

## Supporting Information

### **Fluorine-functionalized and simultaneously reduced graphene oxide as a novel hole transporting layer for highly efficient and stable organic photovoltaic cells**

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#### **Experimental**

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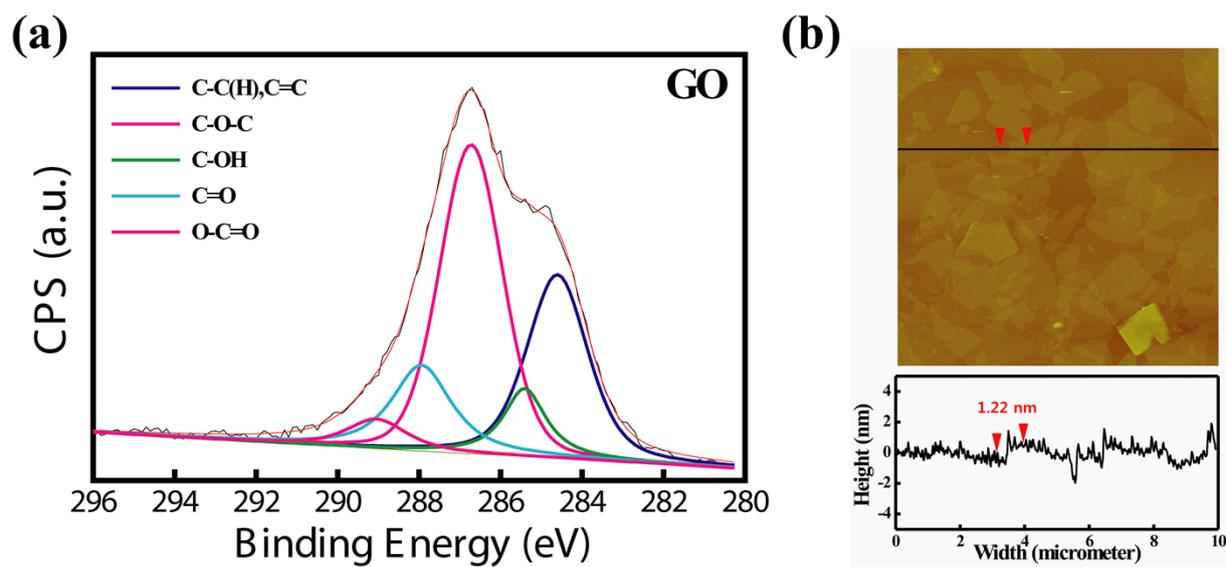
*Preparation of GO and rGO:* Graphene oxide was synthesized using a modified Hummers method. Four grams of graphite flakes were added to a 250 ml round-bottom flask containing 120 ml of H<sub>2</sub>SO<sub>4</sub> and then stirred for 1 h. Four grams of KMnO<sub>4</sub> powder was added to the mixture at 20 min intervals while stirring. The mixture was slowly heated to 40 °C and maintained for 6 h to oxidize the graphite. Subsequently, 150 ml of deionized (DI) water was added to the mixture. Seventeen milliliters of H<sub>2</sub>O<sub>2</sub> solution was added to the mixture, stirred for 30 min, and held under this condition for 24 h. Then, the mixture was centrifuged. The mixture was enclosed in a dialysis tube washed with ultrapure DI water several times to obtain a pH level of 5. Finally, the graphene oxide was dried in a freeze dryer at -60 °C for 48 h. The control rGO (CrGO) was synthesized using phenylhydrazine. First, 0.4 g of the as-synthesized graphene oxide was dispersed in 100 ml of DI water using an ultrasonic bath cleaner at 90 °C. Then, 2 ml of phenylhydrazine was added to the suspension and stirred for 6 h. Finally, the suspension was filtered using a vacuum filter and washed with methyl alcohol. The filtered cake was dried in an oven at 60 °C. Fluorine-functionalized and reduced graphene oxide (FrGO) was also synthesized using the same procedures described above, except using 4-(Trifluoromethyl)phenylhydrazine as the reductant instead of phenylhydrazine at 60 °C.

*Sample characterizations:* X-ray photoelectron spectroscopy (XPS) measurements for the chemical composition of rGOs were performed using a MultiLab 2000 XPS instrument with a monochromatic Al K $\alpha$  source. The graphene sheet thickness and morphology of the rGO films were investigated using atomic force microscopy (AFM, Veeco, Digital Instruments Nanoscope IIIA). The electrical conductivity was analyzed using a four-point probe measurement (FPP-RS8, Dasol Eng.) and a surface profiler (Alphastep IQ, KLA Tencor). The work function and surface images of each sample were obtained using an ultraviolet photoelectron spectroscope (UPS) with a He 1 (h $\nu$  = 21.2 eV) excitation source (AXIS Ultra

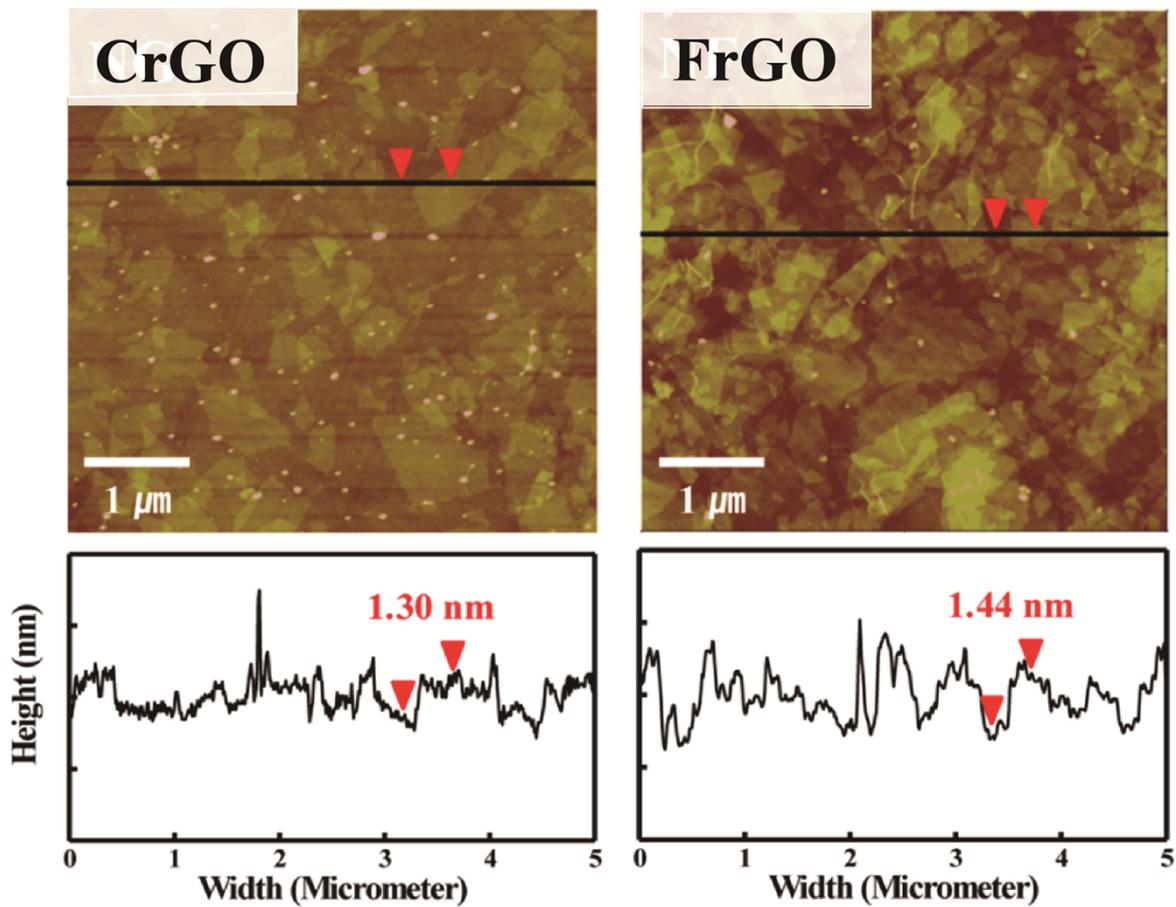
DLD, Kratos Inc.) under  $\sim 10^{-8}$  Torr and using AFM (Veeco, Digital Instruments Nanoscope IIIA), respectively.

*Device fabrication and characterization:* A patterned indium tin oxide (ITO,  $\sim 10 \Omega/\square$ ) substrate was cleaned and UV/O<sub>3</sub>-treated for 30 min. Then, CrGO (1 mg/ml) and FrGO (1 mg/ml) were spin-coated using a gradient spin-rpm from 700 to 3500 rpm for 45 s, followed by drying at 120 °C for 10 min. The conventional PEDOT:PSS (Clevios™ P VP AI 4083) film as a reference hole transporting layer was also fabricated using spin-coating at 5000 rpm for 40 s, and subsequently dried at 120 °C for 10 min. As photoactive layers, poly(3-hexylthiophene) (P3HT, Rieke Metals), poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]-thieno[3,4-b]thiophenediyl]] (PTB7, 1-material), [6,6]-phenyl-C61 butyric acid methyl ester (PC<sub>61</sub>BM, Nano-C), [6,6]-phenyl-C71 butyric acid methyl ester (PC<sub>71</sub>BM, Nano-C), and indene-C<sub>60</sub> bis-adduct (ICBA, 1-material) were used. First, a 1 ml P3HT (25 mg) and PC<sub>61</sub>BM (25mg) blended solution in 1,2-dichlorobenzene (DCB) was spin-coated at 700 rpm for 60 s, followed by solvent annealing for 2 h and thermal annealing at 110 °C for 10 min in an N<sub>2</sub>-filled glove box. For the preparation of PTB7:PC<sub>71</sub>BM active films, a blend solution mixed with PTB7 (10 mg), PC<sub>71</sub>BM (15 mg), and 1,8-diiodooctane (5 vol. %) in 1 ml of chlorobenzene was spin-coated at 2000 rpm for 40s. For the formation of the P3HT:ICBA active films, a blend solution mixed with P3HT (22 mg) and ICBA (22 mg) in 1 ml of DCB was spin-coated at 700 rpm for 60 s, followed by thermal annealing at 150 °C for 10min. Finally, thermal evaporation was used for the metal-cathode formation of Ca/Al (20/100 nm) with an active area of 4.64 mm<sup>2</sup> under a pressure of 10<sup>-6</sup> Torr. The photocurrent density-voltage (J-V) curves were measured using a Keithley 2400 instrument under the standard 100 mW/cm<sup>2</sup> illumination and AM 1.5 G condition and using the standard Si-based solar cell certified by the International System of

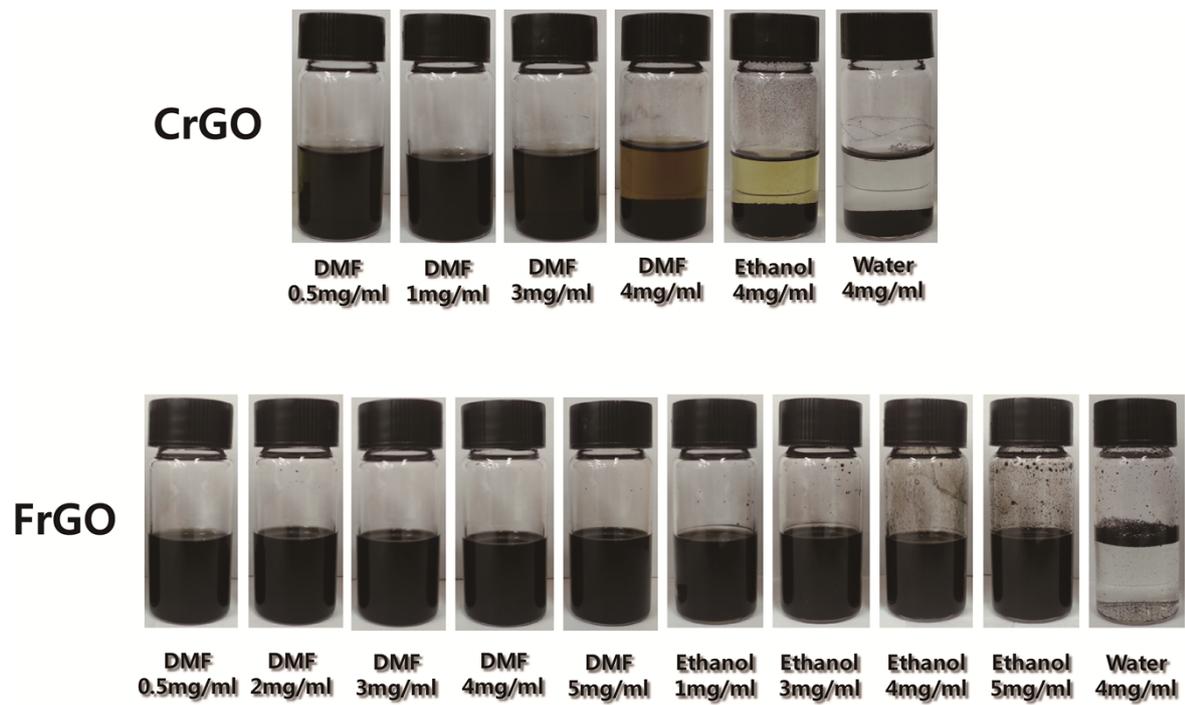
Units (SRC-1000-TC-KG5-N, VLSI standards, Inc). The OPV operation times were recorded as a function of air-exposure time based on the ISOS-D-1 protocol.



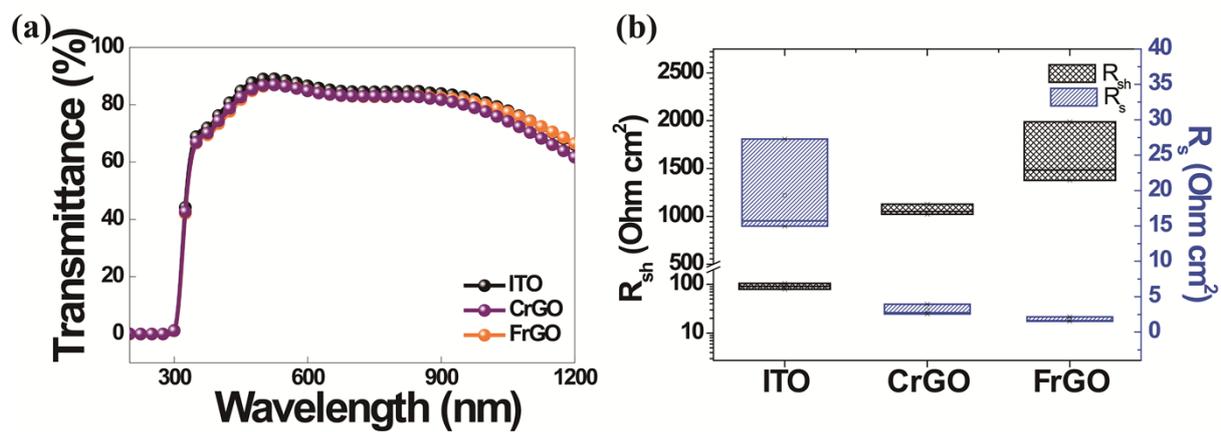
**Figure S1.** (a) XPS spectra and (b) AFM images of GO.



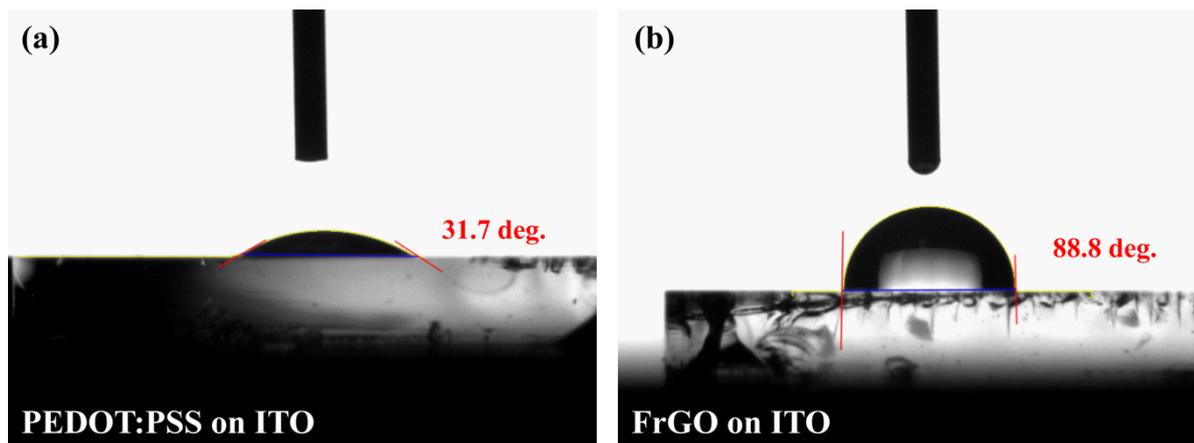
**Figure S2.** AFM images of CrGO and FrGO.



**Figure S3.** Degree of dispersion of the CrGO and FrGO in the various solutions.



**Figure S4.** (a) Optical transmittance spectra of ITO, CrGO, and FrGO. (b)  $R_s$  and  $R_{sh}$  of different anode interfacial layers.



**Figure S5.** Contact angle images of (a) PEDOT:PSS and (b) FrGO on ITO substrate.

**Table S1.** Representative cell performances of solar cells incorporating different hole transporting layers.

	PCE (%)	$V_{oc}$ (V)	FF (%)	$J_{sc}$ (mA/cm <sup>2</sup> )
ITO	0.82	0.41	24.49	8.08
CrGO	2.85	0.53	63.28	8.50
FrGO	3.64	0.60	69.55	8.78

**Table S2.** Photovoltaic characteristics with average values for P3HT-based cells incorporating different HTLs.

	PCE (%)	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	R <sub>sh</sub> (Ωcm <sup>2</sup> )	R <sub>s</sub> (Ω cm <sup>2</sup> )
ITO	0.949 (± 0.133)	0.384 (± 0.032)	30.17 (± 5.906)	8.084 (± 0.287)	19.32 (± 6.902)	91.83 (± 12.49)
CrGO	2.81 (± 0.11)	0.53 (± 0.02)	62.54 (± 2.58)	8.46 (± 0.24)	1067.62 (± 54.24)	3.08 (± 0.74)
FrGO	3.62 (± 0.15)	0.60 (± 0.00)	68.74 (± 1.06)	8.83 (± 0.20)	1616.69 (± 326.10)	1.77 (± 0.34)

**Table S3.** Photovoltaic characteristics for PTB7:PC<sub>71</sub>BM and P3HT:ICBA-based OPVs with FrGO or PEDOT:PSS.

	PCE (%)	V <sub>oc</sub> (V)	FF (%)	J <sub>sc</sub> (mA/cm <sup>2</sup> )
PTB7_FrGO	6.71	0.70	65.10	14.84
PTB7_PEDOT	6.85	0.71	63.76	15.05
ICBA_FrGO	4.57	0.83	63.65	8.65
ICBA_PEDOT	4.67	0.85	60.25	9.08