High efficient organic photovoltaic devices utilizing work-function tuned graphene oxide derivatives as the anode and cathode charge extraction layer

Dimitrios Konios,§a George Kakavelakis,§a Costantinos Petridis,a Kyriaki Savva,a,b Emmanuel Stratakis,a,b and Emmanuel Kymakis* a

1 Center of Materials Technology and Photonics & Electrical Engineering Department, School of Applied Technology, Technological Educational Institute (TEI) of Crete, Heraklion, 71004 Crete, Greece. Email: kymakis@staff.teicrete.gr; Tel: +30-2810-379895
a Institute of Electronic Structure and Laser (IESL), Foundation for Research and Technology-Hellas (FORTH), Greece
§ Authors with equal contribution

Abstract
The effective utilization of work-function (WF) tuned solution processable graphene-based derivatives as both hole and electron transport layers in organic photovoltaic (OPV) devices is demonstrated. The systematic tuning of functionalized graphene oxide (GO) WF took place by either photochlorination for WF increase, or lithium neutralization for WF decrease. In this way, the WF of the photochlorinated GO layer was perfectly matched with the HOMO level of two different polymer donors, enabling excellent hole transport. While the WF of the lithium functionalized GO was perfectly matched with the LUMO level of the fullerene acceptor, enabling excellent electron transport. The utilization of these graphene-based hole and electron transport layers in PTB7:PC71BM active layer devices, led to ~19% enhancement in power conversion efficiency (PCE) compared to the reference graphene-free device, resulting in the highest reported PCE for graphene-based buffer layer OPVs of 9.14%. The proposed techniques open new paths towards novel material and interface engineering approaches for a wide range of new applications, including flexible electronics, OPVs, perovskite solar cells, organic light emitting diodes, and photosensors, as well as traditional electronic devices.

During the past decade, OPV devices based on the bulk heterojunction (BHJ) blend have attracted great interest due to their potential for low fabrication cost but, more importantly their versatility for large-scale fabrication on flexible substrates. 1,2,3,4 Despite the numerous studies on OPVs, their power conversion efficiency (PCE) compared to the silicon and other inorganic materials based photovoltaic technologies remains relatively low (~10%). 5 Aiming to improve the competitiveness of OPVs, extensive research effort has been devoted to the interface engineering of devices and especially to the introduction of charge extracting interlayers between the BHJ layer and the electrodes. 6,7

In contrast to inorganic PVs where surface doping is responsible for Ohmic contacts, OPVs require alternative strategies in terms of the interface engineering. The introduction of buffer layers with electron and hole blocking (or transport)
properties between the donor:acceptor active layer and the anode and cathode respectively, can effectively reduce recombination and current leakage generated at the photoactive layer-electrode interface and enhance the open circuit voltage ($V_{OC}$) of the device. A number of hole transporting layer (HTL) materials for OPVs have been used, including transition metal oxides (e.g. MoO$_x$, NiO) and self-assembled organic molecules, with the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) being the current state-of-art material. On the other hand, the most regularly used electron transport layer (ETL) materials include certain metal fluorides, n-type inorganic (e.g. TiO$_x$, ZnO) and organic (e.g. bathocuproine) semiconductors. However, there are several drawbacks concerning the current state-of-the-art buffer layers, leading to decreased OPV stability, arising, for example, from the acidic and hygroscopic character of PEDOT:PSS or the sensitiveness of sol-gel prepared TiO$_x$ to moisture, and also the increased manufacturing cost, since some metal oxides and metal fluorides require high vacuum thermal deposition and therefore are incompatible with roll-to-roll (r2r) processes and thus with flexible photovoltaics. In addition, the majority of the aforementioned materials do not allow their work function (WF) tuning, preventing the direct energy match with the numerous active layer donors and acceptors and urging the need for universal, tuned WF buffer layer materials.

Recently, graphene oxide (GO), a graphene sheet functionalized with oxygen groups (e.g. epoxy, hydroxyl, carboxyl), and its derivatives have been investigated as alternatives HTLs and ETLs. The availability of the reactive groups on GO sheets enables its further functionalization with molecules, manipulating in this way its optoelectronic properties. In addition, the solution processable character of GO and its derivatives is in accordance with the r2r mass fabrication processes, that are often cited as the advantage of OPVs compared to conventional photovoltaic technologies. More importantly, its tunable WF character makes GO an ideal precursor for creating new materials with WF values perfectly matching the HOMO level of the donor material (a conjugated polymer) and the LUMO level of the acceptor material (usually fullerene derivative). So far, only one study have investigated the photovoltaic performance of devices incorporating simultaneously GO derivatives as HT and ET layers, demonstrating 16% increase in the power conversion efficiency (PCE). Nevertheless, the lack of WF tunability of the produced GO derivatives limits its application on only the well-studied poly(3-hexylthiophene-2,5-diyl) (P3HT): [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM) based cell, since hole or electron transport is not energetically possible with the current cutting edge active layers, such as 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): [6,6]-phenyl-C71-butyric acid methyl ester (PC$_{71}$BM). Therefore low-cost, high-throughput, facile and r2r compatible
methods for WF tuning of the GO buffer layers, which will allow their application in high efficient BHJ OPVs are highly desirable.

In this work, a novel, all graphene-based buffer layer OPV device is realized, investigating the effect of the simultaneously utilization of two different solution processable functionalized GOs as cathode and anode buffer layers, on the PCE of the device. The two r2r compatible graphene-based materials, previously prepared by our group, the first one through laser-induced doping of GO with chloride (GO-Cl) leading to a WF increase from 4.9 to 5.16 eV and 5.23 eV and the second one after a simple and fast functionalization of GO with Li alkali metal (GO-Li) leading to a WF decrease from 4.9 to 4.3 eV, exploited unique electron and hole blocking (or transport) properties respectively. The increased WF of GO-Cl and on the other hand the reduced surface potential of GO-Li provide a direct match with the HOMO level of the donor PTB7 and the LUMO level of the acceptor PC_{71}BM respectively, leading to enhanced photovoltaic performance, outperforming by ~19% the reference graphene free device. To our knowledge, the achieved PCE is the highest reported for all graphene based buffer layers OPV devices, opening new paths to develop a new generation of low cost, high efficient, solution processable all-carbon solar cells.

II. Results and Discussion

Work function tuning

The as synthesized through the modified Hummers method GO was used as the pristine material to perform the functionalization and the subsequent WF tuning. In particular, the as-spun GO layers on ITO/glass substrates were subjected to irradiation by a KrF excimer laser source emitting 20 ns pulses of 248 nm at 1 Hz repetition rate in the presence of chlorine (Cl) precursor gas. To implement and investigate the GO WF tuning, different number of pulses (N_p) was used, increasing from 1 to 65. Figure 1a presents the GO WF change with respect to the applied N_p. It is clear that the WF increases as the exposure is more intense, and tends to saturate at 5.23 eV for N_p=60, because after this point the level of reduction tends to be very important in the tradeoff between the reduction and doping. In particular, the polar character of C-Cl bonds induced by the formation of surface C^{5+}-Cl^{6-} dipoles owing to the different electronegativity between carbon and chloride (2.55 for C compared to 3.16 for Cl) is responsible for the Fermi level downward shift towards the valence band of GO-Cl, and the subsequent increase in the WF.\textsuperscript{30,31} Thus, this simultaneous chloride doping\textsuperscript{20} and the partial
reduction process\textsuperscript{32} gives the possibility of wide a WF tuning allowing the use of GO-Cl as a universal HTL in different optoelectronic devices. \textbf{Figure 1b} demonstrates such dipoles formation in the C-Cl covalent bonds at the edges and/or Cl-C=O groups located outside the graphene basal plane.\textsuperscript{30}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{a) Work function tuning of GO-Cl films as a function of the N\textsubscript{p} exposure. b) 3D chemical structure if the photochlorinated GO, illustrating the formation of C\textsuperscript{δ+}-Cl\textsuperscript{δ-} dipoles.}
\end{figure}

In contrast to laser induced chloride doping of GO, the replacement of -H in the carboxyl groups of GO with Li atoms can effectively reduce the WF of GO. The GO doping was performed using lithium carbonate (Li\textsubscript{2}CO\textsubscript{3}) as a precursor. Lithium has low electronegativity value and low WF (2.9 eV). When bonded in GO, Li atoms lose their valence electrons to the GO plane, with the resulted positive Li\textsuperscript{+} inducing dipoles.\textsuperscript{33} The generated charge transfer from the metal to the GO plane lead to an upward shift of the Fermi level toward the vacuum, yielding a difference in the Fermi level between the two materials of 0.68 eV, which is responsible for the WF decrease to $\sim$4.3 ± 0.1 eV as depicted in the ultraviolet photoelectron spectra (UPS) (\textbf{Figure 2a}) establishing GO-Li as an ideal candidate ETL material for OPVs, since its WF perfect matches the LUMO level of the state of the art electron acceptor materials (PC\textsubscript{71}BM). \textbf{Figure 2b} summarizes our findings on GO functionalization to produce GO-based materials with tunable WF (increased or decreased) values with respect to the pristine materials to be used in a variety of optoelectronic applications.
Figure 2. a) UPS valence (right) band region (the inset represents the expanded view of the shallow valence features) and secondary cutoff (left) region for GO and GO-Li (expanded view of the secondary cutoff region features). b) Energy diagram showing the Fermi level of GO (middle) and its shifting after the functionalization with Cl (left) and Li alkali metal (right). In the case of photochlorination different WF values can be achieved by controlling the number of pulses (in this case $N_p=20$ or 60).

Photovoltaic performance

To assess the viability of the proposed GO WF tuning methods in optoelectronic applications, different structures of PCDTBT:PC$_{71}$BM and PTB7:PC$_{71}$BM-based OPV devices were fabricated. More particular, the effects by the incorporation of GO-Cl (with different WF values) as HTL and the GO-Li as ETL on device performance were investigated and compared with the state of the art buffer layer materials (PEDOT:PSS and TiO$_x$ as HTL and ETL respectively). The device structure and the energy level diagrams of the different materials used in this study are shown in Figure 3.
Figure 3. a) Schematic illustration of the BHJ OPV device with GO-Cl as the HTL and GO-Li/TiO$_x$ as the ETL. b) Energy level diagram depicting the relevant energy levels under flat conditions of all materials used in OPV cells studied and not the actual interfaces.

The averaged photovoltaic characteristics obtained from 10 identical devices, consisting of 6 cells each (60 current density-voltage (J-V) curves in total) are summarized in Table 1, indicate that the incorporation of GO-Cl as HTL and GO-Li as ETL significantly increases the device efficiency by ~12% and ~8% compared to the reference device (PEDOT:PSS as HTL and TiO$_x$ as ETL). As depicted in Figure 3b, the proposed laser induced technique for WF tuning, allowed to produce universal graphene-based HT material with desirable electronic properties. In particular, OPV devices with two different polymer donors a) PCDTBT with HOMO of 5.5 eV and b) PTB7 with HOMO of 5.15 eV were fabricated to clarify the effect of the use of GO-Cl with different WF values on photovoltaic performance. Figure 4a demonstrates the typical illuminated (100 mW/cm$^2$) J-V curves of the PCDTBT:PC$_{71}$BM OPV devices incorporating PEDOT:PSS, GO and GO-Cl with different WF as HTLs. A significant enhancement in the photovoltaic performance upon the increase of GO-Cl WF values can be observed, leading
to a PCE of 6.56% for GO-Cl (5.23 eV) compared to the references devices with PEDOT:PSS (5.49%) and GO (5.59%) HTLs, which can be attributed to the improved hole transport as verified by the hole mobility measurements. The universal applicability of the proposed method is demonstrated by the fact that the less laser exposed GO-Cl sample exhibiting WF of 5.16 eV ($N_p = 20$) was used as HTL in PTB7:PC$_{71}$BM devices achieving a record PCE of 8.28 % for graphene-based HTL devices (Figure 4b). This difference in optimum WF value for GO-Cl applied in the two different photoactive blends can be explained by the induced offset between the two donors HOMO level and the WF of the GO-Cl. In particular, for PTB7-based devices using 20 pulses for GO chlorination induces a ~0.01eV energy barrier between the HOMO of the PTB7 and the WF of GO-Cl, while in the PCDTBT case, the corresponding minimum energy barrier is 0.27 eV (Figure 4c). Therefore, it can be concluded that the ability to fine tune the GO-Cl WF with respect to the polymer-donor energy levels offers a facile route to boost the OPV PCEs.
Figure 4. J-V characteristics of a) PCDTBT:PC$_{71}$BM and b) PTB7:PC$_{71}$BM-based photovoltaic devices with different HTLs. c) Graph demonstrating the WF tuning of GO-Cl films as a function of the N$_p$ exposure and the relevant energy offset between the photochlorination treated films and the polymer donor HOMO level.

Figure 5 shows the illuminated J-V curves of the PCDTBT:PC$_{71}$BM and PTB7:PC$_{71}$BM-based OPV devices with TiO$_x$ and GO-Li/TiO$_x$ as ETLs. The reference PCDTBT:PC$_{71}$BM-based device incorporating TiO$_x$ ETL yielded a PCE of 5.53%, with a short circuit current density ($J_{SC}$) of 11.28 mA/cm$^2$, an open circuit voltage ($V_{OC}$) of 882 mV, and a fill factor (FF) of 55.6%, compared to the GO-Li/TiO$_x$ bilayer ETL based device that yielded a significantly enhanced PCE of 6.25%, with $J_{SC}$ of 12.51 mA/cm$^2$, $V_{OC}$ of 884 mV, and FF 56.5%. In addition, PCDTBT-based devices were prepared by replacing the GO-Li interfacial layer with GO to better clarify the effect of WF tuning in device efficiency. In this case, a significant decrease of the $J_{SC}$ by
~15% and of the FF by ~9% was observed, which can be attributed to the energy offset of 0.6 eV between the LUMO level of the acceptor material (4.3 ± 0.1 eV) and the GO WF (4.95 ± 0.1 eV). For ideal electron transport, the LUMO level of the acceptor material should be absolute equal to the WF of the ETL. Therefore, as the GO-Li WF perfectly matches the LUMO of PC71BM and TiOx ETL, the electrons transport to the cathode is conducted without energy barrier. The Jsc enhancement can be attributed to the improved electron transportation due to the 2D nature of the GO-Li interfacial ETL. Atomic force microscopy measurements have also verified that GO-Li has a planarizing role, creating a perfect interface between the TiOx ETL and the cathode, leading to an improved Ohmic contact and therefore minimizing the contact resistance at the interface. In this context OPV devices were fabricated using PTB7 as polymer donor. After the introduction of GO-Li between the active layer and the TiOx the device PCE was increased from 7.4% to 7.98%, mainly due to a significant increase in the Jsc which is maybe caused by the improve electron extraction as in the case of PCDTBT based devices.

Figure 5. J-V characteristics of a) PCDTBT:PC71BM and b) PTB7:PC71BM-based photovoltaic devices with different ETLs.

To further support the excellent hole and electron extraction capabilities of GO-Cl and GO-Li respectively, OPV devices incorporating graphene-based materials as both HT and ET layers were fabricated. For this purpose, both the performance of the reference device with the configuration of glass/ITO/PEDOT:PSS/PCDTBT:PC71BM or PTB7:PC71BM/TiOx/Al and the one structured as glass/ITO/GO-Cl/PCDTBT:PC71BM or PTB7:PC71BM/GO-Li/TiOx/Al were investigated. Figure 6 depicts the J-V curves for the tested devices. Clearly, in both BHJ active layer there is a significant Jsc improvement (28% for PCDTBT and 18% for PTB7-based devices) upon the addition of graphene-based interlayers. One the one hand, this is because of the WF
match between GO-Li and the LUMO level of PC$_{71}$BM, with the GO-Li modified electrode forming an Ohmic contact with the PCDTBT:PC$_{71}$BM and PTB7:PC$_{71}$BM active layer for improved electron extraction. On the other hand, the WF tuning of GO-Cl produces HTL materials that match the HOMO level of PCDTBT and PTB7 ensuring an Ohmic contact at the interface for efficient hole extraction. On the other hand, the open circuit voltage value was not affected with different buffer layers and this independency is due to the fermi level pinning$^{34}$ of the buffer layer and the active layer. As a result, both graphene-based buffer layers OPV devices significantly outperformed the reference ones, leading to a PCE improvement of 30% for PCDTBT and 19% for PTB7-based devices and to a record PCE of 9.14% for graphene-based buffer layer devices.

The dark J-V curves (Figure S1) also show excellent diode characteristics with very low leakage current and high rectification ratio for the combination of both HT and ET graphene based devices (forward to reverse factor higher than $10^3$) exhibiting that the injected current density in the dark (0.5–1.0 V) is higher than that of the reference device. This is in full agreement with the assumed reduced injection barrier. In order to get an insight for the responsible mechanism of the enhanced device performance, the incident photon-to-electron conversion efficiency (IPCE) curves (Figure 6c) of the devices with different buffer layer combinations was measured and compared with the pristine one. The pristine device exhibits a maximum IPCE of ~69%, while the GO-Cl / GO-Li based devices exhibit an enhanced maximum of ~86% using PTB7 as donor material. This significant and broad enhancement is in agreement with increased $J_{sc}$ observed in the J-V measurements. It should also be noted that the integrated $J_{sc}$ values from the IPCE spectrum for the pristine and the GO-Cl / GO-Li based devices are 15.75 and 18.51 mA cm$^{-2}$. The IPCE calculated values are less than 4% different than the actual measured $J_{sc}$ values, indicating good accuracy of the OPV measurement.
Figure 6. J-V characteristics of a) PCDTBT:PC₇₁BM, b) PTB7:PC₇₁BM-based photovoltaic devices and c) IPCE spectra for the devices using different combinations of hole and electron transport layers of PTB7 based OPV devices.

Table 1. Summary of the averaged photovoltaic parameters of the fabricated OPVs

<table>
<thead>
<tr>
<th>HTL</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDTBT:PC₇₁BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>11.28±0.12</td>
<td>0.880±0.02</td>
<td>55.6±0.3</td>
<td>5.51 (5.61)</td>
</tr>
<tr>
<td>GO</td>
<td>11.52±0.15</td>
<td>0.880±0.02</td>
<td>55.1±0.4</td>
<td>5.59 (5.71)</td>
</tr>
<tr>
<td>GO-Cl (5.04 eV)</td>
<td>11.78±0.14</td>
<td>0.880±0.02</td>
<td>55.1±0.3</td>
<td>5.71 (5.82)</td>
</tr>
<tr>
<td>GO-Cl (5.11 eV)</td>
<td>12.19±0.17</td>
<td>0.880±0.02</td>
<td>55.2±0.5</td>
<td>5.92 (6.07)</td>
</tr>
<tr>
<td>GO-Cl (5.16 eV)</td>
<td>13.32±0.15</td>
<td>0.880±0.02</td>
<td>55.1±0.5</td>
<td>6.46 (6.61)</td>
</tr>
<tr>
<td>ETL</td>
<td>( J_\text{SC} ) (mA/cm(^2))</td>
<td>( V_\text{oc} ) (V)</td>
<td>FF (%)</td>
<td>PCE (%)</td>
</tr>
<tr>
<td>-----</td>
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</tr>
<tr>
<td>GO-Cl (5.23 eV)</td>
<td>13.65±0.19</td>
<td>0.880±0.02</td>
<td>55.3±0.4</td>
<td>6.57 (6.79)</td>
</tr>
</tbody>
</table>

**PTB7:PC_{71}BM**

<table>
<thead>
<tr>
<th>ETL</th>
<th>( J_\text{SC} ) (mA/cm(^2))</th>
<th>( V_\text{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>16.27±0.23</td>
<td>0.760±0.03</td>
<td>59.8±0.6</td>
<td>7.40 (7.60)</td>
</tr>
<tr>
<td>GO-Cl (5.04 eV)</td>
<td>17.13±0.18</td>
<td>0.760±0.02</td>
<td>59.6±0.5</td>
<td>7.78 (7.93)</td>
</tr>
<tr>
<td>GO-Cl (5.11 eV)</td>
<td>17.58±0.25</td>
<td>0.760±0.03</td>
<td>59.6±0.6</td>
<td>7.97 (8.19)</td>
</tr>
<tr>
<td>GO-Cl (5.16 eV)</td>
<td>18.30±0.27</td>
<td>0.760±0.02</td>
<td>59.9±0.8</td>
<td>7.56 (7.74)</td>
</tr>
</tbody>
</table>

**PEDOT:PSS**

<table>
<thead>
<tr>
<th>ETL</th>
<th>( J_\text{SC} ) (mA/cm(^2))</th>
<th>( V_\text{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_x)</td>
<td>11.28±0.12</td>
<td>0.882±0.02</td>
<td>55.6±0.3</td>
<td>5.53 (5.61)</td>
</tr>
<tr>
<td>GO/TiO(_x)</td>
<td>10.73±0.19</td>
<td>0.883±0.05</td>
<td>51.6±0.3</td>
<td>4.89 (5.03)</td>
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<tr>
<td>GO-Li/TiO(_x)</td>
<td>12.51±0.35</td>
<td>0.894±0.05</td>
<td>56.5±0.5</td>
<td>6.25 (6.57)</td>
</tr>
</tbody>
</table>

**GO-Cl & GO-Cl**

<table>
<thead>
<tr>
<th>ETL</th>
<th>( J_\text{SC} ) (mA/cm(^2))</th>
<th>( V_\text{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS &amp; TiO(_x)</td>
<td>11.28±0.12</td>
<td>0.878±0.02</td>
<td>55.6±0.3</td>
<td>5.51 (5.61)</td>
</tr>
<tr>
<td>GO-Cl &amp; GO-Li/TiO(_x)</td>
<td>14.48±0.13</td>
<td>0.880±0.01</td>
<td>56.3±0.5</td>
<td>7.17 (7.31)</td>
</tr>
</tbody>
</table>

**GO-Cl & GO-Cl**

<table>
<thead>
<tr>
<th>ETL</th>
<th>( J_\text{SC} ) (mA/cm(^2))</th>
<th>( V_\text{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS &amp; TiO(_x)</td>
<td>16.27±0.23</td>
<td>0.760±0.03</td>
<td>59.8±0.6</td>
<td>7.39 (7.60)</td>
</tr>
<tr>
<td>GO-Cl &amp; GO-Li/TiO(_x)</td>
<td>19.28±0.31</td>
<td>0.760±0.02</td>
<td>60.5±0.7</td>
<td>8.83 (9.14)</td>
</tr>
</tbody>
</table>

*Average photovoltaic characteristics and standard deviations for the different structured OPV devices. The numbers in parentheses represent the values obtained for the champion OPV cells. To account for experimental errors, the reported averages and deviations for each ETL are taken for 10 identical devices, consisting of six cells each.

The increased value of \( J_\text{SC} \) was also investigated through electron and hole mobility measurements (Figure S2). For that purpose electron- and hole-only devices were fabricated with the following structure: ITO/HTL/Active layer/ETL/Au for the hole-only and ITO/Al/HTL/Active layer/ETL/Al for the electron only device respectively. The values calculated were improved for both electron and hole mobilities. Calculations were based on Mott–Gurney equation:

\[
J_{\text{SCLC}} = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu (V - V_{\text{bi}})^2 \frac{1}{d^3}
\]
in which \( \varepsilon_r \) is the relative dielectric constant, \( \varepsilon_0 \) is the permittivity of free-space, \( m \) is the charge carrier mobility, \( V \) is the applied voltage, \( V_b \) is the built-in potential and \( d \) is the thickness of the active layer. The mobility values for the reference OPV device were \( \mu_e = 7.86 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for the electron and \( \mu_h = 1.30 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for the hole mobility while for the GO-Cl / GO-Li based cells the values were \( \mu_e = 1.59 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for the electron and \( \mu_h = 1.91 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for the hole mobility, respectively. The mobilities were not only increased, especially the electron mobility, but also balanced which is a very important factor in order to prevent charge accumulation in the device. Before further analyzing our results we should first shed light in the functional mechanism taking place. Because holes are collected at the front electrode in the conventional device structure, and taking into account that the most of the excitons are created near by the front contact the holes mobilities should have slightly lower value compared to the electron mobility. Thus, this is the reason that PTB7 based OPV devices (\( \mu_h > \mu_e \)) have lower PCE values in the conventional structure compared to the inverted one and in our case this is maybe the reason for the lower PCE enhancement of PTB7 compared to PCDTBT (\( \mu_h > \mu_e \)). In this context, this is a crucial improvement because electron transport is considered as a factor that limits the photocurrent generation in the conventional PTB7 based devices, since the electron mobility is much lower than the hole mobility. Both electron and hole mobility increases should be attributed on the one hand to GO–Li planaring role\textsuperscript{24} and perfect energy levels matching and on the other hand to perfect WF tuning of GO after the photochlorination process. As a result, when we combined GO-Cl HTL and GO-Li interfacial layer the \( \mu_h/\mu_e \) ratio was significantly reduced, from 1.65 to 1.20 as it is observed in Table 2. We can thus assume, that if we use the inverted structure with the proposed graphene based buffer layers the improvement in the PCE could be much higher than in the conventional structure used here.

**Table 2.** Electron and hole mobilities of the reference and the device with graphene based buffer layers

<table>
<thead>
<tr>
<th>HTL / ETL</th>
<th>( \mu_h ) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>( \mu_e ) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>Ratio (( \mu_h/\mu_e ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7:PC(_{71})BM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS / TiO(_x)</td>
<td>( 1.30 \times 10^{-4} )</td>
<td>( 7.86 \times 10^{-4} )</td>
<td>1.65</td>
</tr>
<tr>
<td>GO-Cl / GO-Li</td>
<td>( 1.91 \times 10^{-4} )</td>
<td>( 1.59 \times 10^{-4} )</td>
<td>1.20</td>
</tr>
</tbody>
</table>

In order to examine and confirm our findings (increased \( J_{sc} \) and balanced mobilities) we studied the charge recombination kinetics at short circuit for the reference and for the devices with graphene based buffer layers. The \( J_{sc} \) can be correlated to illumination intensity (\( I_{light} \)) by,
\[ J_{sc} = \propto I_{light}^n \quad (n \leq 1) \]

At short circuit, the bimolecular recombination should be minimum \((n < 1)\) for maximum carrier sweep out. Any deviation from \(a < 1\) implies bimolecular recombination\(^5\). Figure S3 shows \(J_{sc}\) vs. \(I\) fitted using the power law described above. The fitting of the data yield \(a=0.870\) for reference device, which can be attributed to bimolecular recombination. After the introduction of GO-Cl and GO-Li, \(a\) is 0.968, which imply that bimolecular recombination is significantly reduced. To gain further insight into the origin of the enhanced \(J_{sc}\) in the device, one-dimensional transfer matrix formalism based on optical modeling calculations assuming monochromatic light propagating normal to the device layers was conducted\(^5\). Figure S4 presents the simulated optical electric field distribution, \(|E^2|\), as a function of wavelength in the reference OPV device and using different combinations of buffer layer as reported previously. The optical constants of the PCDTBT:PC\(_{71}\)BM layer were obtained from previous reports.\(^3\) As shown in Figure 7, the optical electric field amplitude is significantly enhanced for the device with the GO-Li interfacial layer and GO-Cl as HTL, compared with that of the reference device with only the TiO\(_x\) as ETL and with PEDOT:PSS as HTL. The highest optical electric field amplitudes are 0.745 and 0.619 V/m for the dual graphene based buffer device and reference, respectively. This electric field enhancement is directly attributed to the better refractive index \((n)\) matching in the sandwich devices using graphene based buffer layer compared to the reference sandwich. In particular, for the reference device PEDOT:PSS \(n\) value is \(~1.5\), PTB7:PC\(_{71}\)BM is \(~1.9\) and TiO\(_x\) \(~2.5\) and for the graphene based buffer layer device GO-Cl \(n\) value is \(~1.9\), PTB7:PC\(_{71}\)BM is \(~1.9\) GO-Li is \(~2\) and TiO\(_x\) is \(~2.5\). In this way, an important part of the incident electric field is reflected at the interface between PEDOT:PSS and active layer while in the case of GO-Cl due to the perfect \(n\) matching the interface parasitic reflection is minimum. Also, GO-Li \(n\) matches with the \(n\) of active layer and TiO\(_x\) acting as a bridge gradually allowing the electric field to pass through the device and thus increasing its intensity.\(^3\) We can conclude that the addition of the graphene based buffer layers increases the electric field amplitude in the photoactive layer, and therefore, more photocurrent is generated in the devices. This effect acts in synergy with the observed balanced charge mobilities. Therefore, the enhancement in PCE upon the addition of a GO-Li interfacial layer and GO-Cl HTL can be attributed to the observed reduced recombination at the interfaces, balanced charge mobilities, and enhanced electric field in the device.
Figure 7. Calculated distribution of the normalized modulus squared of the optical electric field $|E|^2$ inside an OPV device: a) ITO (100 nm)/PEDOT:PSS (35 nm)/PTB7:PC$_{71}$BM (100 nm)/TiOx (10 nm)/Al (100 nm), b) ITO (100 nm)/GO-CI (2 nm)/PTB7:PC$_{71}$BM (100 nm)/TiOx (10 nm)/Al (100 nm), c) ITO (100 nm)/PEDOT:PSS (35 nm)/PTB7:PC$_{71}$BM (100 nm)/GO-Li (2 nm)/TiOx (10 nm)/Al (100 nm) and (d) ITO (100 nm)/GO-CI (2 nm)/PTB7:PC$_{71}$BM (100 nm)/GO-Li (2 nm)/TiOx (10 nm)/Al (100 nm) for a wavelength of 500 nm.

III. Conclusion

In summary, this work demonstrates how the WF tuning of the buffer layers can affect the performance of OPV devices. Two facile, fast, non-destructive and r2r compatible methods are briefly presented, which allowed the WF fine tuning of graphene-based derivatives to develop universal buffer layers that direct match the energy levels of the polymer donor and electron acceptor in the state-of-the-art OPVs. OPVs with a GO-CI as HTL exhibited a PCE of 8.28%, much higher than those of reference devices with GO (7.56%) or PEDOT:PSS (7.40%), while the incorporation of GO-Li as ET interlayer
between the active layer and the TiO₂ optical spacer led to a PCE of 7.98% which was significantly increased compared to the reference one (7.40%). The excellent hole and electron extraction capabilities of GO-Cl and GO-Li were combined to an all graphene-based buffer layer OPV device which exhibited a PCE of 9.14% (8.83% average), significantly outperforming the reference one by ~19%. The described methods can contribute to novel interface engineering approaches, creating graphene- and other 2D materials-based derivatives as excellent potential candidates for a wide range of new applications with tunable optoelectrical properties, including flexible electronic OPVs, perovskite solar cells, organic light emitting diodes, and photosensors, as well as traditional electronic devices.

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