Supporting Information for

Sulfated Graphene Oxide as Hole-Extraction Layer in High-Performance Polymer Solar Cells

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**Instrument and characterization:** XPS was measured on a VG Microtech ESCA 2000 using a monochromic Al X-ray source (97.9 W, 93.9 eV). Elemental analysis was carried out on a Perkin-Elmer 2400 elemental analyzer. The Raman spectra were recorded using the Renishaw Raman spectrometer equipped with 514-nm laser. Fourier transform infrared spectra (FTIR) were recorded on a Perkin-Elmer spectrum GX FTIR system. XRD was performed with a Rigaku MiniFlex II XRD system. UV/Vis absorption was measured with a Shimadzu UV1800 spectrometer. The thermogravimetric analysis (TGA) was carried out on a TA instrument with a heating rate of 10 °C/min in N₂. Atomic force microscopy (AFM) was performed on an Agilent 5500 atomic force microscope. The sample was prepared by spincoating from the corresponding solution on Si substrates. Kelvin probe force microscopy (KFM) was carried out on the same AFM instrument with GO or GO-OSO₃H spincoated on HOPG substrates. Conductivity was measured with the four-probe method using vacuum-filtered films with the thickness of 20-50 µm. Film thickness of PEDOT:PSS and P3HT:PCBM was measured with a KLA-Tencor P-6 Stylus profilometer while the film thickness of GO and GO-OSO₃H was estimated with AFM microscopy. Contact angles were recorded with a FDS OCA15 optical contact angle measuring unit.

**Device Fabrication and Characterization.** ITO glass substrates were cleaned for 10 minutes each sequentially with detergent, de-ionized water, acetone, and iso-propanol, followed by drying with N₂ flow and UV-ozone treatment for 15 minutes. The HEL was then spincoated on the clean ITO glass with the following conditions. PEDOT:PSS layer was spincoated from the solution (Baytron P VP Al4083 from H. C. Stark, filtered through 0.45 µm syringe filter) at 5000 rpm for 40 s, followed by heating at 140 °C for 10 minutes. The GO layer was spincoated from its aqueous solution (1.0 mg/mL) at 2000 rpm for 60 s, followed by heating at 110 °C for 10 minutes. The GO-OSO₃H layer was spincoated from its DMF solution (0.5 mg/mL) at 2000 rpm for 60 s, followed by heating at 110 °C for 10 minutes. The spincoating processes of GO or GO-OSO₃H were repeated until a predetermined film thickness was obtained. After the deposition of HEL, the active layer was spincoated from the solution of P3HT:PCBM = 1:1 in o-dichlorobenzene (15 mg/mL, filtered with a 0.2-µm PVDF syringe filter) at 600 rpm for 60 s, followed by thermal annealing at 120 °C for 10 minutes in a N₂ glovebox. Then, the device was transferred to a vacuum chamber for thermal deposition of Ca (20 nm) and Al (100 nm) at a
The pressure of $10^{-7}$ Torr. The area of each device was 0.12 cm$^2$. The resultant devices were tested in a N$_2$ glovebox using a Keithley 2400 source meter and a Newport Oriel sol 2A solar simulator (AM1.5G, 300 W) calibrated with a standard Si solar cell (standardized by the National Renewable Energy Laboratory) and a KG5 color filter. The EQE spectra of the devices were recorded with a Solar Cell Measurement System from PV measurement Inc.

![Image](image1.png)

**Figure S1.** SEM (a) and TEM (b) images of GO-OSO$_3$H on Si substrate.

![Image](image2.png)

**Figure S2.** The pH titration curve of GO (a) and GO-OSO$_3$H (b) versus the amount of NaOH added.
Figure S3. UV/Vis absorption spectra (a) and photo images (b) of 0.2 mg/mL aqueous solution of GO and GO-OSO$_3$H.

Figure S4. FT-IR spectra of GO and GO-OSO$_3$H.
Figure S5. TGA of GO and GO-OSO$_3$H.

Figure S6. UV/Vis absorption spectra of individual GO-OSO$_3$H (2 nm, black curve), individual P3HT (10 nm, red curve), bilayer of GO-OSO$_3$H (2 nm)/P3HT (10 nm) (blue curve). The sum of individual GO-OSO$_3$H (2 nm) and individual P3HT (10 nm) absorbance (dashed curve) are also shown.

Figure S7. Contact angles of water droplet on bare ITO, PEDOT:PSS, GO, and GO-OSO$_3$H.
Figure S8. AFM image and height profile of a film spincoated from a DMF solution of GO-OSO$_3$H 0.5 mg/mL on a silicon substrate. The image size is 1 µm × 1 µm.