

## Electronic Supplementary Information

# Influence of physicochemical characteristics of reduced graphene oxides on gas permeability of the barrier films for organic electronics

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## Experimental Section

*Materials* : Graphite, potassium persulfate ( $K_2S_2O_8$ ), phosphorus pentoxide ( $P_4O_{10}$ ), potassium permanganate ( $KMnO_4$ ), 1,2-dichlorobenzene (DCB), sodium dodecylbenzenesulfonate (SDBS), zinc acetate dihydrate ( $Zn(CH_3COO)_2 \cdot 2H_2O$ ), ethanolamine, 2-methoxyethanol and molybdenum oxide ( $MoO_3$ ) were purchased from Aldrich. Sulfuric acid ( $H_2SO_4$ ), Hydrogen peroxide ( $H_2O_2$ ), hydrochloric acid (HCl), acetone, and isopropyl alcohol (IPA) were purchased from Daejung. Polyethylene naphthalate (PEN) film was obtained from DuPont Teijin Films. Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) was purchased from Rieke Metal. [6,6]-phenyl-C61-butyric acid methyl ester ( $PC_{61}BM$ ) was purchased from Nano-C. All chemicals were used without further purification.

*Synthesis of GOs* : GOs were synthesized by modified Hummer's method in the detailed process was described in our previous study.<sup>1</sup> To increase the resultant GO yield, graphite flakes (6 g) were preoxidized with  $K_2S_2O_8$  (12 g) and  $P_4O_{10}$  (12 g) in  $H_2SO_4$  (60 ml) in 80 °C for 24 h. After the reaction, the preoxidized graphite was filtered and rinsed with excessive deionized (DI) water until the pH of the filtrate became neutral. They were then stored in a vacuum state at 25 °C. The completely dried expanded graphite (2 g) was dispersed to  $H_2SO_4$  (92 ml) and kept at 0 °C before adding  $KMnO_4$  (12 g). The reaction was performed at 35 °C by stirring at 250 rpm for 2 h. After the reaction, DI water (200 ml) was carefully added to the reaction bath. The reaction was further performed at 45 °C for 2, 4, and 8 h (GO\_452, GO\_454, and GO\_458), 70 °C for 8 h (GO\_708) and 95 °C for 0.5, and 2 h (GO\_950.5, and GO\_952). This step was terminated by releasing  $H_2O_2$  solution (30 ml) into the mixture. The output was centrifuged at 13000 rpm for 20 min, which was followed by three cycles of HCl washing and re-centrifugation. Finally, DI water was used to neutralize GO suspension with centrifugation.

In addition, the 'GO\_000' sample was synthesized and directly released to a mixture of excess ice and H<sub>2</sub>O<sub>2</sub> (10 ml).

*Preparation of rGO/PEN films* : rGO films were prepared by the thermal annealing process and GO aqueous dispersion (7 mg ml<sup>-1</sup>) was spin-cast on the PEN substrate. The GO/PEN films were transferred to an oven to reduce the GO. The samples were then heated to 200 °C at heating rate of 1 °C min<sup>-1</sup>.<sup>2</sup> Hereafter, thermally reduced GOs were denoted rGO\_000, rGO\_452, rGO\_454, rGO\_458, rGO\_708, rGO\_950.5, and rGO\_952, which are thermally derived from GO\_000, GO\_452, GO\_454, GO\_458, GO\_708, GO\_950.5, and GO\_952, respectively.

*Fabrication of devices* : ITO-coated glass substrates were pre-cleaned by bath sonication sequentially with detergent, deionized water, acetone, and IPA. After drying the solvent, substrates were pretreated with UV-ozone radiation for 15 min. The preparation of ZnO sol-gel precursor was described elsewhere.<sup>3</sup> The precursor solution was spin-cast on the ITO substrates at 4000 rpm and followed by annealing at 200 °C for 30 min. As thermal annealing was finished, ZnO-coated substrates were moved to an argon-filled glove box. The P3HT:PC<sub>61</sub>BM blend (1:1) in DCB with a total concentration of 50 mg ml<sup>-1</sup> were stirred overnight followed by filtering. Photoactive materials were spin-cast on top of ZnO films at 800 rpm before being dried in a covered petri dish for the crystallization of active materials.<sup>4</sup> Completely dried films were thermally annealed at 150 °C for 30 min. The devices were fabricated by thermal evaporation of MoO<sub>3</sub> (10 nm) and Ag (100 nm) in a vacuum under 10<sup>-6</sup> torr after thermal annealing of the photoactive layer. Encapsulation barriers (PEN and rGO/PEN) were laminated using epoxy resin. The active area of the devices was 0.055 ~ 0.08 cm<sup>2</sup>, which is defined by the crossing area of the cathode and anode.

*Characterization* : The X-ray diffraction (XRD, D8 Advance, Bruker) patterns for the interlayer distance analysis were recorded using CuK $\alpha$  radiation ( $\lambda = 0.154184$  nm). Elemental analysis were characterized by X-ray photoelectron spectroscopy (XPS, AXIS-His, Kratos). The lateral sizes of rGO samples were characterized using a scanning electron microscope (MERLIN Compact, Zeiss). The lateral sizes of GO samples were characterized by Dynamic light scattering (DLS) analysis using a zeta-potential analyzer (ELSZ-1000ZS, Otsuka). The amount of point defects within the rGO layers were monitored by Raman spectroscopy (Ramanplus, Nanophoton) using the 532 nm wavelength laser. The atomic force microscopy (AFM, NANOSTationII, Surface Imaging Systems) was utilized to confirm the formation of voids and measure the thickness of the rGO layer. The water vapor transmission rate of the films were recorded using a MOCON instrument at 38 °C and 100% relative humidity. The optical transmittance of films was recorded using a UV-vis-NIR spectrometer (Varian, Cary 5000). The current density-voltage (J-V) characteristics of PSCs were measured using an IV sourcemeter unit (Keithley 2634B). The photovoltaic behavior of devices was analyzed under illumination (100 mW cm<sup>-2</sup>) of simulated AM 1.5G from a solar simulator (Abet Technologies model 10500). The devices for lifetime analysis were stored at a temperature of 25  $\pm$  5 °C and a relative humidity of 100%.

## Deconvolution of C1s spectra

To analyze the chemical nature of rGOs, the C1s spectra of each sample were deconvoluted with several peaks, as shown in Figure S1. The rGO raw spectra consist of C=C (284.4 eV), C-C (285.0 eV), C-O (286.3 eV), C=O (287.9 eV) and O-C=O peaks (289.1 eV).<sup>5</sup>

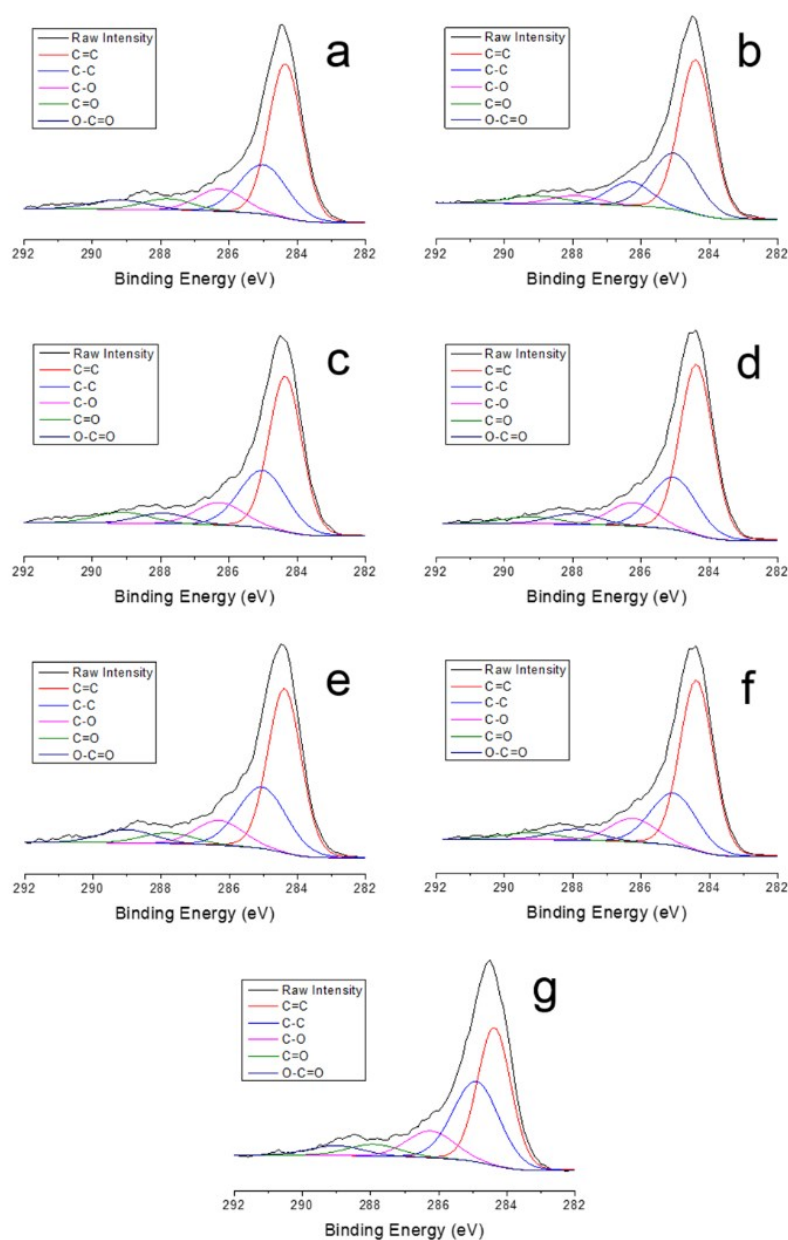


Fig. S1. Deconvoluted C1s XPS spectra of (a) rGO\_000, (b) rGO\_452, (c) rGO\_454, (d) rGO\_458, (e) rGO\_708, (f) rGO\_950.5, and (g) rGO\_952.

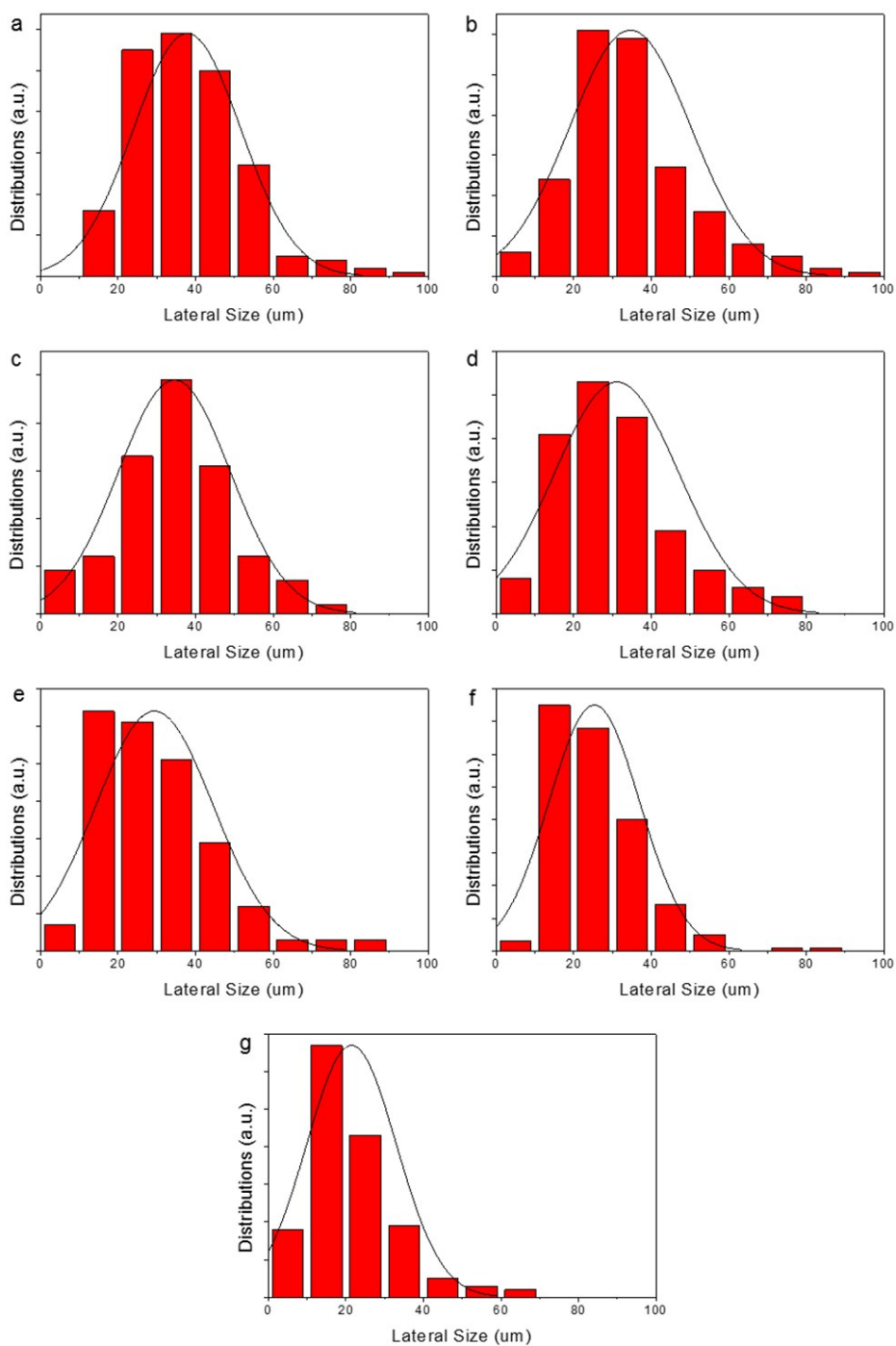


Fig. S2. Size distributions of (a) rGO\_000, (b) rGO\_452, (c) rGO\_454, (d) rGO\_458, (e) rGO\_708, (f) rGO\_950.5 and (g) rGO\_952 measured by analysis of SEM images.

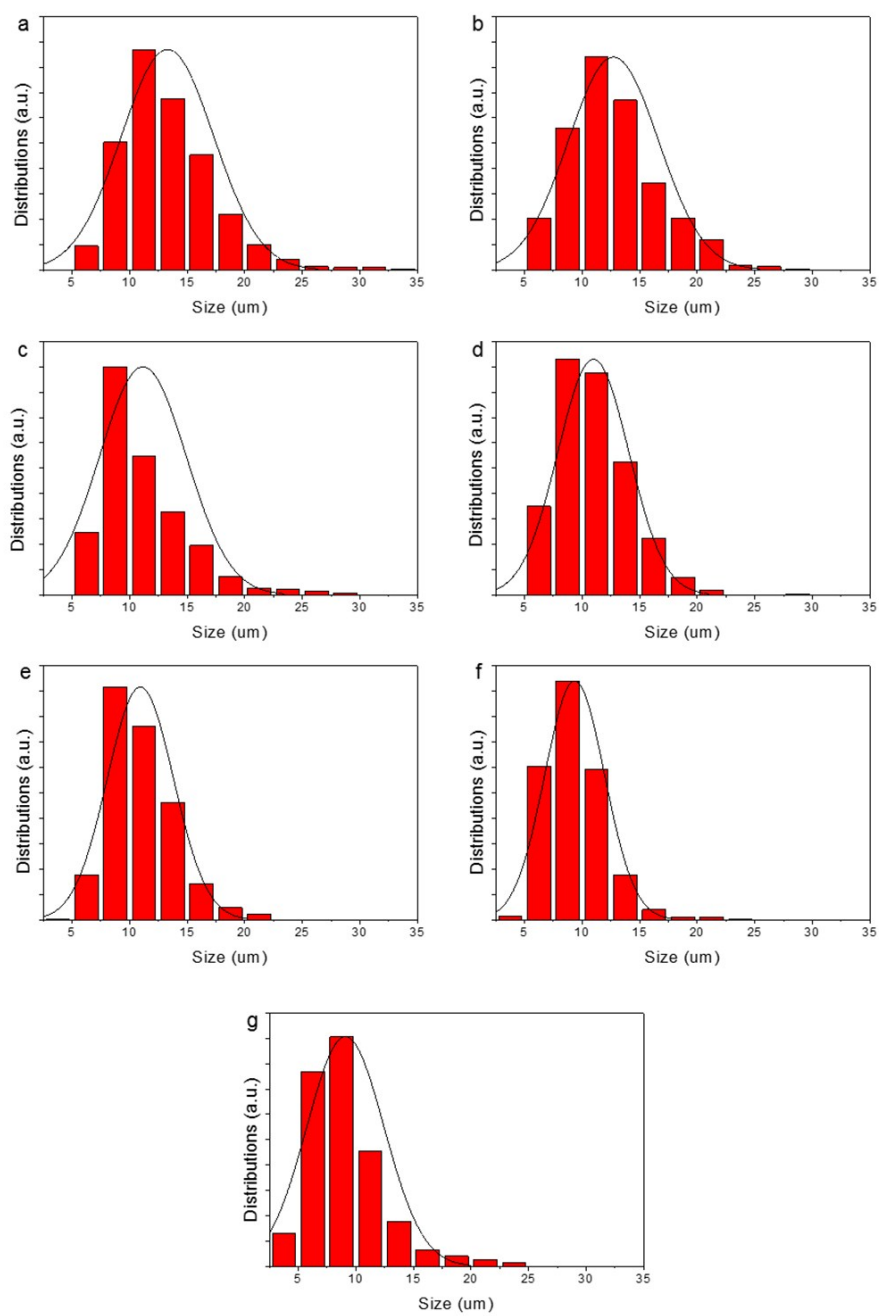


Fig. S3. Size distributions of (a) GO\_000, (b) GO\_452, (c) GO\_454, (d) GO\_458, (e) GO\_708, (f) GO\_950.5 and (g) GO\_952 measured by DLS analysis.

Table S1. Comparison of the size measured by two different methods.

Sample type	Size measured by SEM images ( $\mu\text{m}$ )	Size measured by DLS analysis ( $\mu\text{m}$ )
rGO_000	$37.8 \pm 13.9$	$13.3 \pm 3.8$
rGO_452	$34.6 \pm 15.7$	$12.7 \pm 3.9$
rGO_454	$33.6 \pm 14.9$	$11.1 \pm 3.8$
rGO_458	$30.7 \pm 15.0$	$11.0 \pm 3.1$
rGO_708	$29.8 \pm 15.1$	$10.9 \pm 2.9$
rGO_950.5	$25.3 \pm 11.7$	$9.4 \pm 2.6$
rGO_952	$21.4 \pm 11.6$	$9.1 \pm 3.4$

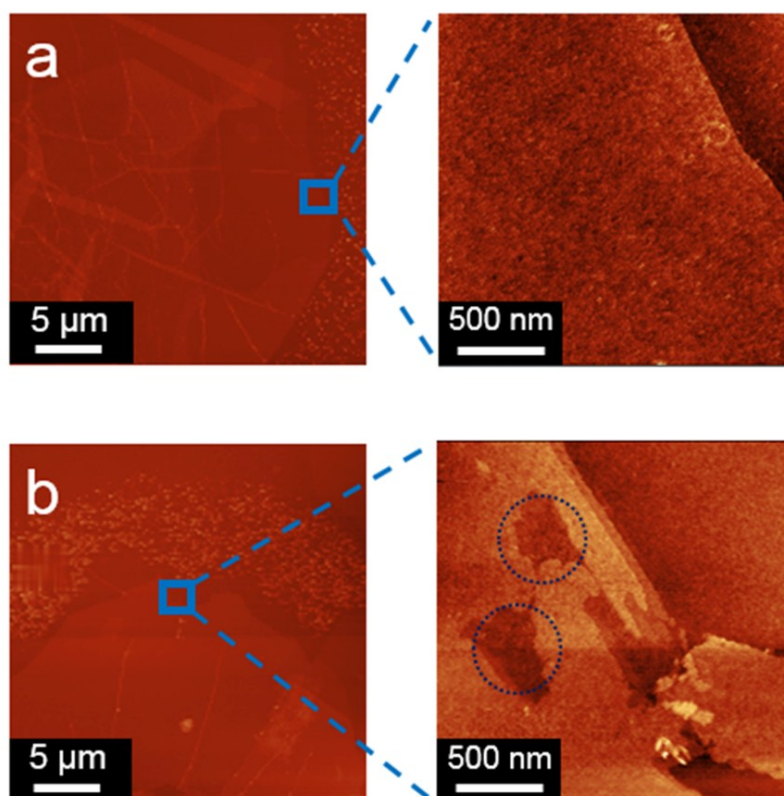


Fig. S4. AFM images of (a) GO\_000 and (b) GO\_952. Magnified regions (right side) were monitored to confirm the generation of large-size voids (dotted blue circles).



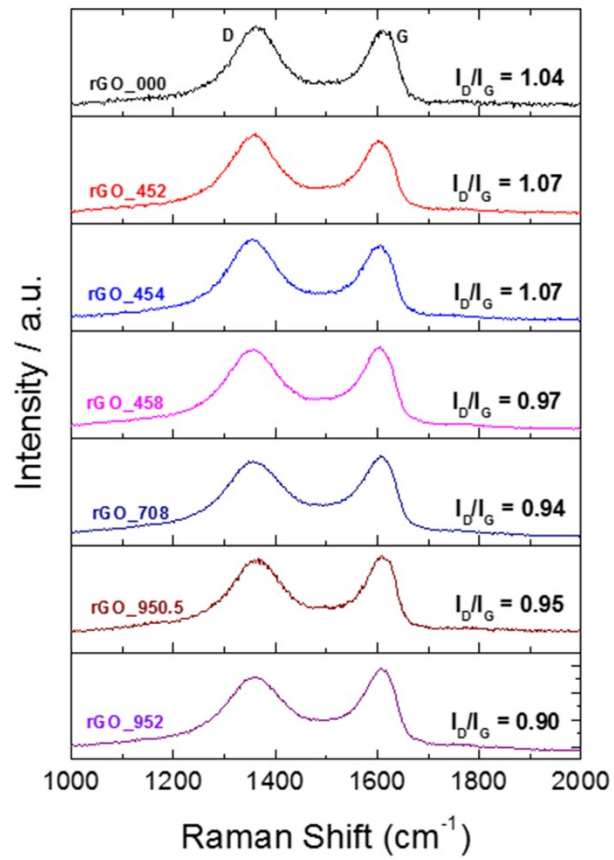
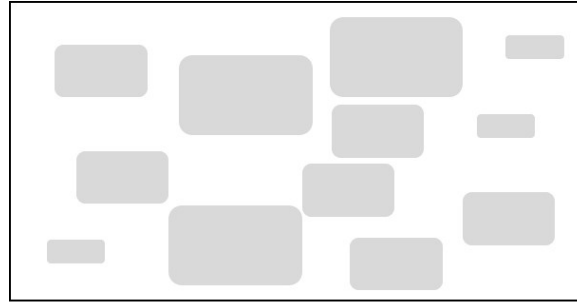


Fig. S5. Raman spectra of rGO films.

### Average surface coverage derivation of rGO in stacked membranes



Covered region :  $\phi_G$   
Uncovered region :  $1-\phi_G$

Fig. S6. Scheme on the unit layer in the rGO-stacked structure. The gray zones represent the rGO sheet coverage.

The average surface coverage of rGOs in a unit layer is calculated by measuring the optical transmittance of rGO films. The unit layer consists of rGO-covered and uncovered regions, as shown in Figure S3. Assuming that the optical transmittance of the individual single-layer rGO sheet is 97.7%, the unit layer ( $T_{unit}$ ) transparency is expressed from the following equation,

$$T_{unit} = 0.977\phi_G + 1 \cdot (1 - \phi_G) = 1 - 0.023\phi_G \quad (S1)$$

where  $\phi_G$  is the aerial ratio of rGO sheets in the unit layer. The  $T_{unit}$  is the summation of the contribution of graphene-covered area ( $0.977\phi_G$ ) and the contribution of graphene-uncovered area ( $1 \cdot (1 - \phi_G)$ ). The number of layers in graphene films ( $n$ ) are calculated from,

$$n = \frac{d_{rGO}}{d_{int}} \quad (S2)$$

where  $d_{rGO}$  is the rGO film thickness and  $d_{int}$  is the interlayer distance. Therefore, the optical transmittance of the rGO-laminated barrier ( $T_{rGO}$ ) is obtained from the following relationship,

$$(1 - 0.023\phi_G)^n = T_{rGO} \text{ (S3)}$$

This equation converts into the following equation,

$$\phi_G = \frac{1 - T_{rGO}^{\frac{1}{n}}}{0.023} \text{ (S4)}$$

By measuring the thickness and optical transmittance of rGO films by extracting the transmittance of PEN substrate, we derived the 2D surface coverage ratio, as summarized in Table S1 and Figure 4.

Table S2. Parameters for calculating the average surface coverage of rGOs.

Sample type	Thickness (nm)	Number of layers	T <sub>rGO</sub> (%)	ϕ <sub>G</sub> (%)
rGO_000	28.7	75.5	42.0	0.497
rGO_452	32.0	84.2	38.7	0.487
rGO_454	21.0	55.3	54.0	0.482
rGO_458	35.5	93.4	36.2	0.471
rGO_708	23.6	62.1	52.1	0.454
rGO_950.5	38.0	100.0	34.9	0.455
rGO_952	37.0	97.4	40.9	0.398

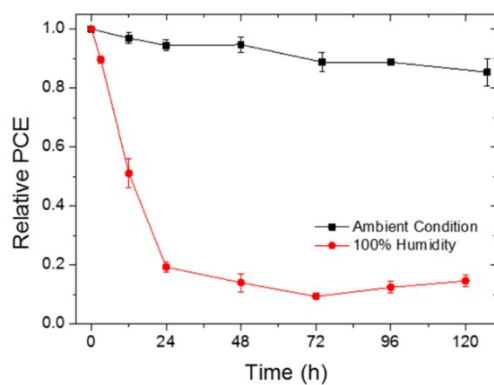


Fig. S7. Change in the device efficiency stored in ambient air or water vapor saturated condition.

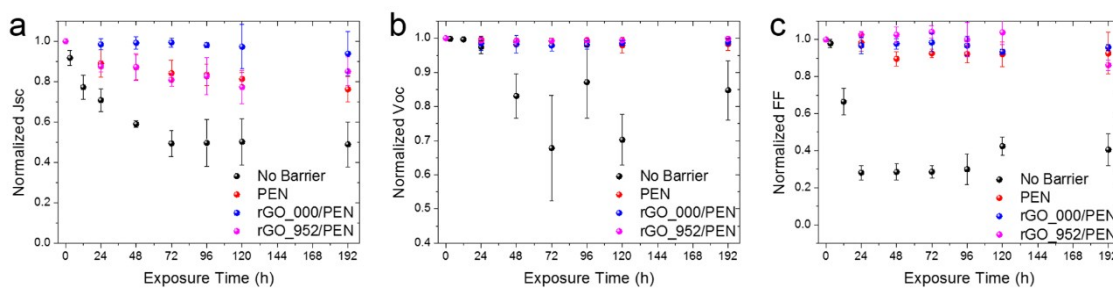


Fig. S8. Decay trend in (a)  $J_{sc}$ , (b)  $V_{oc}$ , and (c) FF and as a function of exposure time to air for different devices.

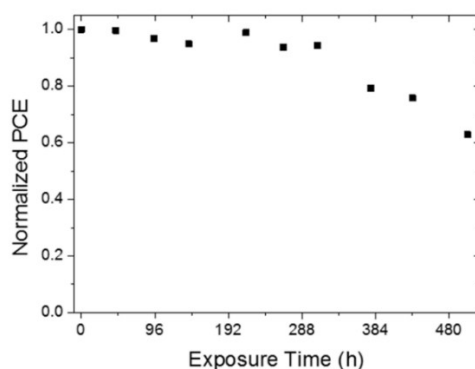


Fig. S9. Long-term stability of rGO\_000/PEN-encapsulated PSC.

## REFERENCES

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