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Supporting Information

Sulfonic Acid-Functionalized, Reduced Graphene Oxide as an Advanced Interfacial Material Leading to Donor Polymer-Independent High-Performance Polymer Solar Cells

Jun-Seok Yeo,[a] Jin-Mun Yun,[a] Yen-Sook Jung,[a] Dong-Yu Kim,[a]* Yong-Jin Noh,[b] Seok-Soon Kim,[c] and Seok-In Na[b]*

[a]Heeger Center for Advanced Materials (HCAM), School of Material Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea
E-mail: kimdy@gist.ac.kr

[b]Professional Graduate School of Flexible and Printable Electronics and Polymer Materials Fusion Research Center, Chonbuk National University, Jeonju-si, Jeollabuk-do, 561-756, Republic of Korea
E-mail: nsi12@jbnu.ac.kr

[c]School of Materials Science and Chemical Engineering, Kunsan National University, Kunsan, Chonbuk 753-701, Republic of Korea

Experimental

Preparation of graphene oxide (GO): Graphene oxide (GO) was prepared using the modified Hummers method. Briefly, graphite (1 g) was mixed with concentrated sulfuric acid (97%, H_2SO_4) under constant stirring. To this mixture, $KMnO_4$ (3 g) was slowly added as an oxidizing agent for 1 h and heated at 40 ^oC for 6 h with constant stirring. After the oxidation was completed, the slurry was poured over ice (500 g) containing H_2O_2 (30 wt%, 10 ml).

The resultant suspension of GO was separated by centrifugation at 10000 rpm for 20 min followed by washing with DI water and acetone at least three times to remove the remaining H_2SO_4 and metal residues. Finally, GO was dispersed in deionized water at a concentration of 2 mg/ml, and used for the preparation of pr-GO and sr-GO.

Preparation of sr-GO: To reduce GO using *p-hydrazinobenzene sulfonic acid hemihydrate* (HBS), HBS (5 g) was slowly added into the aqueous GO solution (2 mg/ml, 50 ml), and then the mixture was stirred at room temperature for 24 h. After the reduction was completed, a small amount of sodium chloride (NaCl) was added into the reaction mixture in order to precipitate the produced sr-GO. The floating sr-GO was centrifuged at 10000 rpm for 10 min and sequentially washed using methanol at least three times to completely remove the remaining reducing agent. Finally, the produced sr-GO was re-dispersed in deionized water at a concentration of ~0.5 mg/ml and used for the material characterization and device fabrication.

Sample characterizations: The surface morphology and thickness of the graphene-based samples was measured using an AFM (Dimension 3100, Veeco) under tapping mode with a silicon cantilever. XPS and UPS (AXIS-NOVA, Kratos) measurements were performed with a monochromatized Al Kα for XPS and the He I (hv = 21.2 eV) excitation source with an energy resolution of 0.1 eV for UPS under a pressure of 5×10^{-8} Torr. The Fermi edge reference was determined for UPS analysis on a cleaned Au surface. The Raman spectra of graphene-based samples were obtained with a Jobin Yvon Horiba LabRam HR800 Raman system using a 514.5 nm laser as the excitation source. Thermal stability of pr-GO, and sr-GO were analyzed using a TA instrument Q50 series with a scan rate of 10 ^{o}C per min in N_2. UV-vis/NIR spectra were measured using a Jasco V-570 UV-vis/NIR spectrophotometer. The electrical sheet resistances were obtained by 4-point-probe measurement (FPP-RS8, Dasol Eng.).

Device fabrication and characterization: The patterned ITO/glass substrates were first cleaned in an ultrasonic bath with acetone, deionized water, and isopropyl alcohol for 10 min each, and subsequently dried in an oven at 100 °C for 30 min. UV/O_3 treatments were applied for 15 min before deposition of the interfacial layer. The graphene-based anode interfacial materials, and PEDOT:PSS (Clevios^{TM} P VP AI 4083, Heraeus) were spin-coated (5000 rpm, 40 s) onto the prepared ITO/glass substrates, and then all the films were baked at 120 °C for 10 min in air. For the photo-active materials, P3HT (4002-EE, Rieke Metals), TQ1 (Solarmer), PTB7 (1-material), PBDTTT-CF (1-material), $PC_{61}BM$ (Nano-C), and $PC_{71}BM$ (Nano-C) were used as received without further purification. At first, a blended solution comprised of P3HT (25 mg) and $PC_{61}BM$ (25 mg) in 1 ml of 1,2-dichlorobenzene (DCB) was spin-cast onto the prepared substrate at 700 rpm for 60 s. Then, a slow evaporation was performed by keeping the active film in a capped-glass jar for 2 h in an N_2-filled glove box, followed by thermal annealing at 150 °C for 10 min. Also, for TQ1-based devices, a solution containing 10 mg of TQ1 and 20 mg of $PC_{71}BM$ in 1 ml of DCB was spin-cast (1500 rpm for 40 s) onto the prepared substrate. For another active film, a chlorobenzene solution (1 ml) consisting of a mixture of PTB7:$PC_{71}BM$ (10 mg:15 mg) or PBDTTT-CF:$PC_{71}BM$ (10 mg:15 mg) and 1,8-diiodooctance (5 vol. %) was spin-cast either at 2500 rpm for 40 s or at 1000 rpm for 40 s on top of a prepared substrate. Finally, a thermal evaporator in vacuum with a pressure of 10^{-6} Torr was used for top electrodes composed of

Ca (20 nm)/Al (100 nm) with an area of 4.64 mm^2. The photocurrent density-voltage curves were obtained using a Keithley 1200 instrument with 100 mW/cm^2 illumination under AM 1.5 G condition. For measurement accuracy, the standard Si solar cell certified by the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc) was used for light intensity calibration. The EQE and IQE spectra were simultaneously obtained using a Quantum Efficiency Measurement System (IQE-200, Oriel). Cell-operation times of non-encapsulated PSCs were recorded as a function of exposure time in an ambient environment using the same instrumental conditions.

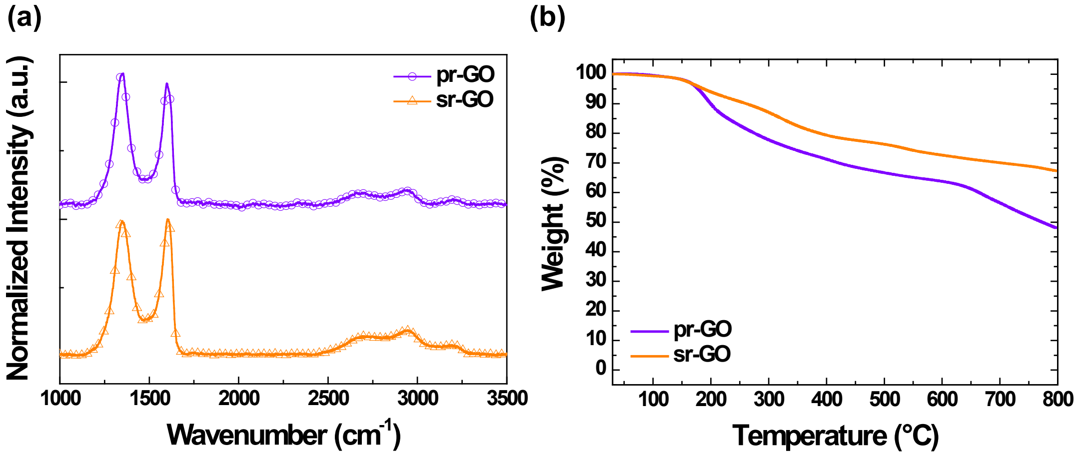

Fig. S1 (a) Raman spectra, and (b) the thermal properties of pr-GO, and sr-GO measured by TGA under an N_2 atmosphere.

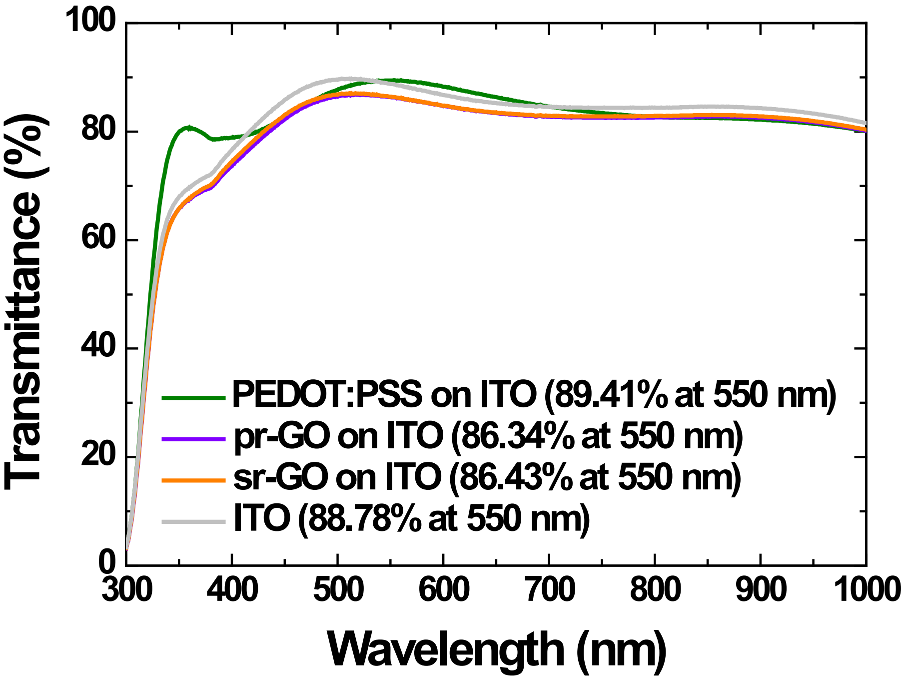

Fig. S2 Optical transmittance spectra with and without various AILs on ITO/glass substrates.

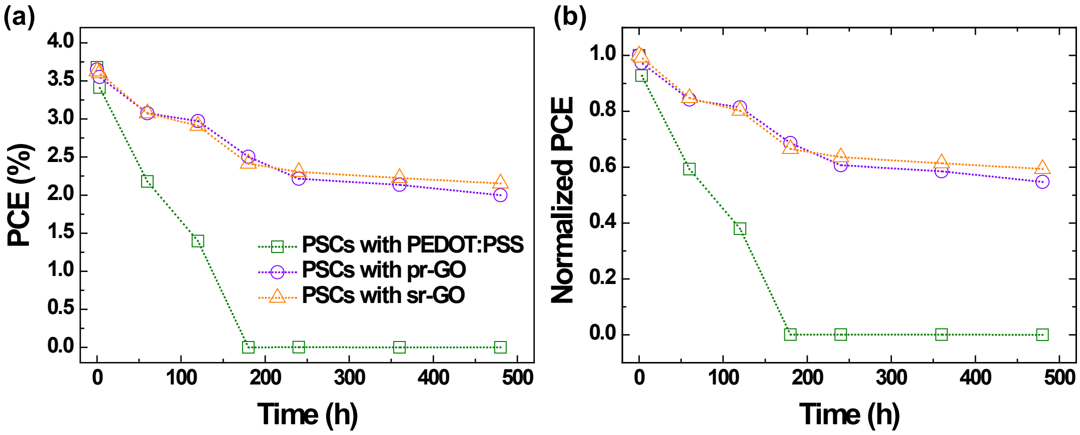

Fig. S3 (a) Changes in PCEs of P3HT-based PSCs with different types of AILS under an ambient atmosphere, and (b) corresponding normalized PCEs.

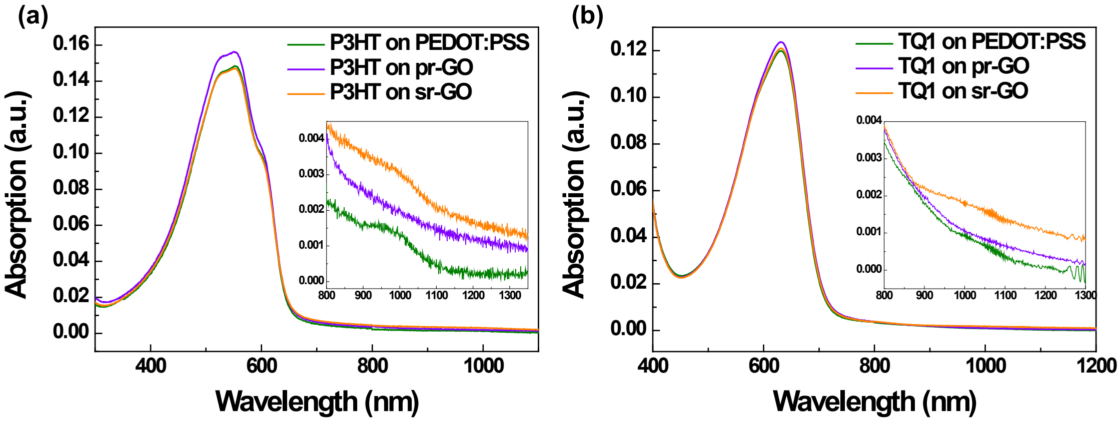

Fig. S4 UV/vis absorption spectra of (a) P3HT, and (b) TQ1 thin films onto PEDOT:PSS, pr-GO, and sr-GO films. The insets show the magnified spectra at the near-IR region.