

Graphene oxide as hole transport layers for P3HT:PCBM solar cells

Cheng-En Cheng^{1,2}, Cheng-Wei Tsai², Tsung-Wu Lin³, Zingway Pei⁴,
Chen-Shiung Chang¹, and Forest Shih-Sen Chien^{2,*}

¹Department of Photonics, National Chiao Tung University, Hsinchu, Taiwan

²Department of Applied Physics, Tunghai University, Taichung, Taiwan

³Department of Chemistry, Tunghai University, Taichung, Taiwan

⁴Graduate Institute of Optoelectronic Engineering, Department of Electrical Engineering,
National Chung Hsing University, Taichung, Taiwan

*fsschien@thu.edu.tw

Abstract—Graphene oxide (GO) is prepared to be the alternative hole transport layers (HTLs) for polymer solar cells (PSCs). The thickness of GO-HTLs are optimized. The PSC with 2-nm UV-treated GO HTL has a higher hole collection efficiency, resulting a compatible photovoltaic performance to a conventional PSC with PEDOT:PSS HTL.

Index Terms—Polymer solar cells, graphene oxide, impedance spectroscopy.

I. INTRODUCTION

Polymer solar cells (PSCs) have attracted great interesting because of their unique advantages, such as low-cost, light weight, and mechanical flexibility [1]. The photovoltaic performance of PSCs is significantly dependent on the interfacial properties between the electrodes and active layers [2]. Introduction of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) at electrode and donor is the most common method to improve the hole collection efficiency in PSCs [3]. However, the high acidity and hygroscopic properties of PEDOT:PSS leads to the poor long-term stability of PSCs with PEDOT:PSS hole transport layers (HTLs) (namely PSC-PEDOT:PSS). To solve this problem, a thin film of graphene oxide (GO) is recently reported as an efficient HTLs for PSCs [4]. Unfortunately, the performance of PSCs with GO-HTL is highly relative to the conductivity of GO. To achieve a high-performance PSC with the GO-HTL, optimization of GO-HTL for PSCs should be significantly considered.

In this study, we have optimized the GO thin films, which are employed as HTLs, for P3HT:PCBM PSCs. First, the thickness of GO-HTL are investigated by 2-nm and 11-nm GO-HTLs for PSCs. The PSC with 2-nm GO-HTL shows higher short-circuit current density (J_{sc}), filling factor (FF) and power conversion efficiency (PCE) than that of PSC with 11-nm GO-HTL. The thicker GO leads to a higher resistance, resulting the lower hole collection efficiency and the worse photovoltaic performance of the PSC with 11-nm GO-HTL. Based on this result, the 2-nm thick GO films are prepared as HTLs for PSCs. The 2-nm GO films are subject to thermal annealing and UV treatment. The PSC with UV-treated GO-HTL [denoted PSC-UV-GO] shows 2%, 9.3%, 36 % and 55% improvements in J_{sc} , open-circuit voltage

(V_{oc}), FF , and PCE, respectively, as compared with the PSC with untreated GO-HTL (denoted PSC-GO). The results of impedance spectroscopy (IS) and electrostatic force microscopy (EFM) evidence that those significant enhancements in photovoltaic performance are attributed to the better hole transit ability and less exciton recombination in the PSC-UV-GO. As the result, the photovoltaic performance of PSC-UV-GO is compatible to PSC with PEDOT:PSS.

II. METHODS

In this study, the PSCs are prepared in a conventional configuration: ITO/HTL/P3HT:PCBM/Al, and the GO is prepared by the modified-Hummer method [6]. To obtain the aqueous GO solution (1.25 mg mL^{-1} , 15 mL), the dry GO is the re-separated in the mixture solution of DI-water and methanol. The pre-patterned ITO substrates are treated by UV-ozone for 30 min for the PEDOT:PSS HTL and air-plasma for 1 min for the GO-HTL deposition, respectively. Both HTLs are obtained on the ITO substrates by spin-coating. Then, the thermal annealing and UV treatments are applied to dry the films and activate the surface. The P3HT:PCBM active layers and Al electrodes are then deposited by spin-coating and thermal evaporation in the nitrogen-filled glove box. The photovoltaic performance and IS of PSCs are conducted under AM 1.5G illumination. The crystallographic structure and chemical composition of all GO films are analyzed by the grazing incident X-ray diffractometry (XRD) in National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The surface morphology and film thickness of GO are obtained by a tapping-mode atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

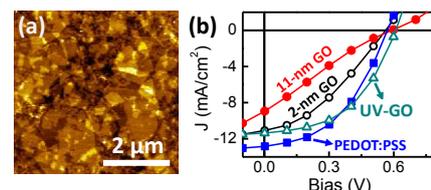


Fig. 1. (a) AFM image of GO thin film on Si substrate. (b) The J-V characteristic curves of PSCs with different HTLs.

TABLE I. PHOTOVOLTAIC PARAMETERS AND PARASITISM RESISTANCE OF PSCs WITH HTLS.

HTLs	Photovoltaic Parameters				Parasitism Resistance	
	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)	R_s (Ω)	R_{sh} (Ω)
2-nm GO	11.1	557	36	2.2	348	2570
11-nm GO	8.9	588	22	1.2	1131	117
PEDOT:PSS	12.8	568	45	3.3	190	3416
UV-GO (2 nm)	11.3	609	49	3.4	186	11846

Figure 1(a) shows the AFM image of GO thin film on Si substrate. It is evidenced that a homogeneous and continuous GO thin layer can be obtained by spin-coating. The J - V characteristic curves of the PSC with 2-nm GO-HTL, PSC with 11-nm GO-HTL, and PSC-PEDOT:PSS are shown in Fig. 1(b), and the photovoltaic parameters and parasitism resistance [series resistance (R_s) and shunt resistance (R_{sh})] from the J - V curves are summarized in Table I. The corresponding parameters of PSCs with GO-HTLs of 2 nm and 11 nm are: 11.1 mA/cm² and 8.9 mA/cm² in J_{sc} , 557 mV and 588 mV in V_{oc} , 36 % and 22 % in FF , 2.2 % and 1.2 % in PCE , 348 Ω and 1131 Ω in R_s , and 2570 Ω and 771 Ω in R_{sh} , respectively. The PSC-GO with 2-nm GO-HTL has a higher J_{sc} because of lower R_s , and higher FF because of higher R_{sh} . The higher R_s in PSC with 11-nm GO-HTL has a thicker GO-HTL and reduces the hole collection efficiency, resulting higher leakage loss and worse PCE . However, as compared with the conventional PSC-PEDOT:PSS, the PCE of PSC with 2-nm GO-HTL is still relative lower than that of PSC-PEDOT:PSS.

To achieve a compatible performance to PSC-PEDOT:PSS, the thermal annealing and UV irradiation are applied to improve the PSC with 2-nm GO-HTL (namely PSC-GO). A peak shift toward to higher degree in X-ray diffraction (XRD) patterns is observed on the annealed GO film, indicating the water molecular was removed between the GO interlayers. The results of EFM analysis show the work function (WF) of GO is increased about 0.13 eV after UV irradiation (both the XRD and EFM of GO films are not shown here). The J - V characteristic curve of PSC-rGO is given in Fig. 1(b). The corresponding photovoltaic parameters and parasitism resistances of PSC-UV-GO are: 11.3 mA/cm² in J_{sc} , 609 mV in V_{oc} , 49 % in FF , 3.4 % in PCE , 186 Ω in R_s , and 11846 Ω in R_{sh} , respectively, which are also listed in Table I. The PSC-UV-GO shows 2%, 9.3%, 36 % and 55% improvements in J_{sc} , V_{oc} , FF , and PCE as compared with the PSC-GO. The overall performance of PSC-UV-GO is compatible to PSC-PEDOT:PSS.

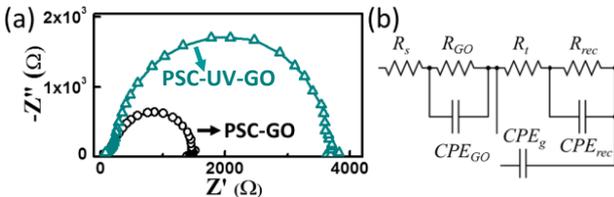


Fig. 2. (a) Nyquist plots of IS of PSC-GO and PSC-rGO. (b) The modified diffused-recombination circuit of a PSC.

The carrier dynamic in PSC-GO and PSC-UV-GO are investigated by IS. Figure 2(a) shows the complex Nyquist plots of IS of PSC-GO and PSC-UV-GO, and the spectrum are analyzed by the modified diffuse-recombination circuit [Fig. 2(b)] [7]. The major components in this circuit are: hole transit in GO-HTL resistance (R_{GO}), transit resistance (R_t), recombination resistance (R_{rec}), which are assigned to the hole transit resistance in GO-HTL, carrier transit ability and exciton recombination in PSCs, respectively. The details of this circuit are well discussed in authors' previous paper [8]. The R_{GO} , R_t and R_{rec} are: 87 Ω , 303 Ω and 1043 Ω for PSC-GO, and 81 Ω , 278 Ω and 3309 Ω for PSC-UV-GO, respectively. The lower R_{GO} and R_t in PSC-UV-GO indicates the higher conductivity of HTL and hole collection efficiency. The increase in R_{rec} in PSC-UV-GO indicates less exciton recombination occurs. We regard that the higher WF of UV-treated GO reduces hole transit barrier between HTL and P3HT, resulting the higher hole collection efficiency and lower exciton recombination. As the results, the PSC-UV-GO has a dramatic improvement in PCE and shows a compatible photovoltaic performance as compared with PSC-PEDOT:PSS.

IV. CONCLUSION

GO are employed as alternative HTLs for PSCs in this study. The PSCs with a 2-nm thick UV-treated GO HTL shows a compatible photovoltaic performance as compared with the conventional PSC with PEDOT:PSS HTL. Based on this approach, the UV-treated GO thin film is expected to be the great candidate as the HTL for the flexible and solution-processable PSCs.

ACKNOWLEDGMENT

This work is supported by Ministry of Science and Technology of Taiwan (Grant NO. NSC 102-2112-M-029-005-MY3).

REFERENCES

- [1] F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **93** (2009), 394.
- [2] H. Ma, H.-L. Yip, F. Huang, A. K.-Y. Jen, *Adv. Funct. Mater.* **20** (2010), 1371.
- [3] G. Li, V. Shrotriya, J. Huang, Y. Yao, and Y. Yang, *Nat. Mater.* **4** (2005), 864.
- [4] J.-M. Yun, J.-S. Yeo, J. Kim, H.-G. Jeong, D.-Y. Kim, Y.-J. Noh, S.-S. Kim, B.-C. Ku, and S.-I. Na, *Adv. Mater.* **23** (2011), 4923.
- [5] G. Eda, C. Mattevi, H. Yamaguchi, H. Kim and M. Chhowalla, *J. Phys. Chem. C* **113** (2009), 15768.
- [6] W. S. Hummers, and R. E. Offeman, *J. Am. Chem. Soc.* **80** (1958), 1339.
- [7] J. Bisquert, *J. Phys. Chem. B* **106** (2002), 325.
- [8] C.-E. Cheng, Z. Pei, C.-C. Hsu, C.-S. Chang, and F. S.-S. Chien, *Sol. Energy Mater. Sol. Cells* **121** (2014), 80.