Water Processable Graphene Oxide: Single Walled Carbon Nanotube Composite as Anode Modifier for Polymer Solar Cells

Jaemyung Kim, Vincent C. Tung, and Jiaxing Huang*

The development of affordable photovoltaic technologies, i.e., solar cells, offers one of the most promising solutions for clean, renewable energy. Solution-processed polymer photovoltaic cells have attracted much attention since they can be manufactured with inexpensive, high-throughput techniques.[1] They are light weight and can also be flexible, making it possible to integrate them with ordinary surfaces at large scale to provide inexpensive power sources. They can also be customized to serve as cheap, disposable, soft generators for remote, autonomous micro devices. With a rapid progress in both materials design and device architectures, it is envisioned that polymer photovoltaic system with power conversion efficiency (PCE) over 10% can be realized.[2]

In a typical polymer solar cell, the transparent anode (e.g., indium tin oxide, ITO) is usually coated with a modifying layer that can block electrons, high-throughput techniques.[1] They are light weight and can also be flexible, making it possible to integrate them with ordinary surfaces at large scale to provide inexpensive power sources. They can also be customized to serve as cheap, disposable, soft generators for remote, autonomous micro devices. With a rapid progress in both materials design and device architectures, it is envisioned that polymer photovoltaic system with power conversion efficiency (PCE) over 10% can be realized.[2]

First, we studied the effects of solution processing conditions for spin coating GO thin films on the device performance. We chose the prototypical poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) bulk heterojunction solar cells, offers one of the most promising solutions for clean, renewable energy. Solution-processed polymer photovoltaic materials, the conjugated polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been predominantly used as an anode modifier due to its exceptional solution processability.[1] Li et al. first reported that graphene oxide (GO) can also be used as a hole transporting layer on ITO for polymer solar cells, potentially replacing PEDOT:PSS.[3] GO is a graphene derivative decorated with oxygen-containing groups such as carboxylic acids, epoxides and hydroxides that can be readily synthesized by oxidative exfoliation of graphite powders to yield stable aqueous dispersion of single layer sheets.[4–6] The apparent thickness of a GO sheet was measured to be around 1 nm by atomic force microscopy (AFM) but its lateral dimension can readily extend to tens of microns.[7,8] The large band gap of GO helps block electron flow towards the anode, thus effectively suppressing the carrier recombination.[3,9] The performance of the GO hole transporting layer was demonstrated to be comparable to PEDOT:PSS. However, since GO is insulating, it also increases the internal resistance of the device, which could lower the fill factor (FF) unless its thickness can be kept at the minimum, ideally down to one monolayer. Our earlier work has shown that GO pieces can be tiled up by Langmuir-Blodgett assembly to obtain high coverage monolayers.[7,10] Since spin coating is routinely used for fabricating polymer solar cells, it would be a more desirable method if very thin GO modifying layers can be made. Li et al. used spin coating to make the GO modifying layers on ITO surface and found that only when the thickness of the GO films was reduced to around 2 nm, were their performances comparable to PEDOT:PSS.[3] However, spin coating such thin GO films (i.e., one to two monolayers) can be extremely challenging because the resulting films also need to fully cover the underlying surface. Here, we report that adding a small amount of single walled carbon nanotubes (SWCNTs) in the GO modifying layer can significantly improve the devices’ FF. Polymer solar cells fabricated with an optimized GO:SWCNTs modifying layer show comparable or even a bit higher performance compared to our best devices using PEDOT:PSS as the hole transporting layer. Allowing thicker GO films to be used as the hole transporting layer can greatly facilitate the integration of GO into polymer photovoltaic devices.

First, we studied the effects of solution processing conditions for spin coating GO thin films on the device performance. We chose the prototypical poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) bulk heterojunction devices[2] as our model system since they have been extensively studied and developed to a relatively more mature stage. In a typical device fabrication process, an aqueous GO stock dispersion was diluted to various concentrations and spin coated on pre-patterned ITO substrates at 2,000 rpm. Then a P3HT:PCBM active layer was deposited on top of the modified ITO, followed by solvent annealing and vacuum deposition of Ca and Al to complete the device (Figure 1a, inset). Although the relationship between GO layer thickness and the device performance was already discussed in Li’s paper,[3] the processing conditions of the GO modifying layer (e.g., dispersion concentration and spin-coating parameters) were not provided, which we found are crucial to device performance. For example, it turned out that a small variation in the concentrations of GO dispersion from 0.1 wt% to 0.2 wt% can result in large variations in thin film coverage and thickness, thus greatly affecting the device performance. Below 0.15 wt%, the GO dispersion yielded non-uniform, incomplete coverage of GO pieces as shown in the AFM image in Figure 1b. Such films were found to produce poor and irreproducible device performances. With 0.15 wt% GO dispersion, it started to yield nearly complete coverage of GO (Figure 1c), leading to reproducible photovoltaic results (Figure 1a, open circle). The open-circuit voltage (VOC), short-circuit current density (JSC), FF, and PCE of the devices were measured to be 0.60 V, 9.3 ± 0.73 mA cm−2, 60.1 ± 3.5%, and 3.28 ± 0.14%, respectively. A slight increase of GO concentration to 0.2 wt% yielded thicker GO thin films (c.a. 3–4 nm) consisting of stacked...
more uniform GO thin films by stitching GO sheets through π–π stacking.\(^\text{[16]}\) Although the synergistic co-assembly between GO and unfunctionalized SWCNTs can be explored to create hybrid thin films, here we discovered that water dispersible, surface functionalized SWCNTs are already sufficiently conductive to improve GO’s performance as an anode modifier. Such SWCNTs are functionalized with 1.0–3.0 atomic% of carboxylic acid groups, and can be readily mixed with GO to yield a uniform GO:SWCNTs composite thin film by spin coating, which is favorable for material processing in fabricating polymer solar cells. Therefore, functionalized SWCNTs are used throughout the studies below.

The GO:SWCNTs dispersions were created by direct mixing of the two components in water by sonication. Surprisingly, incorporating a small amount of SWCNTs (GO:SWCNTs = 1:0.05, w/w) into the GO modifying layer (Figure 2a, inset) resulted in considerable improvement for devices made with both thin (Figure 2a, 0.15 wt% GO) \(J_{SC} = 9.79 \pm 0.43 \text{ mA cm}^{-2}\), FF = 62.7 ± 2.1%, PCE = 3.66 ± 0.18%) and thick (Figure 2b, 0.2 wt% GO) \(J_{SC} = 9.19 \pm 0.48 \text{ mA cm}^{-2}\), FF = 56.4 ± 2.3%, PCE = 3.13 ± 0.11%) GO modifying layers. AFM observation of the GO:SWCNTs thin film (Figure 2c) shows that the overall thickness is largely unchanged after the incorporation of SWCNTs. The GO:SWCNTs films also have very low surface roughness (root mean square roughness = 0.962 nm for Figure 2c), which is crucial for depositing smooth multilayers (Figure 1d). The corresponding \(J_{SC}\), FF, and PCE of the devices decreased to 9.05 ± 0.67 mA cm\(^{-2}\), 43.9 ± 4.8%, and 2.36 ± 0.28% while the \(V_{OC}\) remained the same (Figure 1a, open triangle). The decrease in \(J_{SC}\) and FF is attributed to increased vertical resistance with the thicker insulating GO film. This shows that the processing conditions of GO have to be limited to a very narrow window to ensure both near complete coverage and near monolayer thickness for achieving high device performance. This can be very challenging due to the sheet-like morphology of GO, and its tendency to wrinkle and overlap under capillary forces.\(^{[10,11]}\)

Since it is much easier to achieve complete coverage of GO with larger thickness, if thicker films can be made more conductive along the thickness direction, they could work more reliably as the modifying layer. Although GO can be deoxygenated to greatly increase its conductivity, the reduction process also alters its work function, making it unsuitable as a hole transporting layer.\(^{[12,13]}\) Incorporating a more conductive material such as SWCNTs in GO could solve the problem. The small diameter of SWCNTs (ca. 1 nm) makes them particularly attractive as an adduct for GO thin films because it would not significantly increase the surface roughness if they can be well dispersed. In an earlier work, we discovered that GO can function as a surfactant to disperse unfunctionalized SWCNTs in water.\(^{[14,15]}\) Meanwhile, the SWCNTs also help to create more uniform GO thin films by stitching GO sheets through π–π stacking.\(^{[16]}\) Although the synergistic co-assembly between GO and unfunctionalized SWCNTs can be explored to create hybrid thin films, here we discovered that water dispersible, surface functionalized SWCNTs are already sufficiently conductive to improve GO’s performance as an anode modifier. Such SWCNTs are functionalized with 1.0–3.0 atomic% of carboxylic acid groups, and can be readily mixed with GO to yield a uniform GO:SWCNTs composite thin film by spin coating, which is favorable for material processing in fabricating polymer solar cells. Therefore, functionalized SWCNTs are used throughout the studies below.

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sequential layers to avoid shorting. The AFM image also shows that the amount of the incorporated SWCNTs (GO:SCNWTs = 1:0.05, w/w) was below the percolation threshold. Indeed, it was found that adding this amount of SWCNTs does not improve the lateral conductivity of GO thin films. However, the presence of the SWCNTs was found to greatly improve the vertical conductivity of the GO layer, which is more relevant to the charge flow in the thin film photovoltaic devices. The inset of Figure 2d shows the geometry of the current-voltage measurement of a GO:SWCNTs thin film sandwiched between Al and ITO electrodes. The vertical resistance of the GO layer (open circle) was reduced by an order of magnitude after adding SWCNTs (solid circle). This should lead to lower overall serial resistance in the final device and increased FF. In addition, adding SWCNTs greatly reduces the sensitivity of device performance on the thickness of the GO modifying layer. For example, without SWCNTs, the PCEs of the cells decreased from 3.28 ± 0.14% to 2.36 ± 0.28% when the thickness of GO increased from around 1 nm (spin coated from 0.15 wt% GO dispersion) to around 3–4 nm (spin coated from 0.2 wt% GO dispersion), respectively. However, after adding SWCNTs, the difference between the PCEs of the two types of cells (3.66 ± 0.18% and 3.13 ± 0.11%, respectively) became much smaller. Overall, adding SWCNTs can lead to improved and more reproducible performances of GO modifying layers that are also less sensitive to the solution processing parameters.

With water processability of both GO and the functionalized SWCNTs, it is convenient to tune their relative fraction in the dispersion and thus in the final thin films, too. Table 1 summarizes the effects of SWCNT concentration in the dispersion on the final device performances. The GO concentration was kept at 0.15 wt% to achieve an optimized PCE. The improvement in FF appeared to be already saturated after adding 1:0.05 of SWCNTs into the GO layer. However, it is expected that with thicker GO layers, continued improvement in FF should be observed with higher SWCNTs contents. As the

Table 1. Effects of GO:SWCNTs mass ratio on device performances.

<table>
<thead>
<tr>
<th>GO:SWCNTs mass ratio</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
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<tbody>
<tr>
<td>GO$^a$</td>
<td>0.60</td>
<td>9.30 ± 0.73</td>
<td>60.1 ± 3.5</td>
<td>3.28 ± 0.14</td>
</tr>
<tr>
<td>GO:SWCNTs (1:0.05)</td>
<td>0.60</td>
<td>9.79 ± 0.43</td>
<td>62.7 ± 2.1</td>
<td>3.66 ± 0.18</td>
</tr>
<tr>
<td>GO:SWCNTs (1:0.1)</td>
<td>0.60</td>
<td>10.43 ± 0.40</td>
<td>61.4 ± 2.2</td>
<td>3.80 ± 0.08</td>
</tr>
<tr>
<td>GO:SWCNTs (1:0.2)</td>
<td>0.60</td>
<td>10.82 ± 0.56</td>
<td>62.8 ± 3.1</td>
<td>4.10 ± 0.18</td>
</tr>
<tr>
<td>GO:SWCNTs (1:0.5)</td>
<td>0.58</td>
<td>9.93 ± 0.64</td>
<td>58.8 ± 1.2</td>
<td>3.53 ± 0.17</td>
</tr>
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$^a$Prepared from 0.15 wt% dispersion in water.
SWCNT concentration was increased from 1:0.05 to 1:0.2, the $V_{OC}$ of the cells remained unchanged, while $J_{SC}$ continued to increase, leading to improved PCE values. The initial improvement of $J_{SC}$ can be attributed to reduced vertical resistance by adding SWCNTs; however, further improvement of $J_{SC}$ should be attributed to improved hole extraction from the polymer since the SWCNTs added to the near monolayer thick GO thin film were likely in contact with the active layer as well. With 1:0.2 GO:SWCNTs mass ratio, the device PCE reached 4.10 ± 0.18%, which represents a 25% improvement over devices without SWCNTs. However, when the SWCNT concentration was further increased to 1:0.5 mass ratio, all photovoltaic parameters, including $V_{OC}$, dropped to lower values.

Figure 3 shows the morphological evolution of GO:SWCNTs thin films with increased nanotube content revealed by AFM and scanning electron microscopy (SEM). SEM images (Figure 3a and 3b, left and upper right panels) show that adding SWCNTs at 1:0.2 mass ratio does not affect the overall coverage and uniformity of the GO layer. The SWCNTs can be seen to be evenly dispersed throughout the GO layer (Figure 3b, AFM, lower right panel). However, with excessive amount of SWCNTs (1:0.5 mass ratio), the GO:SWCNTs films become non-uniform with islands of multilayer GO:SWCNTs stacks as well as uncovered areas (Figure 3c). The AFM image reveals that at this concentration, the SWCNTs form network-like aggregates, trapping thicker piles of GO pieces. Uneven coverage and thickness of modifying layers at high SWCNT content should be responsible for their lower performance.

Figure 4a shows the current density-voltage characteristics of solar cells made with ITO modified by GO:SWCNTs (1:0.2 mass ratio, spin coated from 0.15 wt% GO dispersion), GO only (spin coated from 0.15 wt% GO dispersion), PEDOT:PSS, and an unmodified ITO anode. In general, our PEDOT:PSS devices (open diamond) consistently show higher $J_{SC}$ and FF values than devices with only GO as a modifier (open circle) and those without modifying layers (open inverted triangle). However, the GO:SWCNTs devices (solid circle) can have even a bit higher $J_{SC}$ and comparable FF, leading to comparable or even slightly higher PCE values. A potential advantage of using GO based anode modifying layer is its high transparency in the red to near infrared region of the solar spectrum (Figure 4b), which allows more absorption by the active layer.

In summary, GO:SWCNTs thin films were found to be efficient anode modifying layers for polymer solar cells using P3HT:PCBM as a model system. Adding a non-percolating amount of SWCNTs into GO can significantly improve its vertical conductivity, which allows the use of thicker and thus easier-to-make GO films. This helps to reduce the strong dependence of the device performance on GO thickness and solution processing conditions, leading to improved and more reproducible results. GO:SWCNTs can offer comparable performance to the conventional PEDOT:PSS anode modifying layer. It is expected that incorporating p-type SWCNTs into GO may further promote hole extraction and the charge flow in the modifying layer. Since uniform GO:SWCNTs thin films with near complete coverage can be made with much smaller thicknesses (around a few nm) than PEDOT:PSS (typically 40 nm), and offer considerably higher optical transmission in the longer wavelengths, GO:SWCNTs should be an attractive candidate as an anode modifier for low band gap polymer solar cells and
GO can undergo partial deoxygenation upon gentle heating, possibly the interconnect layer in tandem devices. Since GO can undergo partial deoxygenation upon gentle heating, further work is also needed to evaluate the long term stability of devices with GO based modifying layers.

Experimental Section

Materials: GO was synthesized by a modified Hummers’ method and purifed by a two-step washing method as reported elsewhere. The purifed GO, with typical lateral size of a few microns, was dried and redispersed in deionized water to create dispersions. SWCNTs were purchased from Carbon Solutions, Inc. (P3-SWNT, functionalized with 1.0–3.0 atomic% carboxylic acid) and dispersed in water (1 mg/ml) by ultrasonication (Misonix, S-4000) for 2 hours, followed by centrifugation at 110,000 rpm for 1 hour (Eppendorf, 5417C) to collect the supernatant for later use. PEDOT:PSS (Clevios 4083, H.C. Starck), 1,2-dichlorobenzene (anhydrous, Sigma-Aldrich), P3HT (4002-E, Rieke Metals, Inc.), and PCBM (>99.5%, Sigma-Aldrich) were used as received.

Device Fabrication: GO:SWCNTs dispersions were spin coated on pre-patterned ITO anodes (20 Ω/sq) at 2,000 rpm for 40 seconds, followed by thermal annealing at 120 °C for 20 minutes. For control devices, PEDOT:PSS was spin coated at 4,000 rpm for 1 minute, followed by thermal annealing at 150 °C for 30 minutes. The modifed substrates were then transferred into a nitrogen-fflled glove box, and 2 wt% P3HT:PCBM (1:1, w/w) in 1,2-dichlorobenzene was spin cast at 600 rpm for 40 seconds. The active layers were then solvent-anealed by a slow-growth method for 30 minutes. Finally, Ca/Al (20/60 nm) electrodes were thermally evaporated to complete the devices.

Characterization: Two-terminal measurements were performed by using a Keithley 2400 source meter. Photovoltaic measurements were done by illuminating devices (device area = 0.04 cm²) using an Oriel Xe solar simulator (AM 1.5G simulated spectrum) equipped with an Oriel 130 monochromator. Filters were used to cut off grating overtones. A calibrated silicon reference solar cell with a KG5 fter certifed by the National Renewable Energy Laboratory was used to confrm the measurement conditions. At least 25 devices were fabricated for each condition. To minimize the uncertainty with the fabrication processes, the best 15 devices were used to calculate the average values of photovoltaic parameters. The current density-voltage plot of a device that shows closest performance to the average was chosen to represent the group in the fures. Modifying layers deposited on ITO were imaged by SEM (Hitachi FE-SEM S4800) to examine their overall coverage and uniformity. Due to the higher roughness of the ITO surface (c.a. 10 nm), the microstructure of GO and GO:SWCNTs thin fms were examined by AFM (Veeco, Multimode V) on samples deposited on smoother SiO₂/Si substrates. Under the same processing conditions, GO thin fms deposited on SiO₂/Si and ITO showed very similar overall coverage and thickness. The transmittance was measured with a UV/vis spectrometer (Agilent Technologies, 8653).

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