\textsuperscript{[65]} Therefore, the faster charge transfer process also confirms that the charge collection ability of the SWCNT film was greatly boosted by HNO\textsubscript{3} treatment and Cu:NiO\textsubscript{x} coating. We further employed TRPL mapping to study the charge carrier lifetime on a large area (with a size of 18 \(\mu\text{m} \times 18 \mu\text{m}\)). The mapping data was used to directly reveal the decay time of near-surface charges (Figure 2c). The average charge carrier lifetime at the interface of SWCNT/perovskite was reduced from \(\sim 8\) ns to \(\sim 3\) ns.
after HNO₃-doping and Cu:NiOₓ coating, which is in agreement with the TRPL study. And the statistics of the TRPL mapping (Figure 2d) further confirm more effective free charge carrier transfer across the interface after the treatment.
Figure 2 a) PL spectra of pristine-SWCNT/p-PVK, HNO3-doped SWCNT/p-PVK, and HNO3-doped SWCNT/Cu: NiOx/p-PVK. b) TRPL spectra of pristine SWCNT/p-PVK, HNO3-doped SWCNT/p-PVK, and HNO3-doped SWCNT/Cu: NiOx/p-PVK. c) TRPL mapping graphs of p-PVK on pristine SWCNT, HNO3-doped SWCNT, and HNO3-doped SWCNT/Cu: NiOx (scale bar = 5 μm). d) Histograms of the PL decay times of pristine SWCNT/p-PVK, HNO3-doped SWCNT/p-PVK, and SWCNT/Cu: NiOx/p-PVK (p-PVK = passivated perovskite).

In this work, inverted PSCs were fabricated (see details in the experimental section) and the device configuration (SWCNT/CuNiOx(~25 nm)/KI(~2 nm)/CsMAFAPbI3Br3-x(~500 nm)/choline chloride(~3 nm)/PCBM(~20 nm)/BCP(~7 nm)/Ag(120 nm)) is shown in Figure 3a. The corresponding cross-sectional SEM image is shown in Figure 3b. r-PSCs integrated with the modified SWCNTs achieve an outstanding PCE of 19.0% (18.0% for f-PSCs) with negligible hysteresis (Figure 3c) with a \(V_{oc}\) of 1.13 V, a \(J_{sc}\) of ~21.3 mA cm\(^{-2}\), and a FF of ~80%, which is the highest PCE of ITO-free devices reported so far (Figure S6, and Table S2, S3 in supporting information). Furthermore, a stabilized power output measurement yields a photocurrent density of ~21 mA cm\(^{-2}\) at a bias voltage of 0.92 V (voltage at maximum power point) leads to a stabilized PCE of ~19.0% (Figure S7 in supporting information). From the statistics of 60 devices being collected (Figure S8 in supporting information), the PCEs of ~85% SWCNT-based PSCs fall between 17.0% and 19.0%, indicating the good reproducibility of the HNO3-doped SWCNT & Cu: NiOx -based PSCs. Besides, SWCNT-based PSCs exhibit better environmental stability. The SWCNT-based PSCs (unencapsulated) can retain more than 80% of the pristine PCE values after one month (Storage condition: dark, relative humidity = 35% ± 5%, temperature = 25 °C, and devices were measured every 24h.) (Figure 3d) because of the strong interaction between the SWCNT network and perovskite layer,\(^{[66]}\) while the ITO-based PSCs (unencapsulated) only sustain ~60% of original PCEs.
Figure 3  a) Illustration of an SWCNT-based PSC. b) Cross-sectional SEM image of an SWCNT-based PSC (scale bar = 100 nm). c) Photocurrent density-voltage curves of a pristine SWCNT-based PSC, HNO₃-doped SWCNT-based PSC, and HNO₃-doped & Cu:NiOₓ-based PSC (F: forward scan; R: reverse scan). d) Environmental stability of ITO-based and SWCNT-based PSCs (both unencapsulated) (devices were stored under aforementioned conditions). e)
Series resistance and shunt resistance of pristine SWCNT-based PSCs, HNO₃-doped SWCNT-based PSCs, and HNO₃-doped & Cu:NiOₓ-based PSCs. f) Dark $J-V$ curves of PSCs based on different substrates.

**Table 1** Photovoltaic parameters of the champion r-PSCs based on pristine SWCNT films, HNO₃-doped SWCNT films, and HNO₃-doped SWCNT & Cu:NiOₓ films. ($J_{sc}$: short-circuit current density, $V_{oc}$: open-circuit voltage; FF: fill factor, PCE: power conversion efficiency).

<table>
<thead>
<tr>
<th>Device Name</th>
<th>Scan direction</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm⁻²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tr>
<td><strong>Pristine SWCNT</strong></td>
<td>Forward</td>
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<td>18.8</td>
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<tr>
<td></td>
<td>Reverse</td>
<td>0.92</td>
<td>18.2</td>
<td>50.3</td>
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<tr>
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<td>20.1</td>
<td>63.9</td>
<td>14.0</td>
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<tr>
<td></td>
<td>Reverse</td>
<td>1.04</td>
<td>19.5</td>
<td>55.2</td>
<td>11.2</td>
</tr>
<tr>
<td><strong>HNO₃-doped SWCNT &amp; Cu:NiOₓ</strong></td>
<td>Forward</td>
<td>1.13</td>
<td>21.3</td>
<td>78.3</td>
<td>18.9</td>
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<tr>
<td></td>
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<td>1.12</td>
<td>21.4</td>
<td>78.8</td>
<td>19.0</td>
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</table>

We summarize the photovoltaic parameters of PSCs based on various window electrodes on rigid substrates in Table 1. The PCEs of HNO₃-doped SWCNT & Cu:NiOₓ-based PSCs have increased by ~70% as compared with pristine SWCNT-based PSCs. The origins of such a striking enhancement can be explained as follows. The first aspect is associated with the charge transfer process. Commonly, series resistance ($R_s$) and shunt resistance ($R_{sh}$) are considered as two key factors that can directly influence the performance of PSCs. The $R_s$ reflects the current transport and contact between electrodes and the perovskite layer, while $R_{sh}$ reveals the loss of photocurrent through carrier recombination within the device, particularly at the interfaces of each layer.[67] Determined from the statistics of the $R_s$ and $R_{sh}$ (Figure 3e), from pristine SWCNT-based PSCs to HNO₃-doped SWCNT & Cu:NiOₓ-based PSCs, the $R_s$ decreases (from ~125 Ω to ~60 Ω) but $R_{sh}$ increases (from ~2 k Ω to ~12 k Ω), indicating the smoother current flow at the interface of HNO₃-doped SWCNT & Cu:NiOₓ-based PSCs, which is consistent with TRPL data. The observed decrease in the $R_s$ could be attributed to more efficient charge
extraction. However, the sheet resistance of pristine SWCNTs is relatively high, in conjugation with insufficient charge carrier selectivity which can be ascribed to the SWCNTs being not able to generate a strong build-in field to prevent the charge recombination at the interface.\[^{68}\] Due to the \textit{p}-type doping by HNO\textsubscript{3}-treatment, minority carrier concentration at the interface was further reduced, leading to better carrier selectivity and faster transport.\[^{69}\] The HTL (Cu:NiO\textsubscript{x}) with appropriate energy bands and excellent hole extraction capability further contributes to the carrier selectivity and separation of electron-hole pairs. These results suggest that HNO\textsubscript{3}-treated SWCNT and Cu:NiO\textsubscript{x} coating are efficient methods to minimize the \(R_s\) by enhancing the extraction and transport of charge carriers within the SWCNT network. As aforementioned, the \(R_{sh}\) is closely related to the contact of each layer. Because the only difference among these three types of PSCs is the bottom layer (pristine SWCNT film, HNO\textsubscript{3}-doped SWCNT film, and HNO\textsubscript{3}-doped & Cu:NiO\textsubscript{x} coated film), therefore, we focus on the SWCNT/perovskite interface. There are several possible origins for the lowest \(R_{sh}\) value of the pristine SWCNT-based PSCs. The first one is related to the morphology of the film. The pristine SWCNT network contains a negligible quantity of amorphous carbon produced during the preparation of SWCNT films. The complete elimination of the amorphous carbon requires high-temperature annealing (~900°C) after acid treatment.\[^{70}\] For our SWCNTs, the effect of the HNO\textsubscript{3} treatment is to optimize the morphology by forming additional amorphous carbon nanoparticles covering the smaller bundles of CNTs.\[^{70}\] Such a phenomenon was proved by atomic force microspectroscopy (AFM). Pristine SWCNTs, HNO\textsubscript{3}-doped SWCNTs, and HNO\textsubscript{3}-treated & Cu:NiO\textsubscript{x}-coated SWCNTs illustrate a decline in the root mean square (RMS) values of 92.6, 76.7, and 17.4 nm, respectively (Figure S9 in supporting information). Another significant aspect is the introduction of NO\textsubscript{3}\textsuperscript{-}, which can be used to passivate the perovskite layer. The passivation of the nitrate group can be mainly related to the donation of lone unpaired electrons to the vacant orbit of Pb\textsuperscript{2+}.\[^{71}\] As reported, molecules containing a lone pair of electrons on either nitrogen (N) or sulfur (S) functionalities would work as a Lewis base in PSCs, these
molecules could coordinate with undercoordinated Pb^{2+}, producing a Lewis abduct, thus reducing the non-radiative charge recombination.\cite{72,73} Furthermore, electrochemical impedance spectra (EIS) were recorded to investigate the internal electrical processes in PSCs (Figure S10 in support information). The semicircle Nyquist plots are well fitted with an equivalent circuit, and the HNO\textsubscript{3}-doped SWCNT & Cu:NiO\textsubscript{x}-based PSCs demonstrated the lowest charge transport resistance (R\textsubscript{ct}), which is 299.5 Ω, while 937.7 Ω for pristine SWCNT-based PSCs, and 724.5 Ω for HNO\textsubscript{3}-doped SWCNT-based PSCs. Generally, the R\textsubscript{ct} comprises all the contributions related to charge injection and transfer.\cite{74} Therefore, the EIS results are consistent with dark J-V characteristics. As previously stated, the HNO\textsubscript{3}-treatment has reduced the intertube resistance, which could result in better tunneling contacts among carbon nanotubes, and may provide more photocurrent pathways with lower resistance.\cite{75} Consequently, the leakage current would be further suppressed, following the dark J-V data (Figure 3f). From the dark J-V curve, the current leakage of the HNO\textsubscript{3} treated SWCNT-based PSCs is ~1 order of magnitude lower than that of the pristine SWCNT-based PSCs. With the addition of Cu:NiO\textsubscript{x} layer, holes were extracted and transported more efficiently, thus mitigating the current leakage. And further, we note that the PCE of our champion SWCNT-based PSC is slightly lower than that of the ITO-based PSC, mainly due to the optical loss (Figure S11 in support information) and J\textsubscript{sc} loss (Figure S12 and S13 in supporting information).

The mild transfer process of SWCNT films has endowed high compatibility with plastic substrates. f-PSCs based on SWCNT films exhibit high PCEs of ~18.0% with negligible hysteresis (Figure 4a). Comparing with rigid counterparts, f-PSCs have similar V\textsubscript{oc} (1.12 V, versus 1.13 V for r-PSCs), but lower J\textsubscript{sc} (20.8 mA cm\textsuperscript{-2}, versus 21.3 mA cm\textsuperscript{-2} for r-PSCs) and FF (77.3%, versus 79% for r-PSCs), which could be associated with the lower optical transmittance and lower electrical conductivity of flexible TCEs.\cite{76} Plastic substrates, as introduced earlier, can be easily penetrated by vapor, oxygen, and other hazardous substances due to the higher WVTR than rigid glass substrates. Because of the hydrophobic nature of
SWCNT films, the environmental stability of f-PSCs was able to reach the same level as that of r-PSCs (storage condition: dark, relative humidity = 35% ± 5%, temperature = 25 °C, and devices were measured every 24h.) (Figure 4b). As a key criterion for evaluating the performance of f-PSCs, we studied the mechanical robustness of the resultant devices. SWCNT-based f-PSCs were proven to sustain ~85% of initial PCEs after bending 1000 times at a radius of 6 mm. Even at a smaller radius, 4 mm, SWCNT-based PSCs were still able to retain over ~80% of the initial PCEs (Figure 4c). We note that the PCE decline of SWCNT-based PSCs is mainly associated with perovskite cracking (Figure S14 in support information).[77] Hence, our work offers a simple route to make long-term stable and mechanically robust f-PSCs as compared with previously reported methods.[29, 78] Besides these advantages, another appealing advantage of SWCNT film is that it can be integrated with large-area perovskite solar cells easily because the size of such SWCNT films can be extended to the meter-scale.[31] To validate the feasibility of large-area PSCs, 1 cm² SWCNT-based PSCs have been fabricated, delivering a respectable PCE of 17.0% on glass substrates (Figure S15 in supporting information) and 15.8% on flexible substrates (Figure S16 in supporting information).
Figure 4  a) $J-V$ curves of the champion SWCNT-based f-PSC. b) Environmental stability tracking of ITO-based and SWCNT-based f-PSCs (unencapsulated) in air, under 25 °C, relative humidity $= 35\% \pm 5\%$. b) Bending test of flexible ITO-based and SWCNT-based PSCs with the bending radius of 4 mm, 6 mm, and 12 mm.

In summary, we have prepared efficient ITO-free PSCs on both rigid and flexible substrates with small-bundle SWCNT films as window electrodes via a simple dry transfer technique. The PSCs showed improved environmental stability and mechanical robustness. Large-area SWCNT-based PSCs also illustrated respectable device performances. More significantly, the
use of the SWCNT films greatly reduces the material cost of the window electrode and simplifies manufacturing procedures. Future work towards the scalable preparation of highly transparent and conductive SWCNT films will further validate them as a promising alternative to the traditional TCO-based materials for a range of photovoltaic and optoelectronic applications.

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J.Z. and X.H. contributed equally to this work. H.L. provided flexible substrates. B.L., K.J., X.L., and Z.W. performed device characterization. X.H. synthesized and collected SWCNT films. J.Z. fabricated perovskite solar cells. J.Z. and X.H. co-wrote the paper. All authors discussed, analyzed, and commented on the manuscript. The authors acknowledge the financial support from the National Key Research and Development Program of China (2019YFB1503500), the National Natural Science Foundation of China (Grants 52072375, 51625203), Marie Skłodowska-Curie Individual Fellowships 2018 (839136), Royal Society International travel program, the State Key Laboratory of Metastable Materials Science and Technology (201901), Fujian Key Laboratory of Photoelectric Functional Materials (FJPFM-201902), Newton Advanced Fellowship (192097), and EPSRC grant (EP/R025304/1). SDS and KJ acknowledge the Royal Society for funding. All authors acknowledge Dr. Aobo Ren for help with PL, UV-Vis measurement, and TRPL mapping.

Supporting Information

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

Conflict of Interest

The authors declare no conflict of interest.
**Materials and Methods**

**Materials**

ITO-patterned glass substrates (10 Ω sq\(^{-1}\)) were purchased from Huananxiangcheng Ltd. (China) and ITO-patterned PEN flexible substrates (<15 Ω sq\(^{-1}\)) were purchased from Peccell Inc (Japan). Nickel (II) nitrate hexahydrate (98%) was purchased from Alfa Aesar. Sodium hydroxide (99.9%) and pH paper stick indicator were purchased from Fisher Sci Ltd. Lead diiodide (PbI\(_2\), 99.99%) and lead dibromide (PbBr\(_2\), 99%) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI, Japan). Formamidinium iodide (FAI), methylammonium iodide (MAI), Cesium iodide (CsI, 99.999%), copper (II) nitrate trihydrate (98%), nitric acid (HNO\(_3\), 70%), and choline chloride (≥ 99%) were purchased from Sigma-Aldrich. PC\(_{61}\)BM (99.5%) and Bathocuproin (BCP, 98%) were purchased from Ossila. N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.7%), chlorobenzene (CB, 99.8%) and toluene (99.85%), and Isopropanol (IPA, 99.5%) were purchased from Acros. Filter papers were purchased from Whatman Inc. All chemicals and materials were purchased from commercial suppliers and used as received.

**SWCNT film preparation.**

SWCNTs films were prepared according to a floating catalyst CVD process previously reported\(^{[30, 79]}\). And the SWCNT films were formed on a membrane filter at room temperature. The thickness of the SWCNT films was controlled by adjusting the collection time. Glass substrates and PEN substrates were cleaned with deionized water, acetone, and isopropyl alcohol respectively for later use. Then the membrane filter with the SWCNT film deposited was first tailored to a proper size with a scalpel and placed on a pre-cleaned substrate. Then a drop of alcohol was dropped on the transferred SWCNT film to ensure good contact between the substrate and the SWCNT film. After several seconds the membrane filter was removed by
using a tweezer. Finally, a glass/SWCNT or PEN/SWCNT substrate was obtained. For HNO₃ doping, the glass/SWCNT or PEN/SWCNT substrate was transferred to a petri dish, and one drop of HNO₃ was dropped on top of the substrate, followed by drying under 60 °C for 45 minutes. Then these substrates were washed with diluted water and alcohol for later use.

**Calculation of the cost of SWCNT films.**

The raw materials and the energy used during the production (here is FCCVD) are taken into account. As calculated, the total cost of 1 gram SWCNTs is estimated at ~$110. The weight of a single SWCNT film (~85% optical transmittance) used in this work is ~460 µg. Therefore, the cost of each film is ~$0.0506. And the area of one single SWCNT film is 21.23 cm² (equals to 0.002123 m²). Thus, the cost of SWCNT is ~$24 m⁻². While comparing with ITO-coated glass substrates, the cost of glass substrates also needs to be added. The final cost of glass/SWCNT is estimated at ~$40 m⁻². And the price of commercialized ITO glass substrates is ~$900 m⁻² (Price data are extracted from Huananxiangcheng Ltd. China.).

**Copper doped nickel oxide thin film preparation.**

0.25 mol nickel (II) nitrate hexahydrate and copper (II) nitrate trihydrate were dissolved in 50 ml distilled water with continuous stirring, copper (II) nitrate trihydrate was added to the nickel (II) nitrate hexahydrate solution at a molar ratio of 5%. After the solution becomes dark green clear, the pH value was adjusted to 10 by adding 10 M sodium hydroxide solution, the pH value was measured by pH indicator. The solution was kept stirring for another 15 minutes after pH reached 10. Then the solution was filtered by a filter paper to collect the dark green precipitation. The collected precipitation was heated at 80 °C for 1 hour after washing with distilled water three times. To obtain copper doped nickel oxide nanoparticles (Cu:NiOₓ NPs), the heated precipitation was transferred to a furnace to calcinate at 275 °C for 2 hours to obtain black
powders. Finally, the black powder was dispersed in deionized water to form 2 wt% Cu: NiOx NPs solution.

**Perovskite solar cell fabrication.**

ITO-patterned glass substrates (10 Ω sq⁻¹, Huananxiangcheng Ltd.) and ITO-patterned PEN flexible substrates (<15 Ω sq⁻¹, Peccell) were cleaned with deionized water, acetone, and isopropyl alcohol respectively. Then ITO-patterned glass substrates were treated with an oxygen plasma process (Emitech K1050X, 230 V, 100 W) for 5 minutes before fabrication. The rest fabrication processes of ITO-based and SWCNT-based perovskite solar cells were the same. Cu: NiOx NPs solution was spin-coated on ITO-based and SWCNT-based substrates at 2000 rpm for 20 seconds, followed by a post-heating process at 120 °C for 10 minutes. Then, these Cu: NiOx-coated substrates were moved to a UV-ozone cleaning device to receive 5 minutes of UV-Ozone treatment. Then the KI layer was prepared on top of the Cu: NiOx via spin-coating, the spin-coating condition of the KI layer is 2000rpm, 30s with a solution concentration of 2 mg/ml (in water), and heated at 100°C for 10 minutes. Here, the composition of perovskite layer is Cs₀.₀₅FA₀.₈₀MA₀.₁₅Pb(IₓBr₁₋ₓ)₃, the perovskite precursor solution was prepared by dissolving 470.23 mg PbI₂, 66.06 mg PbBr₂, 15.59 mg CsI, 166.64 mg formamidinium iodide, and 19.15 mg methylammonium bromide in a 1 ml solution of 4:1 V/V DMF/DMSO. Then the solution was stirred overnight at room temperature. Then perovskite layer was formed by spin-coating according to a two-step protocol, 1000 rpm for 10 seconds and 4000 rpm for 35 seconds, 80 μl CB was dropped 5 seconds before the end of the second step. Then the film was heated at 100 °C for 60 minutes on a hotplate. A passivation layer, choline chloride was then fabricated on top of the perovskite layer at 4000 rpm, 30 seconds with a solution concentration of 1 mg/mL (in IPA), and heated at 100 °C for 30 minutes. Phenyl-C₆₁-butryic acid methyl ester was employed as the electron transport material, PC₆₁BM (20 mg/ml in CB) was spin-coated at 2000 rpm for 20 seconds, and dried at 100 °C for 5 minutes. Afterward, bathocuproine solution (0.5 mg/mL
in IPA) was spin-coated on top of PC_{61}BM. Finally, a 100 nm thick Ag electrode was deposited in a thermal evaporator (>3 \times 10^{-6} \text{Torr}, Moorefield thermal evaporator) to complete the fabrication process.

**Materials and device characterization. (SWCNT films and PSCs)**

The optical transmittance of SWCNT films was measured by a UV–Vis–NIR spectrophotometer (AGILENT CARY 5000). Raman spectra excited by 633 nm laser was obtained using a Jobin-Yvon Labram HR800 instrument. The sheet resistance of the SWCNT film was determined by Four Probes Tech (4-probe Tech.). The morphology of the SWCNT film was characterized by SEM (Nova Nano SEM 430) and TEM (JEM-2010HR and Tecnai G2 F20, operated at 200 kV). XRD patterns were performed using 45 kV, 40 mA Cu Kα (λ = 0.154187 nm) radiation by PANalytical X’Pert Pro, equipped with an X-ray mirror (parallel beam) and proportional Xe detector(GM-tube). The work function of SWCNT films was determined via Esclab-250 instrument. Photoluminescence data were carried out by Agilent Cary Eclipse Fluorescence Spectrophotometer. AFM images were obtained via AIST-NT SmartSPM 1000 in a tapping mode. The TRPL measurements were measured using a confocal microscope setup (PicoQuant, MicroTime 200). The sample was excited by a 510-nm pulsed diode (PDL 828, PicoQuant, pulse width ~ 100 ps) with an air objective. The signals were focused onto a Hybrid PMT detector connected to a Picoquant acquisition card for time-correlated single-photon counting (time resolution of 200 ps). The J-V characteristics and MPP tracking were performed outside the glovebox at the lab condition by using a Keysight B2901A source meter under simulated one-sun AM 1.5G illumination (100 mW cm−2) with a AAA steady solar simulator (Enlitech, SS-F5-3A). Before J-V measurements, the simulator was cautiously calibrated by using a standard monocrystalline silicon solar cell with a KG-5 filter same as previously reported, to ensure the accuracy of the J_{sc} measured from J-V scans, a mask with an aperture area of 0.09 cm^2 was employed during the measuring process. The sweeping...
conditions are reverse scan (1.20 V → -0.02 V, scan rate 40 mV s⁻¹, and no delay time), forward scan (-0.02 V → 1.20 V, scan rate 40 mV s⁻¹), with no delay time), and a reference cell purchased from Fraunhofer ISE CalLab (ISE001/013-2018). All devices were measured both in the reverse scan (1.20 V→ −0.20 V, step 0.02 V, delay time 100 ms) and forward scan (−0.20 → 1.20 V, step 0.02 V, delay time 100 ms) without any pre-light soaking and pre-bias process. To ensure accuracy, a mask with an aperture area of 0.09 cm² was employed during the measuring process. The data were collected by the IV testing system with software (IVS-KA5000). The stabilized power output was measured at the maximum power output bias voltage. EQE was measured in air on a commercial system (Bentham PV300). And the stability test was conducted without encapsulation. The stability test was performed at 25 °C, and the relative humidity was ~35%. The repeated bending cycle tests are performed by a custom-made stretching machine with an adjustable bending radius.

Reference
