Laminated Carbon Nanotube Networks for Metal Electrode-Free Efficient Perovskite Solar Cells

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ABSTRACT Organic–inorganic metal halide perovskite solar cells were fabricated by laminating films of a carbon nanotube (CNT) network onto a CH3NH3PbI3 substrate as a hole collector, bypassing the energy-consuming vacuum process of metal deposition. In the absence of an organic hole-transporting material and metal contact, CH3NH3PbI3 and CNTs formed a solar cell with an efficiency of up to 6.87%. The CH3NH3PbI3/CNTs solar cells were semitransparent and showed photovoltaic output with dual side illuminations due to the transparency of the CNT electrode. Adding spiro-OMeTAD to the CNT network forms a composite electrode that improved the efficiency to 9.90% due to the enhanced hole extraction and reduced recombination in solar cells. The interfacial charge transfer and transport in solar cells were investigated through photoluminescence and impedance measurements. The flexible and transparent CNT network film shows great potential for realizing flexible and semitransparent perovskite solar cells.

KEYWORDS: perovskite solar cells • carbon nanotubes • laminated • vacuum-free • hole transporter free

In an attempt to reduce the costs of solar cell manufacturing and to increase their potential applications, third-generation photovoltaics are of great interest. These include unconventional light absorber materials with low cost such as dyes,1 conjugated polymers,2 and quantum dots,3 which have triggered continued research efforts. However, these solar cells still lag behind conventional approaches such as Si and GaAs in terms of efficiency. Methylammonium lead halide and mixed halides CH3NH3PbX3 (X = Cl, Br, I) possessing the perovskite structure are an emerging light absorber material with features such as large light absorption coefficient, direct band gap,4 high carrier mobility, and long carrier diffusion length.5 After some early exploration,6,7 solar cells based on a perovskite absorber have reached an efficiency of more than 15%,8,9 approaching the efficiency of commercialized c-Si solar cells. The primary advantage of the organic–inorganic halide perovskites is that they can be deposited through a facile solution process, providing avenues for fabricating low-cost solar cells with attractive efficiency.

Evolving from the solid-state dye-sensitized solar cell structure, new device architectures adopting perovskite as a light absorber are emerging, such as planar junctions,10 where the perovskite material can act as both absorber and charge-transporting material in the solar cell. The hole transport properties of CH3NH3PbI3 have enabled perovskite/Au solar cells with power conversion efficiencies reaching 8%.11,12 This points the way toward a simpler fabrication process that does not involve the utilization of hole-transporting layers. A further simplification of the fabrication process would involve the substitution of the metal electrode layers. Although the perovskite absorber layer is deposited by a simple solution process, the metal electrode of the perovskite solar cell is relatively expensive and deposited by high-vacuum thermal evaporation. To reduce the cost of solar cell fabrication, it is necessary to replace the evaporated metal (Au/Ag) electrode with low-cost materials. Carbon
nanotubes (CNTs), with their excellent electrical conductivity, chemical stability, and unique nanostructure, have been applied as electrodes in CdTe,13,14 dye-sensitized solar cells,15,16 and organic solar cells.17,18 Not only did the CNT electrode show comparable performance to conventional architectures, it also provided the solar cell with more features such as flexibility15 and semitransparency for tandem solar cells.19 The recent development of silicon/CNTs solar cells20 revealed the advantages of CNTs over metallic grids, due to the better local charge collection of the nanometer-scale networks21 and tunable electrical properties with chemical doping.22,23

RESULTS AND DISCUSSION

The CNT network films were synthesized using a floating catalyst chemical vapor deposition (CVD) method. Details of CNT synthesis and the growth mechanism are described in our previous report.24 The CNTs in the film were mainly single and double walled, with diameters in the 1–2 nm range (Supporting Information Figure S1), and were of semiconducting and metallic character. The nanotubes were assembled in bundles with diameters of 5–10 nm, which interweave to form networks. The as-grown CNTs contained a trace amount of Fe catalyst and amorphous carbon on the surface. The Raman spectrum of the as-synthesized CNT film in Figure S2, shows a relatively low defect derived D band intensity as a proof of high purity. Facile transferring is another advantageous feature of the CNT films. According to the floating catalyst growth mechanism, CNTs grew from the floating catalyst particles in the carrier gas flow and formed an aerosol after growth. The aerosol was collected by substrates at the end of the CVD chamber. Once deposited from the aerosol, the CNTs showed strong tube-to-tube interaction and assembled into a freestanding thin film. As shown in Figure 1a, the as-synthesized CNT film was mechanically strong and freestanding. The CNT films are easily peeled off from the substrate by tweezers and transferred to other substrates for device fabrication. Unlike the CNT films attained by filtration or spray or dip coating methods, the as-synthesized freestanding ones do not contain dispersing surfactant, which may hinder charge transport.

The schematic of CNT-based perovskite solar cell structure is shown in Figure 1b. The cell consisted of layers of fluorine-doped tin oxide (FTO)/TiO2 compact layer/mesoporous TiO2/CH3NH3PbI3/CNT film. In brief, a layer of compact TiO2 was deposited by spray pyrolysis on FTO glass followed by a layer of mesoporous TiO2. Subsequently, CH3NH3PbI3 was deposited using a sequential deposition method.9 The freestanding CNT film was placed on top of the perovskite layer, and drops of toluene were added to improve the
adhesion. The toluene does not significantly dissolve the CH$_3$NH$_3$PbI$_3$ and wets the CNT film, drawing it toward the perovskite substrate by surface tension during vaporization. As a result, the CNT film was well adhered to the perovskite surface by van der Waals force. The electron microscopy images of CH$_3$NH$_3$PbI$_3$ perovskite before and after CNT transfer are presented in Figure 1c and d, respectively. Figure 1c shows the formation of a dense layer of CH$_3$NH$_3$PbI$_3$ perovskite nanocrystals on top of the mesoporous TiO$_2$. After transfer, the flexible CNT network could conformally coat the rough surface of perovskite (Figure 1d), enabling an increased interface area between perovskite and CNT as well as an improved electrical contact. Figure 1e showed a false-color tilted SEM image of the perovskite substrate (blue) partly coated with a CNT film (purple). Some folds and wrinkles shown on the CNT film were due to the manual transfer. The single-step direct transfer carried out in ambient atmosphere avoids the requirement of high temperature and high vacuum for metal electrode evaporation.

Photoluminescence quenching is used to demonstrate the charge extraction ability of hole-conducting material in contact with the perovskite. CH$_3$NH$_3$PbI$_3$ was deposited on bare quartz and CNT film-covered quartz substrates. The excitation and luminescence measurement was taken from the quartz side for both samples. As shown in Figure 2a the PL of CH$_3$NH$_3$PbI$_3$ on bare quartz shows strong luminescence at ∼770 nm, which is suppressed in the CNT sample with a quenching ratio of 44 times as a sign of the effective charge transfer from CH$_3$NH$_3$PbI$_3$ to CNTs. Carbon nanotubes are a p-type conducting material at ambient atmosphere with a reported work function between −4.95 and −5.05 eV at room-temperature condition. According to the band edge positions of TiO$_2$, CH$_3$NH$_3$PbI$_3$, and CNTs, the band diagram of the perovskite/CNTs solar cell is shown as an inset in Figure 2b. The CNT films provide a significant driving force for the hole injection from the perovskite layer, collecting and transporting holes to the external circuit. A power conversion efficiency (PCE) of 6.87% with a $V_{OC}$ of 0.88 V, $J_{SC}$ of 15.46 mA/cm$^2$, and fill factor of 0.51 under AM1.5 100 mW/cm$^2$ illumination was achieved by the best device of CH$_3$NH$_3$PbI$_3$/CNTs solar cells (Table S1). The CH$_3$NH$_3$PbI$_3$/Au solar cell was also fabricated by directly depositing a Au electrode on top of the perovskite for comparison. CH$_3$NH$_3$PbI$_3$/CNTs solar cells present higher $V_{OC}$ and $J_{SC}$ than the Au counterpart; however their fill factor is lower (Figure 2a). Higher $V_{OC}$ and $J_{SC}$ might be due to better hole selectivity of CNTs than metallic Au, reducing the chance of interface recombination. The higher sheet resistance of CNT film (2−5 kΩ as measured by four-point probe) could explain the poorer fill factor. Therefore, removing impurities on the CNT surface to reduce the sheet resistance of the CNT film may improve the cell efficiency in the future.

Photovoltaic performance of the CH$_3$NH$_3$PbI$_3$/CNTs solar cell was also tested under different illumination conditions as shown in Figure 2c. The $V_{OC}$ of the solar cell decreased with the decrease of incident light intensity; however, the FF improved at lower light illumination. The correlation between $J_{SC}$ and light...
intensity is plotted in Figure 2d. The $J_{SC}$ of the solar cell shows a quasi-linear relationship below 0.6 sun. However, at higher light intensity the $J_{SC}$ was lower than the linear extrapolation from low illumination, showing limited charge collection efficiency. Lower FF and suppressed $J_{SC}$ can be justified by the high sheet resistance of the CNT film, increasing the overall series resistance ($R_s$) of the solar cell. Under these circumstances, the efficiency shows an increasing trend under low light illumination, reaching 8.85% at 10 mW/cm². This is especially appealing for indoor applications. Even without the conventional hole-transporting material spiro-OMeTAD, this preliminary result positions CNTs as a promising charge collector for perovskite solar cells. Additionally, since the carbon nanotube film was only a thin membrane with tens of nanometers thickness, there is a great potential for flexible perovskite devices.

The low thickness of CNT network films allows for the perovskite solar cells to be illuminated from both directions. The UV–vis transmittance spectra of a CNT film and bare FTO are compared in Figure 3a. The CNT film (20–50 nm) shows a slightly lower transmittance than the FTO in the visible range. Therefore, unlike the conventional Au electrode, the semitransparent CNT counter electrode can also transmit light, which can be harvested in the solar cell. The $J–V$ curves of a CH$_3$NH$_3$PbI$_3$/CNTs solar cell with FTO and CNT side illumination are shown in Figure 3b. When illuminated from FTO side, the solar cell generates a $V_{OC}$ of 0.86 V, a $J_{SC}$ of 16.7 mA/cm², an FF of 0.44, and a PCE of 6.29%. With illumination from the CNT side, the solar cell showed a similar $V_{OC}$ of 0.85 V, a lower $J_{SC}$ of 9.9 mA/cm², an FF of 0.46, and a PCE of 3.88%. The double-sided light response feature of the perovskite/CNTs solar cell is an advantage in applications in building integrated photovoltaic applications such as solar cell windows.

Incident photon to electron conversion efficiency (IPCE) of the CH$_3$NH$_3$PbI$_3$/CNTs solar cells with illumination from different sides is compared in Figure 3c. With FTO side illumination, the solar cell response wavelength ranged from 300 to 800 nm. The ∼800 nm cut-off wavelength corresponds to the 1.55 eV band gap of CH$_3$NH$_3$PbI$_3$ perovskite absorber. At shorter wavelengths, the photocurrent is cut off by FTO and TiO$_2$, as shown in the UV–vis transmittance of FTO. The device shows high photon conversion efficiency, above 70%, for wavelengths from 400 to 600 nm. However, the IPCE is relatively lower at longer wavelength regions possibly due to incomplete absorption of light. UV–vis transmittance spectra of a whole perovskite/CNTs solar cell (Figure S4) show light transmittance starting from 510 nm, which explains the IPCE drop above 510 nm. The lower $J_{SC}$ of the solar cell with light illumination from the CNT side of the solar cell could also be explained by the IPCE results. With illumination from the CNT side, the photoresponse at wavelengths above 350 nm is lower than with the illumination from the FTO side, which is expected...
given the lower transmittance of CNTs with respect to FTO for the 350–800 nm region (Figure 3a). The lower IPCE for CNT side illumination may be related to the poorer charge collection efficiency of CNT film than the mesoporous TiO₂ scaffold. It is conceivable that in a conventional perovskite solar cell the Au back electrode can act as a rear reflector to direct unabsorbed light back into the solar cell and provide higher photocurrent because the perovskite layer in the solar cell is not thick enough for full light absorption in wavelength regions from 300 to 800 nm. Therefore, when an aluminum back reflector is introduced at the CNT side of the CH₃NH₃PbI₃/CNTs solar cell, the J_{SC} of the solar cell increases from 14.74 mA/cm² to 16.40 mA/cm² (Figure 3d).

The porous structure of the CNT film offered the possibility of incorporating hole-transporting materials into the CNT network to improve the heterojunction property of solar cells. Here, we have incorporated conventional hole-transporting material (HTM) spiro-OMeTAD into the CH₃NH₃PbI₃/CNTs perovskite solar cell by simple spin coating. From the cross session SEM image in Figure 4a, it is clear that the HTM not only covered the CNT network but also wrapped around the CNT bundles. The HTM penetrates through the pores of the CNT networks and forms direct contact to the perovskite layer. The light J–V curves of a particular solar cell before and after spiro-OMeTAD coating are shown in Figure 4b. The photovoltaic performance improves significantly with the introduction of spiro-OMeTAD, with V_{OC} increasing from 0.86 V to 1.00 V, J_{SC} from 13.9 mA/cm² to 18.1 mA/cm², and FF from 0.43 to 0.55. Hence, the efficiency is nearly doubled, from 5.14% to 9.90% (Table S2). The CNT/spiro-OMeTAD composite film provided better coverage over the perovskite surface compared to the porous CNT networks; therefore it maximized the contact interface with the perovskite, which could have a positive effect on both charge separation and collection, resulting in an improvement of J_{SC}. The spiro-OMeTAD infiltrates beneath the CNT network and forms a direct contact with CH₃NH₃PbI₃. The higher Fermi level of the hole-transporting material could contribute to the higher V_{OC} for the spiro-OMeTAD devices. The CNT/spiro-OMeTAD solar cells were also tested under rear illumination and showed a lower efficiency of 5.6% (Figure S8) and suffer from light absorption losses in the spiro-OMeTAD layer.

Impedance spectroscopy has been deployed to further understand the electrical characteristics in CNT and CNT/spiro-OMeTAD solar cells. The obtained spectra for both samples clearly show different shapes in all the measured voltages. The measurements in the CNT device result in two arcs separated in frequencies; in contrast, the CNT/spiro-OMeTAD presents a more merged spectrum (Figure 4c). This is probably due to an extra element in the hole transport process: the injection of the holes from the spiro-OMeTAD to the

Figure 4. (a) Cross section SEM image of CNT film after spiro-OMeTAD infiltration. (b) J–V curves of a solar cell with and without spiro-OMeTAD at 1 sun. (c) Nyquist plot of solar cells with and without spiro-OMeTAD measured at 800 mV applied bias under 0.1 sun; fittings represented by solid lines follow the equivalent circuit shown in the inset. (d) Hole-transporting material resistance (R_{HTM}) and recombination resistance (R_{rec}) extracted from fitting of the impedance spectra at different voltages under 0.1 sun illumination.
EXPERIMENTAL SECTION

Synthesis of CNT Film. CNT network films were synthesized using the floating catalyst chemical vapor deposition method using a tube furnace. Ferrocene (0.36 M) as catalyst and sulfur (0.036 M) as growth promotion agent were dissolved in xylene to form a uniform precursor solution. The temperature for CVD was set to 1150 °C. Then 2500 scm Ar and 600 scm H2 were introduced into the quartz tube as carrier gas. When the temperature and gas flow stabilized, the precursor solution was injected into the quartz tube at a preheating zone of the furnace with a temperature of 180 °C. The precursor vaporized and was transported into the center zone of the furnace by the gas flow for CNT growth. CNTs grew from the floating Fe catalyst in the carrier gas flow. After growth, the CNTs formed an aerosol carried by the gas flow. The CNT aerosol was carried to the end of the quartz tube with a temperature of 100–150 °C, where it was collected on a nickel foil and assembled into a freestanding thin film. More information on CNT film synthesis can be found in a previous report. 

Preparation of TiO2 Substrates. Fluorine-doped tin oxide substrates were laser etched to form the desired pattern. The etched substrates were subsequently cleaned with Decon soap solution, then deionized water, followed by ethanol. A thin layer of compact TiO2 (80–100 nm, blocking layer) was deposited by aerosol spray-pyrolysis at 450 °C using compressed air as a carrier gas. These substrates were immersed in a 40 mM TiCl4 solution for 30 min at 70 °C, followed by rinsing with deionized water and ethanol. A mesoporous TiO2 layer (~400 nm) composed of 20 nm-sized particles was then deposited by spin coating and subsequently annealed at 500 °C for 30 min.

Preparation of CH3NH3PbI3 Absorber. The organic-inorganic perovskite CH3NH3PbI3 was deposited by a sequential method as reported in the literature. PbI2 (1 M) was dissolved in N,N-dimethylformamide overnight under stirring conditions at 70 °C. The solution was spin coated on the TiO2 substrates at 6000 rpm for 5 s, followed by annealing at 70 °C for 30 min. Subsequently, the films were dipped in a 8 mg/mL solution of CH3NH3I in 2-propanol (IPA) for 20 min. The films were then rinsed further with IPA and dried at 70 °C for 30 min.

Deposition of CNT Film. The edges of the perovskite region were covered by tape. The taped substrates were put under the lifted CNT film and covered by the film. Several drops of toluene were added to wet the CNT film and perovskite surface. After toluene vaporization, CNTs on the unwanted region were removed by wiping with a cotton stick. Both the CNT and FTO were soldered for better electrical contact.

Deposition of spiro-OMeTAD: Hole Transporting Material. Spiro-OMeTAD was dissolved in chlorobenzene (120 mg mL−1) and spin-coated on substrates with a speed of 4000 rpm. Additives such as Li[CF3SO2]2N (29 μL mL−1 from a stock solution of 520 mg mL−1), tert-butylpyridine (29 μL), and FK102 dopant
(24 μL, stock solution 300 mg mL⁻¹) were added to the above solution.

**Solar Cell Characterization.** Photocurrent–voltage measurements were carried out using a San-Ei Electric XEC-3015 under AM 1.5 G and the illumination area was defined by a 4 × 4 mm mask. Incident photon to current conversion efficiency was measured using a PVE300 (Bentham), with a dual xenon/quartz halogen light source, measured in dc mode with no bias light used. Incident light intensity was calibrated using a photodiode detector (silicon calibrated detector, Newport).

**Impedance Measurement.** IS measurements were carried out under low light intensity (0.1 sun) with an Autolab 302 N. The applied dc bias potential ranged from 100 to 1000 mV. A voltage perturbation with 20 mV (rms) amplitude was applied with a frequency swipe from 1 MHz to 1 Hz. The spectra were fitted using Z-View software.

**Material Characterization.** HRTEM images of CNTs were recorded using a transmission electron microscope (JEM-2010). Top view and cross sectional images of solar cells were recorded using a field emission scanning electron microscope (JSM-7600F). UV–vis absorption spectra were collected with a Shimadzu UV3600 spectrophotometer. Raman and photoluminescence measurements were taken using a spectrometer (Horiba JY-T64000) under an excitation laser with a wavelength of 532 nm.

**Conflict of Interest:** The authors declare no competing financial interest.

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**Supporting Information Available:** HRTEM and Raman spectrum of the CNT film, SEM images and UV–vis spectrum of CH₃NH₃PbI₃/CNTs and CH₃NH₃PbI₃/spiro-OMETAD/CNTs solar cells, capacitance Bode plots, and series resistance estimates of solar cells are included. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**


