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Photovoltaic Performance of Flexible Graphene-Electrodes Prepared by a Simple Chemical Vapor Graphitization

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When the graphene oxide (GO) film on plastic substrate was treated with HI-gas, a reduced graphene oxide (RGO) film with the conductivity 14.1 S/cm and the transparence of 34.7% at 550 nm was successfully obtained. Despite the low conductivity of the RGO electrode, the flexible organic solar cells fabricated on the RGO electrode showed a power conversion efficiency of ∼0.37% (FF: 0.25, V_{OC}: 0.58 V and J_{SC}: 2.41 mA/cm^2), indicating the possibility of using RGO as a flexible and transparent electrode for polymer-based flexible solar cells.

Keywords Flexible transparent electrode; graphene oxide; reduced graphene oxide; solar cell

1. Introduction

Recently, the discovery of isolate individual graphene nanosheets [1], many research groups tried to “how to make a mass-producible and easy-processable graphene?”. The major challenge is the mass production of graphene oxides (GOs) by fast and reliable methods by treating graphite with solution-based a strong oxidizers, followed by an exfoliation process [2]. However, GO is an electrical insulator due to the destroyed π-conjugated systems of π-plane within the graphene nanosheets. These physical properties can be overcome through chemically reduction by reducing reagents [3] and/or thermal annealing of GO under inert gas atmosphere [4]. Among the reported reduced graphene oxide (RGO) electrodes, record efficiency of polymer solar cell in power generation has exceeded 1.12% using a small test cell made by annealed at 1100°C under argon gas on graphene-coated quartz electrode [5]. Despite lower efficiencies, graphene-based electrodes are being developed for their low-cost manufacturing and flexible device. Avoidance of the high temperature processing for flexible organic solar cells has become conceivable through breakthroughs that allow the gas-phase reduction of GO. With this mind, we have demonstrated the success of graphene-based solar cells on flexible polyethylene terephthalate (PET) substrates through a simple chemical vapor graphitization. In this article, we could fabricate a flexible organic solar cell

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using poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The RGO electrode was successfully formed onto PET under a gas-phase of HI at a low-temperature (∼40°C), providing a replacement of transparent conductive metal oxides for collection of hole carriers.

2. Experimental

The GO nanosheets, GO film, and RGO film used in this work were obtained by the Moon's method, respectively [6]. Current the air-dried RGO thin film used in this study had conductivity of approximately 10.6 S/cm at chemical reduction. In order to enhance the conductivity, the RGO thin film onto PET substrate was annealed in a vacuum oven at 140°C for 15 h. After annealing treatment, it lead to a conductivity of about 14.1 S/cm (MCP-T600; Mitsubishi Chemical). Thickness of GO and RGO film can be measured by atomic force microscopy (AFM: PSIA XE-100).

3. Results and Discussion

As the reduction proceeded, color of GO thin film changed from light brown to black. Figure 1(a) showed AFM image of the RGO thin film uniformly coating the PET substrate surface. Root mean square (RMS) for surface roughness was 43.8 nm. The white regions in the AFM images indicated the edge or wrinkles of the RGO sheets. UV-vis spectroscopy (Duksan Mechasys, Optizen III) was used to compare the structures of the graphene before and after vapor-reduction. The transmittance of UV-vis spectra of the GO and RGO thin films depicted as Fig. 1(b) were 57.5% for the ∼56 nm thick GO film and 34.7% for the ∼29 nm thick RGO film at 550 nm, respectively. RGO film shows shrinkage of the film thickness from about 2 times due to the removal of the oxygen-containing functional groups on GO nanosheets. This finding means that the electronic conjugation within the graphene sheets is restored upon reduction [6].

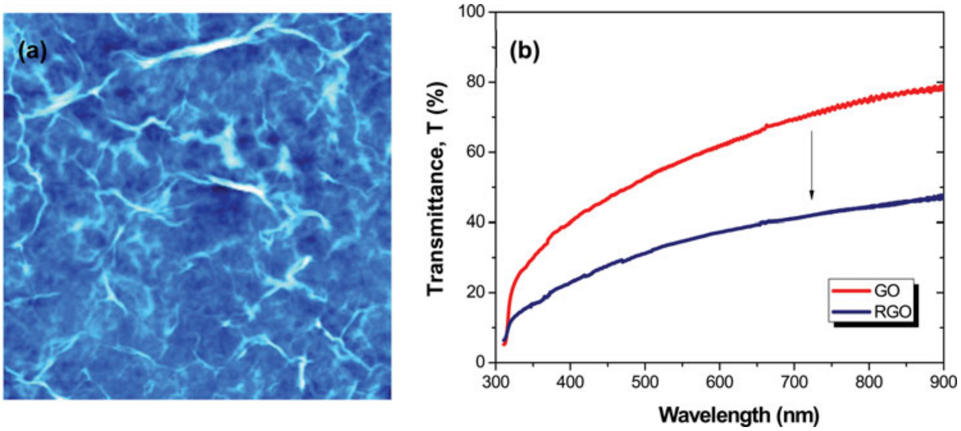


Figure 1. (a) Representive AFM image of the surface sectional profile of RGO thin film onto PET substrate (tapping mode, 25 × 25 μm scan size). (b) Optical transmission spectra of GO and RGO thin films onto PET substrate.

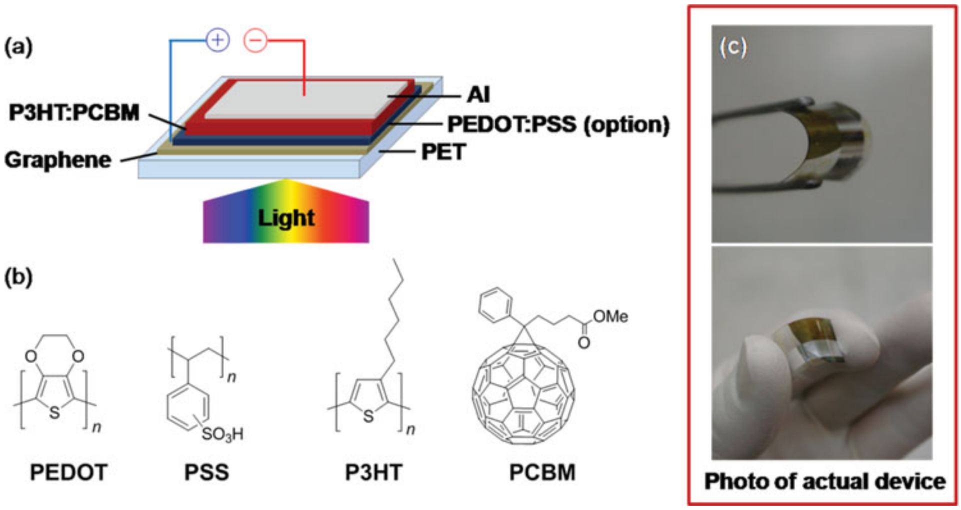


Figure 2. With and without an PEDOT:PSS hole transport layer. (b) The chemical structures of PEDOT:PSS and the active layer components P3HT and PCBM are also shown. (c) The photo-image shows graphene-based solar cell (Device III) being flexed.

The device structure of the bulk heterojunction solar cell is illustrated in Fig. 2. These devices studied in this work consists of, from bottom up, air-dried-RGO coated PET as a substrate with PEDOT:PSS (Device I) and vacuum-annealed-RGO coated PET as a substrate without PEDOT:PSS (Device II) and with PEDOT:PSS (Device III) thin-film as a hole transporting layer, P3HT:PCBM (1.25:1 w/w ratio) as an absorber, and aluminum (100 nm) top electrodes. Where applicable, annealing was performed at 120°C for 10 min for PEDOT:PSS layer and at 130°C for 5 min for P3HT:PCBM layer in an inert atmosphere each (see Fig. 2(c)).

The current devices were illuminated by 100 mW/cm^2 with air mass 1.5 filters (AM 1.5), as a solar simulator (450 W Xenon lamp (Oriel Instruments) and Keithley 2400 source meter). The course of illuminated J-V curves is far away from dark J-V curves, which indicates a relatively non-optimized device. Short-circuit current densities (J_{SC}), fill factors (FF), open-circuit voltage (V_{OC}) as well as the overall energy-conversion efficiency (η) drastically increase with increasing conductivity of the RGO cathode and PEDOT:PSS (Device II vs. Device III) (see Fig. 3). In experiments comparing η of Device I with Device III, the Device III has enhanced over 4.6 times more than that of the Device I. This is attributed to the increased conductivity of RGO electrode under vacuum annealing at 140°C (see Table 1).

The conductivity of the electrodes is important to consider as they can affect both the photocurrent and fill factor device parameters. The higher conductivity leads to the energy gain from the lateral charge collection through the P3HT:PCBM active layer become much more apparent. For cells with and without PEDOT:PSS layer for Device III and Device II, the V_{OC} are increased to 0.58 V and 0.47 V, respectively. This result is further evidence that the PEDOT:PSS layer to the vacuum-annealed-RGO thin film efficiently transfer photogenerated positive charge carriers from within the device. Compared to Device II without PEDOT:PSS layer, the efficiency of the Device III with PEDOT:PSS layer was improved, which indicates the effective work function of the cathode system. The energy

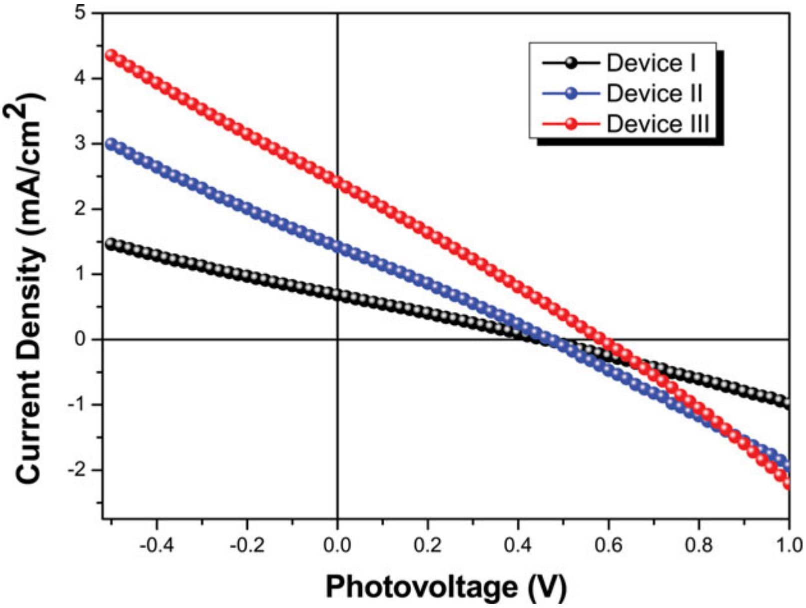
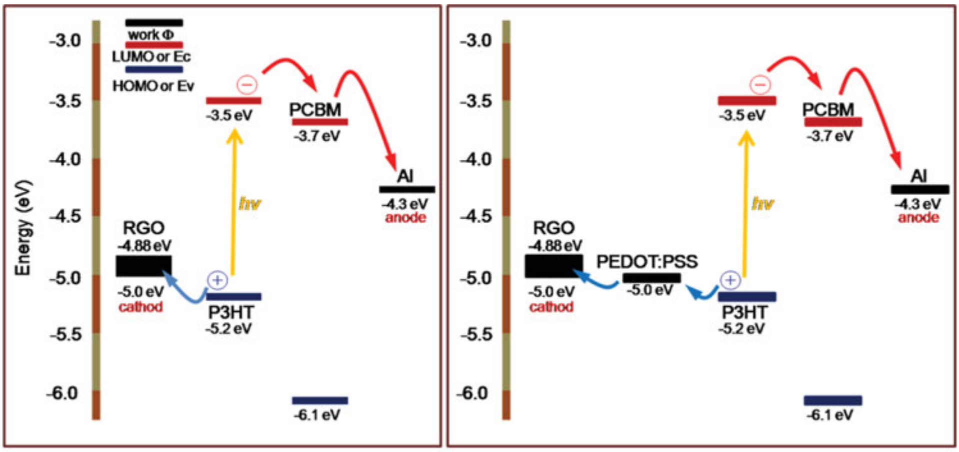


Figure 3. *J-V* characteristics of devices having the semi-transparent RGO cathode under simulated solar light illumination (AM 1.5).

level of the cathode system for Device III (RGO/PEDOT:PSS/P3HT:PCBM/Al) should provide cells with efficient pathways for carrier collection. According to the previous reports, the work function of RGO is located at −5.0 – −4.8 eV depending on film preparation conditions (see Figure 4) [7]. Here, we assumed a local work function of −4.8 eV. The Device II (RGO/P3HT:PCBM/Al) show lower open-circuit voltages than those that do employ PEDOT:PSS (−5.0 eV). It is possible that this is related to a small amount of recombination occurring preferentially on the RGO electrode. The PEDOT:PSS layer would block holes traveling from P3HT to RGO more effectively compared to Device II, that is. We compare Device III with the device in Refs [5,8,9] through a thermal annealed at 1100°C only to show efficiencies on RGO electrodes, but it is difficult to compare it with the devices in Refs. [5,8,9] onto quartz substrate because of the use of other materials and different device structures. Su et al. [5] investigated the P3HT:PCBM blend solar cell on 1100°C-thermal-annealed-RGO doped with large-aromatic donor molecule and showed a

Table 1. Short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and relative power conversion efficiency (η) for photovoltaic cells with semi-transparent RGO cathode under white illumination (AM 1.5) through semi-transparent RGO cathode

	Conductivity of RGO films (S/cm)	intensity (mW/cm^2)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
Device I	10.6	100	0.68	0.46	0.260	0.08
Device II	14.1	100	1.42	0.47	0.263	0.18
Device III	14.1	100	2.41	0.58	0.264	0.37



(a) **Device II** (b) **Device III**

Figure 4. Energy level diagram for Device II and Device III.

remarkable efficiency of 1.12% under 100 mW/cm^2. The other 1100°C-thermal-annealed-RGO electrode onto quartz for solar cells reported the 0.1 – 0.84% [8–11]. In comparison, our flexible Device III are processed at low temperatures with a vacuum annealing RGO layer at 140°C and have a high overall-efficiency of 0.37% in spite of a relatively low transmittance. In addition, our results might provide a new solution to solve the mass-productibility graphene-based flexible devices "thermal annealing-economic trade off" existing in Reduced Graphene Oxide to some degree, suggesting this method will open a new direction for future low-cost plastic opto-electronic devices. Table 1 provides a summary of the current devices measured photovoltaic performances.

4. Conclusion

We have first described a new and convenient method to fabricate flexible thin-film, semi-transparent, and conductive RGO films as hole-collector through low temperature processing. Moderate vacuum annealing can enhance its electrical conductivity. We have also presented the results of highly efficient organic photovoltaic cells based on flexible GRAPHENE electrode on plastic substrate, which indicate that this fabrication method may be suitable for flexible electrode. This method has the advantages of being ultralow-cost processing, large area, lightweight, and compatibility with flexible substrates for the plastic electronic devices, suggesting this method will open a new direction for future low-cost plastic electronic devices.

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