

# Buffer Layer of PEDOT:PSS/Graphene Composite for Polymer Solar Cells

Bin Yin<sup>1</sup>, Qian Liu<sup>1</sup>, Liying Yang<sup>1</sup>, Xiaoming Wu<sup>1</sup>, Zunfeng Liu<sup>2</sup>, Yulin Hua<sup>1</sup>, Shougen Yin<sup>1, \*</sup>, and Yongsheng Chen<sup>2</sup>

<sup>1</sup> Key Laboratory of Display Materials and Photoelectric Devices (Tianjin University of Technology), Ministry of Education, Institute of Material Physics, Tianjin University of Technology and Tianjin Key Laboratory for Photoelectric Materials and Devices, Tianjin 300384, China
<sup>2</sup> Key Laboratory for Functional Polymer Materials and Center for Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

High-efficiency polymer solar cells were made with a hydrophilic graphene oxide (GO) doped in poly(ethylene dioxythiophene) (PEDOT)-polystyrene sulfonic acid (PSS) composites using a structure of indium tin oxide/PEDOT:PSS:GO (40 nm)/poly(3-hexylthiophene-1,3-diyl) (P3HT)-[6,6]phenyl-C61-butyric acid methyl ester (PCBM) (1:0,6,100 nm)/LiF (1 nm)/Al (70 nm). The energy conversion efficiency  $\eta$  was enhanced from 2.1 to 3.8% by doping GO into the PEDOT:PSS buffer layer under AM1.5G 100 mW cm<sup>-2</sup> illumination in air. The pre-annealing of GO makes energy conversion efficiency 1.8 times that of the device based on a pristine PEDOT:PSS buffer layer. Because of the low price and ease of preparation, soluble graphene will be a promising buffer layer used in photovoltaic applications. Furthermore, it can be used in other electronic applications.

**Keywords:** Graphene, Buffer Layer, Energy Conversion Efficiency, Organic Photovoltaic Device, Organic Solar Cell.

## **1. INTRODUCTION**

Polymer solar cells have attracted considerable attention due to their potential as a renewable, alternative source of electricity and their preference in low cost, light weight, mechanical flexible, and easy processing conditions as compared to the conventional inorganic solar cells.<sup>1</sup> In recent years, with significant advances in the fundamental understanding of the basic operation mechanism and great efforts to optimize performance, organic solar cells have reached power conversion efficiencies of 5-6% by use of the bulk heterojuction (BHJ) structure.<sup>2,3</sup> The commonly accepted light-electric conversion process is as follows. The active layer absorbs light and generates excitons, then the excitons diffuse to the donor/acceptor (D/A) interface and dissociate into electrons and holes, which transport in the donor and acceptor phases, and then are collected by the respective electrodes.<sup>4</sup> For the hole collection in common solar cells, a buffer layer of the PEDOT:PSS is often used to modify the indium tin oxide (ITO) electrode in view of the superior injection/collection properties of the PEDOT:PSS/active layer compared with those

sion of PEDOT:PSS can form a uniform, conductive, transparent, and stable thin film, which can smooth and stabilize the surface of the ITO electrode, enhance the adhesion to the organic layer, and favor the hole injection/collection to the electrode.<sup>6,7</sup> Therefore, the electrical properties of the PEDOT:PSS film plays a great role in the whole performance of the photovoltaic devices. The conductivity of the films cast from the aqueous PEDOT:PSS solution often reaches up to 10 S  $cm^{-1}$ ; however, the charge transport properties of the PEDOT:PSS still need to be improved in order to improve the whole device performance.<sup>8,9</sup> Recently, several approaches have been developed to improve the conductivity of PEDOT:PSS including thermotreatment,<sup>10</sup> secondary doping of inert solvents such as glycerol, sorbitol, dimethyl sulfoxide (DMSO), N,N'-dimethyl formamide (DMF), tetrahydrofuran (THF), polymers such as poly(vinylpyrrolidone) and polyethylene oxide,<sup>11</sup> and conducting nanomaterials such as carbon nanotubes.<sup>12, 13</sup> In this paper, we modify the PEDOT:PSS with a newly discovered nanomaterial graphene oxide (GO) and use it as the hole collecting buffer layer of the organic photovoltaic cells. By introducing graphene into the PEDOT:PSS buffer layer of the

of the ITO/active layer interface.<sup>5</sup> The aqueous disper-

<sup>\*</sup>Author to whom correspondence should be addressed.

photovoltaic device having a structure of ITO/PEDOT:PSS (40 nm)/P3HT:PCBM (1:0.6, 100 nm)/LiF (1 nm)/Al (70 nm), the energy conversion efficiency  $\eta$  increased from 2.1 to 3.8%, almost by ~80%.

Graphene exhibits a high charge mobility of 10.000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at room temperature, long phase coherence and elastic scattering lengths, and quantum confinement effects.<sup>14</sup> Electrons in graphene obey a linear dispersion relation and behave like massless relativistic particles,<sup>15</sup> resulting in the observation of a number of very peculiar electronic properties such as the quantum Hall effect,<sup>16</sup> ambipolar electric field effect,<sup>17</sup> and photovoltaic acceptor.<sup>18</sup> Its one-atom thickness and large two-dimensional plane provide it large specific area, and therefore, very large interfaces and low percolation threshold can be achieved when it is added into the polymer matrix. Graphene can be prepared using several methods, such as micromechanical cleavage,<sup>17</sup> epitaxial growth,<sup>19</sup> and chemical oxidation.<sup>20</sup> In view of the aqueous nature of the PEDOT:PSS solution, a functionalized graphene (graphene oxide, GO) was used in this paper prepared by a modified Hummers method<sup>20</sup>—an chemical oxidation method as described elsewhere,<sup>21</sup> which can be very soluble in aqueous solution and, therefore, is expected to be well dispersed in the PEDOT:PSS matrix.

## 2. EXPERIMENTAL DETAILS

#### 2.1. Preparation of Graphene Oxide

GO was prepared by using a modified Hummers method from flake graphite (average particle diameter 4  $\mu$ m, 99.95% purity, Qingdao Tianhe Graphite Co., Ltd.).<sup>1</sup> Briefly, graphite (5 g) and NaNO<sub>3</sub> (A.R., 3.75 g) were placed in a flask. Then, H<sub>2</sub>SO<sub>4</sub> (A.R., 375 mL) was added with stirring in an ice water bath.  $KMnO_4$  (A.R., 22.5 g) was slowly added over about 1 h. Cooling was completed in 2 h, and the mixture was allowed to stand for 5 days at room temperature with vigorous stirring. During the five days, the mixture changed from green to dark brown to brick brown. The liquid obtained was added to an  $H_2SO_4$ aqueous solution (700 mL, 5 wt%) over about 1 h with stirring, and the temperature was kept at 98 °C. The resultant mixture was further stirred for 2 h. Then, the mixture was cooled to 60 °C, H<sub>2</sub>O<sub>2</sub> (15 mL, 30 wt% aqueous solution), added to the above liquid, and stirred for 2 h at room temperature.

In order to remove ions of oxidant origin, especially manganese ions, the resultant liquid was purified by repeating the following procedure cycle at least 15 times: centrifugation, removal of the supernatant liquid, addition of mixed aqueous solution (2 L) of  $H_2SO_4$  (3 wt%)/ $H_2O_2$  (0.5 wt%), and dispersion using vigorous stirring and bath ultrasonication for 30 min at a power of 140 W. Then, the procedure was cycled 3 times using HCl aqueous solution (3 wt%) and 2 times using  $H_2O$ . The resultant solution

was transferred to acetone to remove the remaining acid. Then, through a drying process, the GO was obtained.

#### 2.2. Instruments and Measurements

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed using a TGA/DSC STA904 at a heating rate of 5 °C min<sup>-1</sup> under a nitrogen flow. All current-voltage (J-V) characteristics of the photovoltaic devices were measured in air using a Keithley SMU 2400 unit. A Xenon lamp with a filter (broadpasss GRB-3, Beijing Changtuo Scientific limited company) to simulate AM1.5G conditions was used as the excitation source with a power of  $100 \text{ mW cm}^{-2}$  white light illumination from the ITO side. Light source illumination intensity was measured using a calibrated broadband optical power meter (FZ-A, wave length range 400-1000 nm, Photoelectric Instrument Co, Beijing Normal University, China). All the fabrication and measurements were conducted in air at room temperature. The calculation of the power conversion efficiency  $\eta$  as performed using the following equation:

$$\eta = V_{\rm oc} J_{\rm sc} FF/P_{\rm in}$$

where  $V_{oc}$  is the open circuit voltage,  $J_{sc}$  is the short circuit curnet density, *FF* is the fill factor, and  $P_{in}$  is the incident light power. *FF* is determined according to  $FF = (V_m J_m)/(V_{oc} J_{sc})$ , where  $V_m$  and  $J_m$  are the voltage and the current density in the maximum power point of the J-V curve in the fourth quadrant.

#### 2.3. Fabrication of the Photovoltaic Device

The photovoltaic device was fabricated by use of a common process. The active layer was prepared by spin coating a P3HT(10 mg mL<sup>-1</sup>)/PCBM (1:0.6) solution in DCB onto an ITO glass substrate that was pre-coated with PEDOT:PSS (Baytron P, Bayer Germany):GO. Then, LiF and Al were vapor deposited on the active layer. The chemical structures of GO and PEDOT:PSS are shown in Figure 1(a). The schematic representation of the PEDOT:PSS:GO-based solar cell is shown in Figure 1(b), which has a structure of ITO (~17  $\Omega$  sq<sup>-1</sup>)/PEDOT:PSS:GO (40 nm)/P3HT:PCBM (1:0.6, 100 nm)/LiF (1 nm)/Al (70 nm). The effective area of each cell was ~8 mm<sup>2</sup>. For comparison, a photovoltaic device based on a buffer layer of pure PEDOT:PSS having the same device structure was also prepared.

### 3. RESULTS AND DISCUSSION

The experimental results are shown in Figure 2. The performance details are listed in Table I.

The J-V curves of the photovoltaic devices based on PEDOT:PSS and PEDOT:PSS:GO buffer layers under



Fig. 1. (a) The chemical structures of graphene and PEDOT:PSS. (b) Schematic structure of photovoltaic device based on PEDOT:PSS/graphene buffer layer.

AM1.5G 100 mW cm<sup>-2</sup> illumination are shown in Figure 2(b). The device based on the pristine PEDOT:PSS buffer layer gives  $\eta$  of 2.1%,  $J_{sc}$  of 6.9 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.60 V, and *FF* of 0.50. By doping GO, the PEDOT:PSS:GO buffer layer makes the  $\eta$  value increase to 2.4% with  $J_{sc}$  of 10.2 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.56 V, and *FF* of 0.42. The  $J_{sc}$  value increases by 48%, and the  $\eta$  value increases by ~14%. Obviously, the improvement in the device performance can be attributed to the addition of GO. The J-V curves of the two devices in dark are shown in Figure 2(a). The dark current at the same bias value increase greatly with the PEDOT:PSS:GO buffer layer, showing an improved charge collection ability of the PEDOT:PSS:GO buffer layer compared with the pristine PEDOT:PSS composite.

When graphene was introduced with functional groups, such as -COOH and -OH as well as -C=O, -C-O-C-, and  $-CH_2-$  groups, its conductivity and charge carrier mobility were decreased to display an insulating nature, impeding the performance of the photovoltaic device based on the PEDOT:PSS:GO buffer layer. A recent report has

shown that rapid heating of GO results in its expansion and exfoliation to produce conducting single-functionalized graphene sheets.<sup>22</sup> In view that the functional groups can be partially removed from the graphene sheet at an elevated temperature under an inert atmosphere, and the conductivity of the graphene sheet can be recovered,<sup>23</sup> we investigated the thermal properties and the weight loss properties of GO using TGA and DSC under an Ar atmosphere, as shown in Figure 2(c). It can be seen that there is about 30% weight loss between 180 and 250 °C from the TGA curve, accompanying which, we can see an obvious exothermic peak in the DSC curve. The weight loss at this temperature range can be attributed to the removal of functional groups from the graphene sheets.

We then carried out an annealing treatment on the PEDOT:PSS/GO buffer layer before the P3HT:PCBM active layer at 250 °C for 10 min, the J-V curves of the device in dark and under illumination are also shown in Figures 2(a) and (b), respectively. The device based on the PEDOT:PSS:GO buffer layer after an annealing treatment shows an  $\eta$  value of 2.3%,  $J_{\rm sc}$  of 10.2 mA cm<sup>-2</sup>,  $V_{\rm oc}$  of



**Fig. 2.** J-V curves of photovoltaic devices based on different buffer layer in (a) dark and (b) under a simulated AM1.5G 100 mw illumination, and (c) TG and DSC curves of the GO in the range of 35–960 °C at a heating rate of 5 °C min<sup>-1</sup> in nitrogen flow.

0.62 V, and *FF* of 0.37, indicating that the overall performance of the annealed device is almost the same as that of the un-annealed one, except for a slight decrease in the  $\eta$  and  $V_{oc}$ . It has been reported that an annealing treatment at 250 °C will increase the conductivity of the PEDOT:PSS film,<sup>10</sup> Therefore, we investigated the photovoltaic device based on the pristine buffer layer of PEDOT:PSS with an annealing treatment at 250 °C for 10 min, the *J*–*V* curves of the device in dark and under illumination are also shown in Figures 2(a) and (b), respectively. This device shows an  $\eta$  value of 1.3%,  $J_{sc}$  of 4.6 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.60 V, and *FF* of 0.46, indicating that the annealing treatment on the PEDOT:PSS buffer layer at 250 °C for 10 min

**Table I.** Performance details ( $V_{oc}$ ,  $J_{sc}$ , FF, and  $\eta$ ) of the photovoltaic devices having different buffer layers.

Buffer layer	$V_{\rm oc}~({ m V})$	$J_{\rm sc}~({\rm mA~cm^{-2}})$	FF	η (%)
PEDOT:PSS	0.60	6.9	0.50	2.1
PEDOT:PSS/GO	0.56	10.2	0.42	2.4
(PEDOT:PSS/GO) annealing	0.62	10.2	0.37	2.3
PEDOT:PSS annealing	0.6	4.6	0.46	1.3
GO-annealing/PEDOT:PSS	0.62	14.2	0.43	3.8

greatly decreases the overall performance of the photovoltaic device. Moreover, the current density from the J-Vcurve of the device in dark (Fig. 2(a)) decreases more than that of PEDOT:PSS buffer layer without annealing treatment at the same bias. This indicates the decrease in the charge collection ability of the buffer layer, which may be caused by the decomposition of the PEDOT:PSS.

In order to reactivate the performance of GO and avoid the decomposition of the PEDOT:PSS composite with annealing treatment at same time, the GO was first heated at 250 °C for 10 min, then mixed with PEDOT:PSS solution by use of ultrasonic dispersion, and finally used as the buffer layer of the photovoltaic device. The device J-Vcurves of this treatment in dark and under illumination are shown in Figures 2(a) and (b), respectively, showing an  $\eta$  value of 3.8%,  $J_{\rm sc}$  of 14.2 mA cm<sup>-2</sup>,  $V_{\rm oc}$  of 0.62 V, and FF of 0.43. It can be seen that the energy conversion efficiency based on pre-annealing of GO is  $\sim$ 1.8 times of that of the pristine PEDOT:PSS buffer layer, especially when the  $J_{sc}$  value reaches 2 times. The higher dark current density of this device compared with the pristine PEDOT:PSS device at the same bias also indicates that pre-annealing of GO sheets greatly improves the hole collection ability of the PEDOT:PSS buffer layer. It is worth noting that the devices based on the PEDOT:PSS/graphene composite buffer layer show lower fill factor than those based on the pristine PEDOT:PSS buffer layer. This indicates that besides the high conductivity of the GO sheet, there may be other factors of GO influencing the device performance. For example, GO in the buffer layer and PCBM also form a bilaver heterojunction subcell, besides the bulk heterojunction formed by P3HT:PCBM.<sup>24</sup>

#### 4. CONCLUSIONS

In summary, a one atom thick carbon material, graphene, was used as a buffer layer compounded with PEDOT:PSS. We achieved a performance of 3.8%, which is 1.8 times of that of the device based on a pristine PEDOT:PSS buffer layer. Thus, the composite is a promising buffer layer for use in photovoltaic applications. Furthermore, such a buffer layer can also be used in other electronic applications. The device performance should be further improved by optimization in composite fabrication details.

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