Printable Free-Standing Hybrid Graphene/Dry-Spun Carbon Nanotube Films as Multifunctional Electrodes for Highly Stable Perovskite Solar Cells

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ABSTRACT: Perovskite solar cells (PSCs) have attracted immense attention owing to their outstanding power conversion efficiency (PCE). However, their counter electrodes are commonly produced by evaporating metals, such as Ag and Au, under high vacuum conditions, which make the PSCs costly, thereby limiting their large-scale production. In this study, a free-standing hybrid graphene/carbon nanotube film was carefully designed to replace noble metal PSC counter electrodes to reduce the cost and increase the stability of PSCs. A highly conductive and stable hybrid carbon thin film can be easily transferred to the various desired substrates by a simple rolling process. The PSCs with hybrid graphene/carbon nanotube films showed a high PCE of 15.36%. Moreover, the devices exhibited excellent stability and could retain 86% of their initial PCE after storage for 500 h in a high-moisture atmosphere (RH 50%). The outstanding stability of PCEs can be attributed to the efficient moisture blocking by the multilayered graphene/carbon nanotube present in the hybrid film. The thin, flexible, and easy-to-synthesize free-standing hybrid graphene/CNT film with high conductivity showed great potential for realizing the low-cost production of highly stable PSCs.

KEYWORDS: dry-spinning CNTs, graphene, free-standing hybrid graphene/CNT film, perovskite solar cell, stability

1. INTRODUCTION

Perovskite solar cells (PSCs), as the most important class of solar cells, have been developed rapidly since the influential study by Koijima et al.1 As promising energy conversion devices, PSCs have gained immense attention owing to their relatively high solar harvesting performance and simple manufacturing process.2–5 Typical PSCs comprise methylammonium lead iodide (MAPbI3) as the active perovskite layer,6–8 a dense and mesoporous TiO2 layer as the electron transfer layer (ETL), and 2,2′,7,7′-tetakis(N,N-di-p-methoxyphenylamine)-9,9′-spiropentfluorene (spiro-OMeTAD) as the hole transfer layer (HTL). These layers are sandwiched by the electrodes, which typically comprise fluorine-doped tin oxide (FTO)-coated glass and thermal-evaporated metals, such as Ag and Au.9–13 The industrial production of PSCs is limited due to the high cost of Ag and Au, which are used as the counter electrodes. In addition, the vapor deposition process usually requires high vacuum, which consumes a significant amount of energy and time. In addition, the metal electrodes in PSCs react with iodide ions and accelerate the iodine electromigration process, thereby accelerating the device degradation.14–16 Therefore, it is imperative to develop cost-effective, easy-to-synthesize, moisture blocking, and chemically inert electrodes to replace precious metal electrodes.

Carbon materials, such as carbon nanotubes (CNTs), carbon paste, and graphene, are excellent alternatives to noble metal counter electrodes; furthermore, they increase the stability of PSC devices owing to their suitable work function, good conductivity, and hydrophobic properties.17–22 Vertically superaligned carbon nanotubes (VACNTs) are a type of multilayered CNTs. Large-area carbon films can be directly deposited on arbitrary VACNT surfaces using the dry-spinning technique23 and have been used in conductors, heaters, capacitors, and batteries.24–27 Luo et al. prepared 50-layer CNTs by dry-spinning, doped them with iodine to increase their conductivity for replacing the commercial carbon paste used in mesoporous PSCs, and achieved a power conversion efficiency (PCE) of 9.64%.28 The studies reported on the use of carbon films as electrodes have focused on improving the film conductivity and device stability of CNTs. Single-atomic-thickness graphene with a high hole mobility of 24,000 cm²
CNTs under a N2H4 atmosphere to prepare a well-dispersed al. conducted the reaction of graphene oxide and oxidized∼ synthesized fi combining CNTs and graphene to develop highly conductive the perovskite complex and challenging.

humidity (RH) for a week.31 However, large-area graphene is maintain 80% of the initial PCE under 85% high relative moisture when it is used in glass/FTO/TiO2/perovskite/ CuSCN/graphene/Au devices as an interfacial layer. It can

Lee et al. demonstrated that graphene can e

Some researchers have prepared hybrid structures by combining CNTs and graphene to develop highly conductive films for application in photovoltaic devices. Li et al. synthesized ~500 μm thick VACNTs onto ~3 μm thick commercial graphene paper for application as an electrode in lithium-ion batteries and dye-sensitized solar cells.35 Tung et al. conducted the reaction of graphene oxide and oxidized CNTs under a N2H4 atmosphere to prepare a well-dispersed graphene–CNT solution. They spin-coated this solution on a PET substrate, and the resulting electrode was used to replace the conventional indium tin oxide electrodes in polymer solar cells. A PCE of 0.85% was achieved because of the high sheet resistance of the electrode (600 Ω sq−1).36 Recently, Li et al. used a plasma-enhanced CVD method to grow graphene flakes on the surface of CNTs and prepared a hybrid CNT@G nanoparticle solution. To this solution, spiro-OMeTAD was added, and the mixed solution was coated on the perovskite active layer.37 The CNT@G interlayer improved the stability and PCE of the device (from 15.67 to 19.56%). However, generally, chemical reaction methods are used to fabricate hybrid graphene and CNT structures. These methods require spin-coating techniques to coat the solution on the target device. However, such techniques inevitably produce waste materials.

In this study, we developed a printable free-standing hybrid graphene/dry-spun CNT film as an ideal top electrode and moisture-blocking layer for PSCs. The free-standing hybrid graphene/CNT film was easy to synthesize and could be easily transferred to the target substrate without any chemical or water process. The effect of the graphene layers on the PSCs’ performance was investigated. The hybrid film could be easily transferred onto the solar cells using a laminating method. In addition, the hybrid film reduced the resistance and improved the stability of the device under a humid atmosphere. The PSCs with the free-standing hybrid graphene/CNT films showed PCE up to 15.36% and maintained 86% of the initial PCE under humid conditions (RH 50%) for 500 h. Multilayer graphene can efficiently prevent moisture intrusion. The free-standing hybrid graphene/CNT film was found to be a promising alternative to metal electrodes and served as an efficient moisture-blocking layer for PSCs.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Graphene and VACNTs. Graphene and VACNTs were synthesized by a low-pressure chemical vapor deposition method in a quartz tube furnace (ISAC Research, Inc.). H2, and CH4 gases were used to synthesize graphene on copper, whereas C2H2, H2, and Ar gas were used to synthesize the VACNTs on a SiO2 substrate. The synthesis procedure was the same as that used in our previous study.25

2.2. Preparation of the Hybrid Graphene/CNT Films. Figure 1 shows the schematic of the fabrication procedure for the free-standing hybrid graphene/CNT films. Herein, multilayered graphene was transferred using a poly(methyl methacrylate) (PMMA)-based wet transfer method.38 First, 4.5 wt % PMMA solution was spin-coated on the surface of graphene at 1000 rpm. Then, the copper substrate was etched using a copper etchant (Sigma-Aldrich). After rinsing the so-obtained PMMA/graphene with DI water at least three times to remove the residual etchant, another precut graphene/Cu film was used to scoop the floating PMMA/graphene in DI water and the resulting PMMA/graphene/graphene/Cu film was carefully blown using an air gun. The PMMA/graphene/graphene/Cu film was then heated on a hot plate for a few minutes to further evaporate DI water and enhance the π–π interaction between the graphene and the graphene. The above process was repeated several times to obtain multilayered graphene. Finally, the top PMMA layer was removed by immersing the composite film in an acetone solution for 20 min (two layers of graphene was obtained, as shown in Figure 1). The cross-stacked CNT sheets on the top of the multilayered graphene/Cu film were directly drawn out from the VACNTs using a dry-spinning.
Films.

Commercial FTO glasses (SnO\textsubscript{2}:F, 14\Ω\·sq\textsuperscript{-1}) were spin-coated on the FTO glass at 4000 rpm for 25 s. Then, 0.5 mL of diethyl ether (Thermo Fisher Scientific Co., Inc., >99%) was dropped on the rotating surface in 15 s after beginning the coating program to prevent the rapid vaporization of DMF. Subsequently, the devices were heated at 65 °C for 1 min and 100 °C for 2 min to form a uniform perovskite crystal.\textsuperscript{11} The HTL layer was prepared by adding 72.3 mg of spiro-OMeTAD (Sigma-Aldrich, 99%) to 1 mL of chlorobenzene (Sigma-Aldrich, 99.8%) and was then doped with a solution of 28.8 \µL of 4-tert-butyl pyridine and 17.5 \µL of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI). The Li-TFSI solution was prepared by mixing 520 mg of Li-TFSI in 1 mL of acetonitrile (Sigma-Aldrich, 99.8%). The HTL solution was coated on the perovskite layer at 3000 rpm for 30 s.\textsuperscript{41,42} Finally, the free-standing hybrid film was transferred onto the PSCs using a laminator with several drops of chlorobenzene, as shown in Figure 1. Lamination at an optimum pressure was used to discharge the air bubbles between the hybrid film and PSCs. Devices with thermally evaporated Ag (100 nm) top electrodes were also fabricated as reference devices. Images of the PSCs with the hybrid graphene/CNT films are shown in Figure S1.

2.3. Fabrication of PSCs with the Hybrid Graphene/CNT Films. Commercial FTO glasses (SnO\textsubscript{2}:F, 14 Ω·sq\textsuperscript{-1}, AMG) were sequentially cleaned with acetone, ethyl alcohol, and 2-propanol for 25 min in an ultrasonic bath. Then, the glasses were further cleaned with UV−ozone for 20 min. A solution of 0.15 M titanium diisoproxipoxide bis(acetylacetonate) (75 wt % in isopropanol) in 1-butanol (Sigma-Aldrich, 99.8%) was spin-coated on the FTO glass at 2800 rpm for 20 s as a compact TiO\textsubscript{2} layer (c-TiO\textsubscript{2}). A mesoporous TiO\textsubscript{2} layer (mp-TiO\textsubscript{2}), which was prepared by diluting 1.2 g of TiO\textsubscript{2} paste (ShareChem Co., SC-HT040) into 10 mL of the chemically pure ethyl solvent, was coated onto c-TiO\textsubscript{2} at 2000 rpm for 20 s. After each step, the samples were heated on a hot plate at 125 °C for 5 min, followed by annealing at 530 °C for 1 h. The perovskite layer was prepared by mixing 461 mg of PbI\textsubscript{2} (Alfa Aesar, 99.9985%), 159 mg of CH\textsubscript{3}NH\textsubscript{3}I (Sigma-Aldrich, ≥99%), 71 \µL of dimethyl sulfoxide (DMSO, Alfa Aesar, ≥99.8%), and 520 \µL of N,N-dimethylformamide (DMF, Sigma-Aldrich, ≥99%) to prepare a CH\textsubscript{3}NH\textsubscript{3}I·PbI\textsubscript{2}·DMSO adduct solution. The TiO\textsubscript{2}-coated FTO glasses were treated with UV−ozone for 20 min before coating the perovskite layer at 4000 rpm for 25 s. Then, 0.5 mL of diethyl ether (Thermo Fisher Scientific Co., Inc., >99%) was dropped on the rotating surface in 15 s and an atomic force microscope (AFM) was used to characterize the film thickness and surface roughness.

2.4. Characterization of the Hybrid Graphene/CNT Films and Photovoltaic Measurements of the PSCs. Field-emission scanning electron microscopy (FE-SEM) along with energy-dispersive X-ray spectroscopy (EDS) (Hitachi, S-4700) was used to analyze the surface morphologies of the hybrid graphene/CNT films and cross-sectional structure of the target PSCs. A four-point probe system (CMT-SR2000N, AIT) was used to measure the sheet resistance of the PSCs. A source meter (94043A, Oriel Sol3A Class AAA) was used to measure the photovoltaic performance of PSCs under AM 1.5G (100 mW cm\textsuperscript{-2}) illumination with a source meter (94043A, Oriel Sol3A Class AAA) at room temperature under AM 1.5G (100 mW cm\textsuperscript{-2}) illumination with a source meter (94043A, Oriel Sol3A Class AAA) at room temperature. The incident photon-to-current conversion efficiency of the devices was measured using an Oriel QE-200 spectrometer. A silver paste was used to reduce the contact resistance during the measurement, and the active area was defined by a metal mask, which was 0.09 cm\textsuperscript{2}. The incident photon-to-current conversion efficiency of the devices was measured using an Oriel QE-200 spectrometer.
Figure 3. (a) PSC architecture with the hybrid graphene/CNT film counter electrode; (b) energy band diagram of the various layers in the PSCs; and (c) cross-sectional FE-SEM image and the Sn, Ti, Pb, I, and C EDS elemental mapping images of the PSCs with the hybrid graphene/CNT films.

spectral system (Newport Stratford, Inc.) with a 250 W quartz tungsten halogen lamp, a monochromator, and an optical chopper. Photoluminescence (PL) measurements were conducted on a Hitachi F-4500 fluorescence spectrophotometer with a pulsed 470 nm excitation laser. Electrochemical impedance spectroscopy (EIS) measurements were conducted over the frequency range of 2 MHz−1 Hz with a signal amplitude of 5 mV. The applied bias voltage was set at 0.7 V under the dark conditions (Wonatech Co., Ltd., Korea). The EIS spectra of the samples were fitted using Z-View software to obtain the equivalent circuit. A humidity and temperature chamber (AAA82113, Jeio Tech, Korea) was used for the stability test.

3. RESULTS AND DISCUSSION

Raman spectroscopy was used to evaluate the quality of graphene and CNTs, and the spectra are shown in Figure S2. Graphene showed typical D, G, and 2D bands at 1354, 1585, and 2710 cm$^{-1}$, respectively. Monolayer graphene showed an $I_{2D}/I_G$ ratio >2.5 and a very weak D band, confirming that high-quality monolayer graphene was successfully synthesized. With an increase in the number of graphene layers to 5, the 2D band broadened and $I_{2D}/I_G$ ratio became <1. In addition, the five-layer graphene showed a strong D band, indicating an increase in the number of defects in the transferred graphene.$^{43,44}$ Figure S2c shows the Raman spectrum of the CNTs with characteristic D and G bands at 1351 and 1587 cm$^{-1}$, respectively. Moreover, the $I_{D}/I_G$ ratio of ≈0.95 indicates that the CNTs were well graphitized.$^{45,46}$

During the transfer of the hybrid film on a substrate, the graphene or CNT layers on the top showed different surface morphologies. Figure 2 shows the FE-SEM images of hybrid graphene/CNT films after transferring on a substrate. The morphology of eight-layer CNTs on the top is shown in Figure 2a,b. The CNT surface was nonuniform and rough. It was not a continuous CNT-covered surface, and some interspaces between the adjacent CNTs could be clearly seen. These interspaces increased the sheet resistance (199 Ω sq$^{-1}$) of the eight-layer CNTs. In addition, moisture intrudes through these interspaces to the layer beneath. This adversely affects the performance and long-term stability of the PSCs. This problem can be solved by preparing hybrid graphene/CNT films and transferring them onto PSCs with graphene layers on the top. An ideal graphene layer is a whole, intact, and pinhole-free film compared to the CNT layer. In addition, graphene has a high specific surface area and hence can efficiently prevent moisture from infiltrating. Figure 2c,d shows the morphology of hybrid graphene-4/CNT-8 hybrid film. The surface of the film was continuous, flat, smooth, and clean, indicating that the underlying CNT layers supported the top graphene layers well with almost no wrinkles on the surface. This result is consistent with that obtained in our previous study.$^{25}$ However, single-layer graphene could not cover all of the CNT interspaces, as shown in Figure S4a,b, and cross-stacking CNT layers could be clearly observed. The sheet resistances of the hybrid films were measured, and the results are shown in Figure S3. The sheet resistance of the hybrid graphene-1/CNT-8 film was 88 Ω sq$^{-1}$. In the case of films with enough graphene layers (for example, four-layer graphene), graphene could completely cover all of the poor conductive interspaces of the CNT sheets, as shown in Figure 2c,d, resulting in the formation of a large number of charge-transfer tunnels. The hybrid graphene-4/CNT-8 film showed a low sheet resistance of 54 Ω sq$^{-1}$. Thus, more graphene layers on the top could increase the film conductivity and block moisture efficiently. In this study, all the hybrid films were transferred on the PSCs with graphene layers on the top surface. Hybrid graphene-4/CNT-8 films with cracks on the graphene surface were fabricated to prove the presence of graphene by rubbing the film surface on the wiper. The images are shown in Figure S4c,d. The underlying cross-stacking CNT layers could be clearly observed only in the crack parts.

Figure 3a shows the PSC architecture with the hybrid graphene/CNT film as the counter electrode. The energy band diagrams of the various layers in the PSCs are shown in Figure 3b. Under sunlight lamination, the photogenerated electrons...
and holes in the perovskite active layer could be effectively injected into the electron transfer TiO$_2$ layer and hole transfer spiro-OMeTAD layer, respectively. Finally, the electrons were collected at the FTO electrode, and holes were collected at the hybrid graphene/CNT counter electrode because of its suitable work function of $\sim$4.9 V.\cite{77,48} Figure 3c shows the cross-sectional FE-SEM images and elemental mapping images of the PSCs with the hybrid films. The EDS mapping images showed the elemental composition of each layer. The TiO$_2$ layer had an average thickness of $\sim$250 nm. A pinhole-free perovskite layer with a thickness of $\sim$400 nm was formed. The top hybrid graphene/CNT layer was flat and showed a thickness of $\sim$600 nm along with the spiro-OMeTAD layer.

The photocurrent–voltage (J–V) curves of the PSCs with different hybrid films under AM 1.5 illumination of 100 mW/cm$^2$ are shown in Figure 4. The photovoltaic parameters of the PSCs with the hybrid graphene/CNT films as counter electrodes and (b) statistical J–V parameters of the PSCs with the hybrid graphene-1/CNT-8 and graphene-4/CNT-8 films from 20 devices.

![Figure 4](https://dx.doi.org/10.1021/acsami.0c17141)

Figure 4. (a) J–V curves of the PSCs with different hybrid graphene/CNT films as the counter electrodes and (b) statistical J–V parameters of the PSCs with the hybrid graphene-1/CNT-8 and graphene-4/CNT-8 films. The measurements were conducted on 20 independent devices. The PSCs with the hybrid graphene-4/CNT-8 film showed better performance ($V_{OC} = 1.07 \pm 0.01$ V, $J_{SC} = 21.65 \pm 0.15$ mA cm$^{-2}$, FF = $66.06 \pm 0.36$, and PCE = $15.28 \pm 0.13$%) than the PSCs with the hybrid graphene-1/CNT-8 film ($V_{OC} = 1.00 \pm 0.02$ V, $J_{SC} = 20.50 \pm 0.31$ mA cm$^{-2}$, FF = $56.84 \pm 0.47$, and PCE = $11.62 \pm 0.25$%). With an increase in the number of graphene layers to four, the FF and $J_{SC}$ of the devices increased significantly, especially the FF. This is because the four-layer graphene efficiently covered the nonconductive interspaces of the CNTs. The PSCs with the graphene-4/CNT-8 film showed low series resistance.

The incident photon-to-electron conversion efficiency (IPCE) spectra of the PSCs with the different hybrid graphene/CNT films are shown in Figure 5a. The photocurrent was generated at $\sim$800 nm. This is consistent with the optical band gap of perovskite materials. The IPCE spectra of the PSCs with the hybrid films showed a loss in the red region from 500 to 750 nm compared to the PSCs with the reference Ag electrode, as shown in Figure 5b. This indicates that the carbon film could not reflect the incident sunlight back to the active perovskite layer for reabsorption. A back reflective metal

PSCs with the hybrid films are listed in Table 1. First, we investigated the performance of PSCs with eight-layer CNT films. As shown in Figure S5, the PSCs with only eight-layer CNTs exhibited the lowest average PCE of 8.96% with a fill factor (FF) of 45.44%, a short-circuit current density ($J_{SC}$) of 19.71 mA cm$^{-2}$, and an open-circuit voltage ($V_{OC}$) of 1 V due to the relatively high sheet resistance of the CNTs, and the charge could not be transferred efficiently. The performance of PSCs improved when hybrid films with highly conductive graphene layers were used. With the introduction of one-layer graphene (hybrid graphene-1/CNT-8 film), the FF of the PSCs increased from 45.44 to 56.84%, whereas the $J_{SC}$ increased from 19.71 to 20.50 mA cm$^{-2}$, yielding an average PCE of 11.62%. The PSCs with four-layer graphene (hybrid graphene-4/CNT-8 film) showed excellent photovoltaic performance with the highest PCE of 15.36%, impressive FF of 66.42%, $J_{SC}$ of 21.88 mA cm$^{-2}$, and $V_{OC}$ of 1.07 V, which is 90% of the PCE of the PSCs with the reference Ag electrode (as shown in Figure S6a); the best-group devices show relative high performance among the reported PSCs with CNTs or graphene electrodes (see Table S1, Supporting Information).

The improved performance of the PSCs can be attributed to the increased film conductivity and enhanced charge extraction. However, when the number of graphene layers was increased to five, the device performance deteriorated slightly. The PSCs with the hybrid graphene-5/CNT-8 film showed an average PCE of 15.12% with a FF of 65.82%, a $J_{SC}$ of 21.34 mA cm$^{-2}$, and a $V_{OC}$ of 1.07 V. This deterioration in the device performance was mainly due to the wrinkles and impurities produced during the graphene transfer process. These defects increased after the graphene transfer process and acted as charge trap states.\cite{18,31} Figure 4b shows the statistical J–V parameters of the PSCs with the hybrid graphene-1/CNT-8 and graphene-4/CNT-8 films. The PSCs improved when hybrid films with highly conductive graphene/CNT layers to four, the FF and $J_{SC}$ of the devices increased significantly, especially the FF. This is because the four-layer graphene efficiently covered the nonconductive interspaces of the CNTs. The PSCs with the graphene-4/CNT-8 film showed low series resistance.

<table>
<thead>
<tr>
<th>cell types (CE)</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
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<tr>
<td>graphene-1/CNT-8</td>
<td>1.00 ± 0.02</td>
<td>20.50 ± 0.31</td>
<td>56.84 ± 0.47</td>
<td>11.62 ± 0.25</td>
</tr>
<tr>
<td>graphene-2/CNT-8</td>
<td>1.03 ± 0.02</td>
<td>20.57 ± 0.26</td>
<td>57.96 ± 0.37</td>
<td>12.26 ± 0.28</td>
</tr>
<tr>
<td>graphene-3/CNT-8</td>
<td>1.03 ± 0.02</td>
<td>20.99 ± 0.22</td>
<td>61.44 ± 0.39</td>
<td>13.36 ± 0.23</td>
</tr>
<tr>
<td>graphene-4/CNT-8</td>
<td>1.07 ± 0.01</td>
<td>21.65 ± 0.15</td>
<td>66.06 ± 0.36</td>
<td>15.28 ± 0.13</td>
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<tr>
<td>graphene-5/CNT-8</td>
<td>1.07 ± 0.01</td>
<td>21.34 ± 0.19</td>
<td>65.82 ± 0.57</td>
<td>15.12 ± 0.35</td>
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Table 1. Photovoltaic Parameters of PSCs with Different Hybrid Graphene/CNT Films as Counter Electrodes
The electrode can increase the photogenerated current by 13%.49 The integrated photocurrent densities of the PSCs with the hybrid films with 1–5 graphene layers were 19.42, 19.59, 19.83, 20.43, and 20.16 mA cm−2, respectively. All of the integrated photocurrent densities obtained from the IPCE spectra were consistent with the JSC measured by the solar simulator (less than 6% deviation). All of the groups showed similar spectra. The PSCs with the hybrid graphene-4/CNT-8 film showed the highest IPCE value over the wavelength range of 400–650 nm.

Steady-state photoluminescence (PL) measurements were conducted to investigate the charge-carrier electrical behavior, especially the charge extraction efficiency, of the PSCs.50 The PL spectra of the PSCs are shown in Figure 5b. All of the samples exhibited a similar PL emission peak at ∼770 nm. The pristine perovskite film showed a very intense emission peak. However, after the addition of the charge extraction layers, such as spiro-OMeTAD, graphene-1/CNT-8/spiro-OMeTAD, graphene-2/CNT-8/spiro-OMeTAD, graphene-3/CNT-8/spiro-OMeTAD, graphene-4/CNT-8/spiro-OMeTAD, and graphene-4/CNT-8/spiro-OMeTAD, the PL emission of the PSCs quenched strongly and the PL emission peak intensity decreased. Among all of the devices with the hybrid films, the PSCs with the hybrid graphene-4/CNT-8 film showed the
highest quenching, indicating that the hybrid graphene-4/CNT-8 film in combination with the spiro-OMeTAD layer could efficiently extract the holes excited in the perovskite film. The charge could be transferred rapidly owing to the high conductivity of the hybrid film.

EIS measurements were performed to investigate the interface charge transfer and recombination behavior of the PSCs with different hybrid graphene/CNT films as the counter electrodes. Figure 5c shows the Nyquist plots of the PSCs with different carbon films as the electrodes, and the fitted equivalent circuit is shown in Figure 5d. Only one semicircle was observed in the high-frequency region. This semicircle corresponded to the charge-transfer resistance ($R_t$) and series resistance ($R_s$) of the device. Given that the counter electrodes were the only different parts in the devices, the difference in their Nyquist plots could mainly be attributed to the presence of different carbon films. Lower $R_t$ values corresponded to larger FF values, and the film sheet resistance affected the measured $R_s$ values. The measured $R_t$ values of the hybrid films increased in the order graphene-4/CNT-8 film < hybrid graphene-5/CNT-8 film < hybrid graphene-3/CNT-8 film < hybrid graphene-2/CNT-8 film < hybrid graphene-1/CNT-8 film. The devices showed significantly different $R_s$ values. The PSCs with the hybrid graphene-4/CNT-8 film showed the smallest diameter and hence the lowest charge-transfer resistance. Considering that the fitted $R_t$ values were close, the performance of the PSCs was mostly affected by their interfacial charge-transfer resistance. The hybrid graphene-4/CNT-8 film-based PSCs with a low charge-transfer resistance could extract and transfer charge efficiently. Thus, a large FF improved the performance of the PSCs.

Long-term stability is essential for practical applications of PSCs. The decomposition of the active perovskite layer and corrosion of the top metal electrode occur easily in humid environments. Figure 6a shows the water contact angle (WCA) of different electrodes. Ag electrodes showed a low WCA of 88.4°, while all carbon electrodes showed hydrophobic properties with WCAs of more than 90°. In particular, a four-layer graphene hybrid film shows a high WCA of around 107°, which can be seen as a cause of high stability. The stability tests of the PSCs with the reference Ag electrode and CNT-8, hybrid graphene-1/CNT-8, and graphene-4/CNT-8 films as counter electrodes were conducted at an RH of 50 ± 2% and 25 °C in a humidity and temperature chamber. As shown in Figure 6b, the PCE of the reference cell with the Ag electrode decreased quickly to 17% of the initial PCE after 7 days. However, the PSCs with the graphene-4/CNT-8 film showed relatively high stability and could retain 86% of the initial PCE even after 500 h at RH 50%. The PCE of the PSCs with CNT-8 and hybrid graphene-1/CNT-8 film decreased to 35 and 56% of the initial value of PEC, respectively, under the same conditions. Single-layer graphene cannot prevent moisture efficiently because it cannot be fully transferred, as shown in the FE-SEM images. The hybrid graphene-4/CNT-8 films with the hydrophobic four-layer graphene served as an efficient moisture-blocking layer for the PSCs. Figure 6c shows a photo before and after the 500 h stability test of the PSC using Ag and hybrid graphene-4/CNT-8 films as counter electrodes. After storing 500 h in the RH 50 ± 2% chamber, it can be confirmed that the unit cells of the PSC with silver electrodes have been severely degraded. On the other hand, for PSCs with hybrid graphene-4/CNT-8 films, no degradation of unit cells is made, indicating that hybrid films can effectively block moisture and will not react with active layers.

4. CONCLUSIONS
In this study, printable free-standing hybrid graphene/dry-spun CNT films to be transferred easily and fast on arbitrary substrates were successfully synthesized using a simple fabrication method. The hybrid graphene/CNT films were used in PSCs to replace noble metal electrodes and served as moisture-blocking layers. The film conductivity significantly affected the device performance. The performance of the PSCs with the hybrid graphene-4/CNT-8 film exhibited the best PCE of 15.36% (FF = 66.42%; $J_{SC} = 21.88$ mA cm$^{-2}$; $V_{OC} ≈ 1.07$ V). In contrast, the PSCs with eight layers of CNTs showed a PCE of 8.96% (FF = 45.44%; $J_{SC} = 19.71$ mA cm$^{-2}$; $V_{OC} ≈ 1.00$ V). The effect of the number of graphene layers on the performance of the PSCs was investigated. The PSCs with the hybrid graphene-4/CNT-8 film exhibited the best performance among all of the PSCs investigated because of the significant increase in the FF and $J_{SC}$. The improved photovoltaic performance of the PSCs can be attributed to the high conductivity of the hybrid film and low series resistance of the whole device. In addition, the PSCs with the hybrid graphene-4/CNT-8 film maintained more than 86% of the initial efficiency after storage under RH 50% at 25 °C for 500 h without encapsulation. Moreover, the free-standing hybrid graphene/CNT film could be transferred to arbitrary solar cells without damaging the underlying layer and showed excellent flexibility; therefore, it has great potential for developing low-cost and flexible PSCs.

ASSOCIATED CONTENT
 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c17141.

Image of PSCs with hybrid graphene/CNT films, Raman spectra, sheet resistance, FE-SEM images, and additional performance data of PSCs with the hybrid films (PDF)

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Author Contributions

The main experiments were conducted by M.T., and the various property measurements were performed by C.Y.W., J.W.C., Prof. J.-Y.S., and Prof. J.-M.K. Prof. S.H.K. analyzed the measurement results, and Dr. M.S. and Prof. H.W.L. organized all in this study and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CNTs, carbon nanotubes
VACNTs, vertically superaligned carbon nanotubes
graphene-1/CNT-8, 1 layer graphene/8 layer CNTs
graphene-2/CNT-8, 2 layer graphene/8 layer CNTs
graphene-3/CNT-8, 3 layer graphene/8 layer CNTs
graphene-4/CNT-8, 4 layer graphene/8 layer CNTs
graphene-5/CNT-8, 5 layer graphene/8 layer CNTs

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