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### Supporting Information for Highly stable perovskite solar cells with all-carbon hole transport layer

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1. Photographs of a graphene oxide (GO) solution and single-walled carbon nanotube (SWNT) film



**Figure S1.** (a) and (b) Photographs of the graphene oxide (GO) solution and singlewalled carbon nanotube (SWNT) film, respectively. The GO modified by octadecylamine (ODA) was well-dispersed in the chlorobenzene solution at a concentration of 5 mg/mL. The SWNT film had a transmission of 70% at a wavelength of 550 nm. The scale bar in each figure represents 0.5 cm.

# (a) (b) + + + PMMA (c) + + Au PMMA

2. Connection between SWNTs and electrode.

**Figure S2.** (a) Top view SEM image of Au coated SWNTs network with thin PMMA layer. (b) and (c) Cross sectional SEM images of SWNTs network covered by PMMA layer with thickness of ~100 nm and SWNT/PMMA/Au layer with PMMA layer thickness of ~80 nm. Black arrows indicate the SWNTs and the scale bar in each figure represents 1  $\mu$ m.

Figure S2(a) shows the top view of Au coated SWNTs network with thin PMMA layer. The bundles of SWNTs are protruded on the surface, which plays an important role for electronic connection to electrode layer. Figures S2(b) and (c) show cross sectional SEM images of a SWNT film covered by PMMA layer with thickness of ~100 nm and SWNT/PMMA/Au layer with PMMA layer thickness of ~80 nm, respectively. It is seen that the SWNTs can connect to Au in the cross-sectional images, indicated by arrows. The electrical connection covered by insulating PMMA layer comes from the characteristics network structure of SWNTs.

### 3. Absorption spectra of perovskite and perovskite/SWNT/GO films



**Figure S3.** Optical absorption spectra of a perovskite thin film (black solid line) and a perovskite/SWNT/GO film (red solid line).

### 4. Optical absorption spectrum of GO



**Figure S4.** Optical absorption spectrum of the GO. The inset shows the same absorption spectrum as a function of the photon energy. A drastic increase in absorption occurred at approximately 3 eV, indicating that the optical gap for the major portion of the GO was approximately 3 eV.

5. Turn-on voltages of perovskite solar cells using SWNT and SWNT/GO transport layer



**Figure S5.** J-V characteristics of perovskite solar cells using SWNTs and SWNT/GO transport layer under dark conditions, which shows the increase of turn-on voltage from about 0.3 to 0.7 V by the introduction of GO.

## 6. Photovoltaic performance of perovskite solar cells with various hole-transport layers



**Figure S6.** (a) J-V curves of perovskite/GO and perovskite/PMMA solar cells. (b) J-V curves of perovskite/SWNT/PMMA and perovskite/GO/PMMA solar cells.

The J-V curves of perovskite solar cells with various hole-transport layers were measured in order to understand the role of each layer. Figure S6a shows the J-V curves for perovskite solar cells with the GO (perovskite/GO) and PMMA (perovskite/PMMA) layers. The PCEs of the perovskite/GO and perovskite/PMMA were relatively low at 2.6 and 1.2%, respectively. The detailed photovoltaic parameters from the J-V curves are shown in Table S1. The lower PCE values for the perovskite/GO and perovskite/PMMA cells compared to those of the perovskite/SWNT cell (4.9%, Fig. 3a) are attributed to the large series resistance loss due to the lower electronic conductivity of the GO and PMMA (see  $R_s$  in Table S1).

Figure S6b shows the J-V curves for perovskite solar cells with GO/PMMA (perovskite/GO/PMMA) and SWNT/PMMA (perovskite/SWNT/PMMA) layers. The detailed photovoltaic parameters evaluated from these J-V curves are also shown in Table S1. The PCE of the perovskite/GO/PMMA is low at 0.7%, also due to the very large series resistance loss (see  $R_s$  in Table S1). The PCE of the perovskite/SWNT/PMMA cell is much higher, however, at 7.4%, but still lower than those of the perovskite/SWNT/GO (9.8%) and perovskite/SWNT/GO/PMMA (10.4%) cells (Fig. 3a). The lower  $J_{sc}$  and  $V_{oc}$  values for the perovskite/SWNT/PMMA cell without a GO layer (see in Table S1) compared to those for the cell with the GO layer can be attributed to relatively large carrier recombination losses and the low built-in potential, as discussed in the main text.

Samples	J <sub>sc</sub> (mA/cm²)	V <sub>oc</sub> (V)	Æ	η (%)	<b>R</b> <sub>s</sub> (Ω)	${\it R}_{ m sh}$ (k $\Omega$ )
PMMA	4.71	0.69	0.38	1.2	1241	4.7
GO	8.16	0.76	0.42	2.6	459	4.2
GO/PMMA	4.0	0.85	0.20	0.7	8396	4.4
SWNT/PMMA	15.6	0.82	0.58	7.4	168	7.2

**Table S1.** Parameters of perovskite solar cells with PMMA, GO and SWNT layer.  $R_s$  and  $R_{sh}$  are series and shunt resistance, respectively.

#### 7. Stability of perovskite/SWNT/GO solar cells



**Figure S7.** (a) and (b) J-V curves of perovskite/SWNT/GO solar cells protected by PMMA layers of different thicknesses before and after exposure to air for 10 days.

The stability of the photovoltaic performance of perovskite/SWNT/GO solar cells protected by PMMA layers of different thicknesses was evaluated in air (humidity: 70–80%, temperature: 298 K). The J-V curves before and after exposure to air for 10 days are shown in Figures S7 (a) and (b), respectively. Drastic decreases in the PCE values and significant degradation of the photovoltaic performance are observed for the perovskite/SWNT/GO solar cells with thinner PMMA layers (30 and 40 nm). In contrast, almost no decrease in the PCE values and photovoltaic performance degradation is observed after 10 days for the perovskite/SWNT/GO solar cells with thicker PMMA layers (60, 90, and 160 nm).

Figure S8 shows the PCEs as a function of PMMA layer thickness before and after exposure to air for 10 days. The difference of the PCE value ( $\delta\eta$ ) is also shown in Fig. S8. The  $\delta\eta$  drastically decease with increasing PMMA layer thickness. The degradation of photovoltaic performance is much reduced with thicker PMMA layer, as also shown in Table S2



**Figure S8.** PCEs of perovskite/SWNT/GO/PMMA solar cells before (blue squares) and after exposure to air for 10 days (green rhombuses). The difference of the PCE value  $(\delta \eta)$  in initial and after 10 days is also shown (red circles).

Thickness Efficiency	30 nm	40 nm	60 nm	90 nm	160 nm
$\eta_{0}$ (%)	8.3	10.3	10.8	10.8	10.5
$\eta_{\rm t}$ (%)	3.5	7.7	9.2	9.7	10.0
δη (%)	4.8	2.6	1.6	1.1	0.5

**Table S2.** PCEs value of solar cells as a function of layer thickness before and after exposure to air for 10 days, and the difference of PCE value ( $\delta\eta$ ) in initial and after 10 days.

We checked performance of five perovskite/SWNT/GO/PMMA solar cells to further conform the stability. The *J-V* curves of five solar cells labeled as a, b, c, d, and e are shown and corresponding conversion efficiencies are 12.1, 11.0, 9.7, 10.7, and 10.6% as shown in Fig. S9. After 10 days under the air condition, the conversion efficiencies are decreased as 11.5, 10.3, 9.2, 10.0, and 9.9% in Fig. S9(b), respectivity. The detail parameters of photovoltaic performance are also shown in Table S3. These small changes suggest that the higher stability of perovskite/SWNT/GO/PMMA based solar cells was achieved.



**Figure S9.** (a) and (b) *J*–*V* curves of five perovskite/SWNT/GO solar cells protected by PMMA layers before and after exposure to air for 10 days.

Samples	J <sub>sc</sub> (mA/cm²)	V <sub>oc</sub> (V)	FF	η (%)
a (0 day)	20.4	0.96	0.62	12.1
a (10 days)	20.5	0.95	0.60	11.5
b (0 day)	18.5	0.93	0.64	11.0
b (10 days)	18.0	0.93	0.61	10.3
c (0 day)	18.6	0.87	0.60	9.7
c (10 days)	18.5	0.86	0.58	9.2
d (0 day)	18.9	0.90	0.63	10.7
d (10 days)	18.7	0.89	0.61	10.0
e (0 day)	19.6	0.91	0.60	10.6
e (10 days)	19.5	0.91	0.56	9.9

**Table S3.** Parameters changes of 5 solar cells before and after exposure to air for 10 days.

## 8. Hysteresis of perovskite/SWNT/GO/PMMA solar cells and spiro-OMeTAD based perovskite solar cells

Figure S10 shows *J-V* curves of perovskite solar cell obtained from forward scan (from short-circuit to open-circuit under forward bias voltage, FS) and reverse scan (from open-circuit to short-circuit under the forward bias voltage, BS) at the scan rate of 50 mV s<sup>-1</sup>. The difference between J-V curves is observed under the different sweep direction. The hysteric index (HI) is defined as, <sup>[1]</sup>

$$HI = \frac{J_{\rm BS}(V_{\rm OC}/2) - J_{\rm FS}(V_{\rm OC}/2)}{J_{\rm BS}(V_{\rm OC}/2)},$$

where  $J_{BS}(V_{oc}/2)$  is the photocurrent density at  $V_{oc}/2$  bias for the backward scan, while  $J_{FS}(V_{oc}/2)$  is the photocurrent density for the forward scan at  $V_{oc}/2$  bias. The evaluated HI in perovskite/SWNT/GO/PMMA and perovskite/Spiro-OMeTAD are 0.015, and 0.033, respectively. The hysteresis in perovskite/SWNT/GO/PMMA solar cell is similar with that perovskite/Spiro-OMeTAD solar cell.



**Figure S10.** Forward (red line) and backward (blue line) J-V characteristics of perovskite solar cells. (a) with Spiro-OMeTAD hole-transport layer, and (b) with SWNT/GO/PMMA layer.

### 9. Raman spectra of GO (graphene oxide)



**Figure S11.** Raman spectra of the GO before (black line) and after modification using ODA (red line). The two Raman peaks at 1600 and 1350 cm<sup>-1</sup> correspond to the G and D peaks, respectively. There is little change in the Raman spectrum of the GO after ODA modification, indicating that the GO structure is not strongly affected during the modification process.

#### Reference

[1] R. S. Sanchez, V. G.-Pedro, J.-W. Lee, N.-G. Park, Y. S. Kang, I. M.-Sero and J. Bisquert, *J. Phys. Chem. Lett.*, 2014, **5**, 2357.