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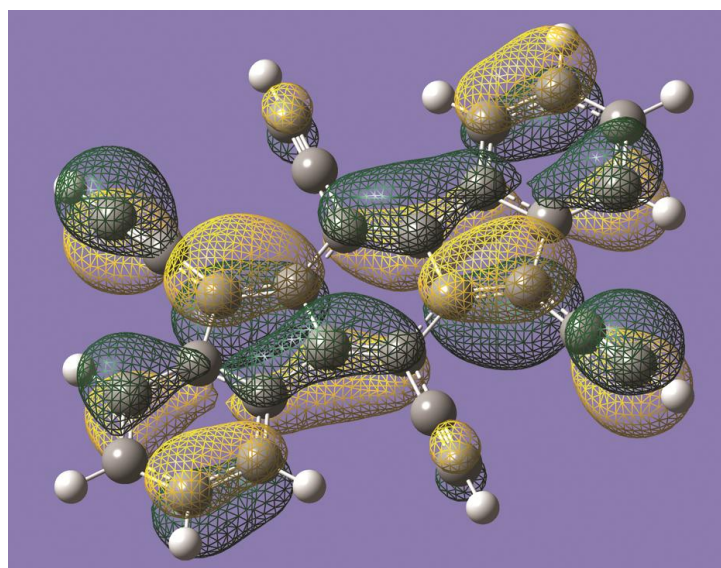
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Chemically modified graphene oxides as a hole transport layer in organic solar cells†

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We demonstrate O₂ plasma treated graphene oxides with a work function of 5.2 eV as a high performance hole transport layer in organic solar cells. The high transparency and high work function simultaneously increase short circuit current, threshold voltage and fill factor, resulting in a 30% increase in cell efficiency.

Organic solar cells (OSCs) have emerged as a promising low-cost renewable energy source due to their potential for large-area solar energy conversion.¹ The technology now offers in excess of 8% power conversion efficiency at the single cell level.^{1d,2} In bulk hetero-junction OSC devices, the interface formed between the photoactive layer and the electrodes is essential for its high efficiency and stability.³ Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been most commonly used as a solution-process hole transport layer (HTL) to improve anode contact and to increase hole collection in organic electronic devices. Several problems of the PEDOT:PSS HTL include high acidity, hygroscopic properties, and inhomogeneous electrical properties, resulting in poor long-term stability.⁴

Recently, graphene oxide (GO) was shown preliminarily to be a mechanically-flexible hole-transporting material in OSCs.⁵ GO is a graphene sheet functionalized with oxygen groups in the form of epoxy and hydroxyl groups on the basal plane and various other types at the edges. It contains a mixture of sp²- and sp³-hybridized carbon atoms. In particular, manipulation of the size, shape and relative fraction of the sp²-hybridized domains of GO provides opportunities for tailoring its optoelectronic properties.⁶ In this work, GO films on ITO substrates were treated with oxygen plasma, the changes of surface properties and their effects on the performance of poly(3-hexylthiophene):phenyl-C61-butyric

acid methyl ester (P3HT:PCBM) solar cells were carefully investigated. X-ray photoelectron spectroscopy (XPS), scanning Kelvin probe microscopy (SKPM), hole-only devices and dark current analysis were used to correlate the performance of OSCs with chemically modified GO as HTLs.

ITO on glass (10 Ω⁻¹) was purchased from AimCore Technology Co., Ltd. The substrates were cleaned in a sonication bath in acetone, isopropyl alcohol and deionized water sequentially, and then dried by blowing nitrogen. PEDOT:PSS (Clevios 4083) was purchased from H. C. Starck and used as received. It was spin coated onto the cleaned, O₂ plasma-treated ITO substrates at 2000 rpm for 90 s (thickness ~45 nm), and then annealed on a hot plate at 150 °C for 15 minutes in air. GO was purchased from Nanjing Jcnano Technology Co., and was suspended in water with ultrasonication at a power of 160 W. GO aqueous dispersion with a concentration of ~2 mg mL⁻¹ was prepared, and then was spin coated at 3000 rpm onto ITO. The GO films were baked on a hot plate at 120 °C for 15 min. For O₂ plasma treatment, GO/ITO was treated at 30 W from 10 s to 60 s. Fourier transform infrared (FT-IR) spectra were recorded with a Nexus model Thermo Scientific Nicolet™ iSTM spectrometer (see Fig. S1, ESI†). X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG ESCALAB MK2 system with a monochromatized Al Kα source under a pressure of 5 × 10⁻⁷ Pa. Atomic force microscopy (AFM) height images (Fig. S1, ESI†) and SKPM images were obtained using a Bruker Metrology Nanoscope III-D atomic force microscope.

Regio-regular P3HT (weight-averaged molecular weight, *M_w* < 50 000 g mol⁻¹, Rieke Metals Inc.) and PCBM (purity >99%, Solenne B.V.) were used as received. P3HT and PCBM blend solution was prepared in a 1 : 1 ratio with a total concentration of 30 mg mL⁻¹ in *ortho*-dichlorobenzene. The thickness of the active layer was 143 nm determined by a Bruker 150 surface profiler. The samples were baked at 160 °C for 30 min in a glove box before being transferred to the evaporation chamber. 10 nm Ca and 100 nm Al were deposited sequentially at 5 × 10⁻⁴ Pa with a metal mask. The area of metal electrodes was 3.14 mm² and 19.6 mm² respectively. All devices were characterized with a computer-controlled Keithley 2400 source measure unit, and the illumination intensity was 100 mW cm⁻² (AM 1.5G Oriel solar simulator). External quantum efficiency was characterized on the QTest Station 2000ADI system (Crowntech Inc., USA).

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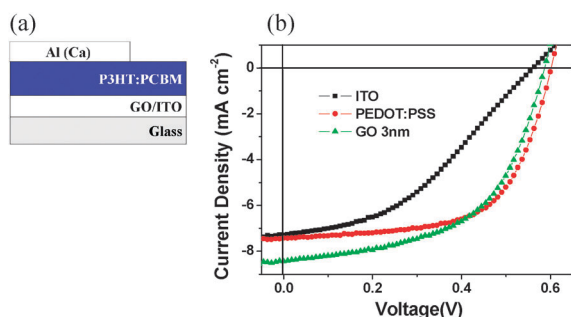


Fig. 1 (a) Device configuration of OSCs with GO as a HTL. (b) Representative J - V curves of OSCs without and with PEDOT:PSS or GO as HTLs.

Fig. 1a shows the device configuration. The typical J - V curves of devices with no HTLs or with either PEDOT:PSS or GO under 100 mW cm^{-2} air mass 1.5 global illumination are shown in Fig. 1b. For each type, over 20 devices were made from several films. It can be seen that the ITO-only device exhibits an average power conversion efficiency (η) of 1.63%. The insertion of a 3 nm thick GO thin film between ITO and P3HT:PCBM results in a substantial increase in short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF), leading to an enhancement in the power conversion efficiency to 2.71%. For comparison, typical device performance of ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al has an efficiency value of 2.77%. The overall efficiencies of OSC devices incorporating GO and PEDOT:PSS are within the measurement errors.

Consequently, GO layers were treated by O_2 plasma, and were used as HTLs in P3HT:PCBM OSCs. The J - V curves of devices with and without O_2 plasma treated GO layers are shown in Fig. 2. When the GO was treated with O_2 plasma at 30 W for 10 s, a simultaneous enhancement in J_{sc} (9.91 mA cm^{-2} vs. 8.42 mA cm^{-2}), V_{oc} (0.60 V vs. 0.58 V) and FF (60% vs. 55%) was observed, resulting in a significant improvement in the OSC efficiency (3.59% vs. 2.71%). Further increase of the treatment time to 30 s and 60 s decreases the efficiency quickly to around 2%, which is similar to the efficiency of devices with O_2 plasma treated ITO as anodes (Fig. S2, ESI[†]).

Obviously, the improvement in devices with O_2 plasma treated GO mainly comes from the increased J_{sc} and FF. An increase of J_{sc} from 8.42 mA cm^{-2} to 9.91 mA cm^{-2} was observed upon the incorporation of the GO with O_2 plasma treatment. To gain further insight into the relative performance of

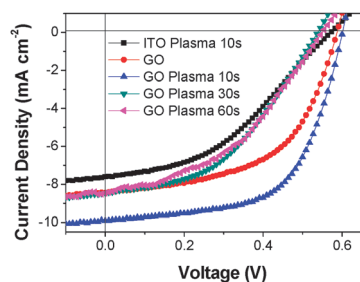


Fig. 2 Representative J - V curves of OSCs based on ITO with O_2 plasma treatment, GO film without O_2 plasma treatment or with different time of O_2 plasma treatment.

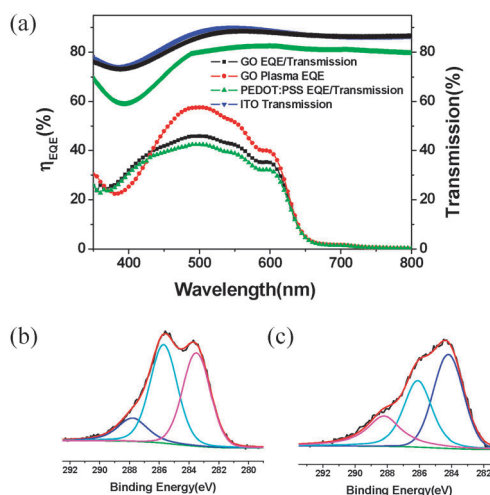


Fig. 3 Optical spectra comparing the transmission characteristics of PEDOT:PSS, and GO overlaid on external quantum efficiency measurements on OSCs using PEDOT:PSS, GO, or GO with O_2 plasma treatment as HTLs (a). XPS analysis of the GO films without (b) and with (c) O_2 plasma treatment. Deconvolution reveals the presence of C-C ($\sim 284.8 \text{ eV}$), C-O ($\sim 286.2 \text{ eV}$), C=O ($\sim 287.8 \text{ eV}$) species in the films.

the PEDOT:PSS and GO HTLs, optical transmission spectra and external quantum efficiency (EQE) data were recorded for the OSCs illuminated by monochromatic light (Fig. 3a). The transmission spectra show that across the entire visible spectrum, GO is significantly more transparent than the PEDOT:PSS HTL in OSCs. In terms of EQE of devices with different HTLs (also shown in Fig. 3a), the spectral response of OSCs with O_2 plasma treated GO tracks approximately the P3HT:PCBM absorption spectrum with a maximum EQE of more than 50% in the spectral range of 460 to 560 nm.

Besides the improvement in J_{sc} , the FF of the devices with treated GO is found to be higher than that of devices with pristine GO. The work function of GO thin films was determined by SKPM. The surface potential is uniform over both the active layers, and the average work function value obtained from the measurements on 6 different GO film samples was found to be 5.0 eV, which is consistent with the previous report.^{5a} The average work function value on 6 different GO thin film samples with O_2 plasma treatment at 30 W for 10 s was found to be 5.2 eV, which is apparently higher than the typical value of pristine GO. XPS is used to characterize the GO layer with and without O_2 plasma treatment. The XPS spectra of carbon atoms in GO layers are shown in Fig. 3b and c. In both spectra, the presence of C-C ($\sim 284.8 \text{ eV}$), C-O ($\sim 286.2 \text{ eV}$), C=O ($\sim 287.8 \text{ eV}$) species were observed in the films.⁷ After O_2 plasma treatment, the C=O species increased from 15% to 22%, the C-C species decreased from 49% to 44%, and the C-O species kept similar levels (36% vs. 34%). The higher work function of GO with O_2 plasma is due to the higher electronegativity of O atoms, which produce more surface C=O dipoles *via* extraction of electrons from graphene.⁸

Fig. 4a shows $J^{1/2}$ - V curves of the hole-only devices (ITO/HTL/P3HT:PCBM/ MoO_3 /Au) with different HTLs.

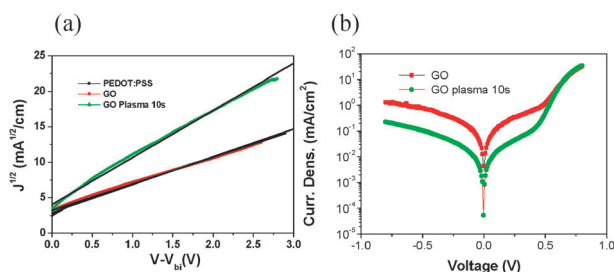


Fig. 4 (a) $J^{1/2}$ - V characteristics of hole-only devices with PEDOT:PSS, GO and GO with O_2 plasma treatment as HTLs. (b) J - V characteristics of OSC devices with GO and GO with O_2 plasma treatment as HTLs in the dark.

In the trap-free region over the trap-filled limit, which is the limit of the presence of carrier traps, space charge limited current (SCLC) can be characterized by the Mott-Gurney square law,⁹

$$J = (9/8)\epsilon_r\epsilon_0\mu_h(V^2/L^3)$$

where ϵ_0 is the vacuum permittivity, ϵ_r is the dielectric permittivity of the active layer, L is the thickness of the active layer, and μ_h is the hole mobility. At a typical electric field of 10^5 V cm⁻¹ (corresponding to an applied voltage of 1 V across a 100 nm-thick device), the apparent hole mobilities calculated from the currents in the square law region of 1.42×10^{-5} , 1.28×10^{-5} and 4.06×10^{-5} cm² V⁻¹ s⁻¹ have been determined for the devices with PEDOT:PSS, GO and GO with O_2 plasma treatment as HTLs, respectively. The hole mobility increases in the device with O_2 plasma treated GO. In OSCs, hole carriers separate from the exciton and move into the ITO through the HTL. A higher work function of O_2 plasma treated GO results in the increase of the apparent hole mobility and the enhancement of hole extraction. The increase of the apparent hole mobility induced improved FF. The enhanced hole extraction significantly increases the peak EQE around 500 nm in P3HT:PCBM films (Fig. 3a), and then increases the short circuit current. Furthermore, in the leakage dominated regime (<0.5 V), the dark current density of the OSCs with O_2 plasma treated GO is nearly 1 order lower than that of the OSCs with pristine GO films (as shown in Fig. 4b), which indicates that GO HTL treated with O_2 plasma is efficient in blocking electrons and collecting holes. Therefore, the GO treated with O_2 plasma can be expected to be an efficient hole-selective interfacial material.

In conclusion, the efficiency of OSC with GO or PEDOT:PSS as HTLs is comparable, and the efficiency of devices with O_2 plasma treated GO can be further improved by more than 30%. The higher transparency and higher work function of GO with O_2 plasma treatment simultaneously increase the short circuit current and fill factor of OSCs, as proved by XPS, SKPM, UV-vis spectra, hole-only devices and dark-current analysis.

The results show that the development of electronically tuned graphene oxides is an efficient method for developing high efficiency OSCs.

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