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Polymer photovoltaic devices with transparent graphene electrodes produced by spin-casting

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ABSTRACT

Large-area, smooth, transparent and conductive graphene films were produced by a spin-coating method using graphene solutions. Bulk heterojunction polymer organic photovoltaic devices using these pure graphene films as a transparent anode were fabricated and studied. A direct pure graphene film electrode ensured that the device fabrication cost remained low and the processing was simple. The photovoltaic device displayed a power-conversion efficiency of 0.13%.

Conversion of solar energy into electricity is becoming more important in our age of rising energy crises and global climate change. Bulk heterojunction polymer organic photovoltaic cells (OPVs) fabricated using solution processing have shown the potential to harness solar energy in a cost-effective way [1]. Some of the important advantages of these OPVs include ease of processing, compatibility with flexible substrates, et al. Transparent electrode materials are the essential components of OPVs. Presently, the state-of-the-art transparent anode uses indium tin oxide (ITO) for OPVs. However, ITO is becoming increasingly expensive due to the conventional fabrication process and the limited availability of the element indium [2]. As such, much research has been devoted to find a simple solution-based route to fabricate an inexpensive transparent electrode for optoelectronics.

Graphene, as a rapidly rising star in material science [3,4], is a very promising transparent electrode material because of its excellent optical and electrical properties [5,6]. Recently, graphene-based materials used as window electrodes for OPVs have been prepared [7–9]. Direct pure graphene films produced by spin-casting graphene solutions as electrodes ensure that the fabrication cost remains low and that the processing is simple. However, the fabrication of graphene electrodes so far for OPVs is associated with either high temperature chemical vapor deposition process or using graphene composite materials. While currently the best reported OPVs use polythiophene polymers as the active electron donating material, so far no study has been reported using pure, spin-coated graphene films as electrodes for polymer OPVs. Herein, we demonstrate polymer OPVs using pure graphene films as the transparent anode fabricated by spin-coating graphene solutions directly, with poly-(3-hexylthiophene) (P3HT) as the electron donor and phenyl-C61-butyric acid methyl ester (PCBM) as the acceptor.

Compared with exfoliation of graphite [10] and epitaxial growth on silicon carbide [11], easy chemical synthesis and solution processable functionalized graphene (SPGraphene) can greatly facilitate the fabrication of graphene-based nano-electronic devices. Reproducible and uniform graphene films can be generated by a spin-coating method. After spin-coated

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deposition, the insulating SPGraphene films are reduced through exposure to hydrazine vapor and then annealed in inert conditions to render the material electrically conductive (Supplementary material) [5].

Fig. 1 shows the UV–vis–Near IR (NIR) spectra of the spin-coated SPGraphene film on quartz substrate (~40 nm) and the reduced graphene films (~25 nm) from these films with different reduced methods. Overall, the spectra showed increasing red shift with better reduction. For example, compared with SPGraphene (λ_{max} – 220 nm), the film (hydrazine + 700 °C treatment, λ_{max} – 272 nm) demonstrated a red shift of 52 nm. Also the absorption in the whole spectral region increases significantly, indicating that much of the electronic conjugation within the graphene sheets is restored [12].

We find that independent of temperature annealing, the graphene films (~25 nm) have a flat optical transmittance profile across the whole visible and NIR region of the spectrum (Fig. 2). The graphene films reduced with hydrazine
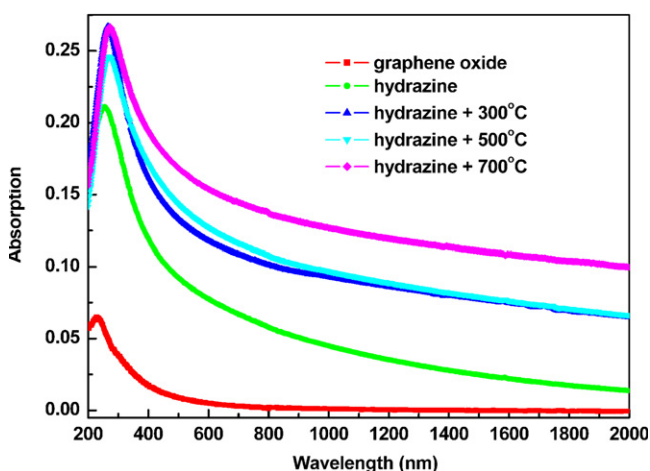
and different temperatures of 300, 500 and 700 °C annealing have transmittances of 75%, 73% and 69% at a wavelength of 550 nm, respectively. This darkening of the reduced material has been observed previously and is due to the partial restoration of the π-electron system in the graphene structure [5]. Such films are also likely to find application for transparent conductors in the NIR.

The electrical conductivity of the as-prepared graphene film is closely related to the annealing temperature. At a given film thickness of ~25 nm, concomitant increase of film conductivity was observed with an increase in the annealing temperatures from 300 to 700 °C. By plotting sheet resistances versus different annealing temperatures, the electrical char-

Table 1 – Comparison of the sheet resistance and conductivity of the films (~25 nm thickness) versus different reduced methods.

Graphene films	Sheet resistance (Ω/sq)	Film conductivity (S/cm)
Hydrazine	$1.80 * 10^{10}$	$2.53 * 10^{-4}$
Hydrazine + 300 °C	$6.18 * 10^{5}$	$6.47 * 10^{-1}$
Hydrazine + 500 °C	$7.25 * 10^{4}$	5.74
Hydrazine + 700 °C	$1.79 * 10^{4}$	$2.23 * 10$

Fig. 1 – UV–vis–NIR absorption spectra of SPGraphene film (~40 nm) and the graphene films (~25 nm) with different reduced methods.

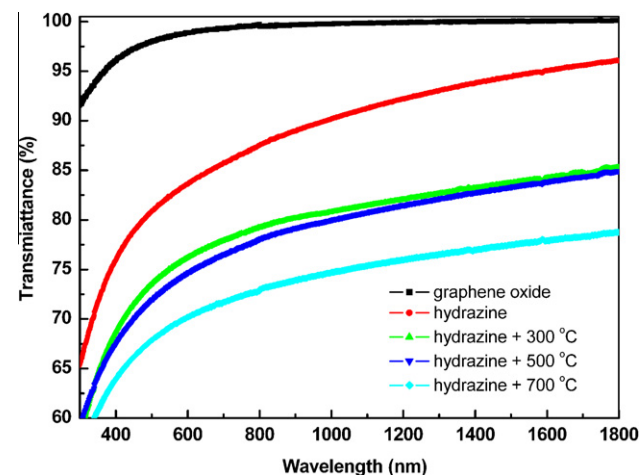Fig. 2 – Optical transmittance spectra of SPGraphene film (~40 nm) and graphene films (~25 nm) with different reduced methods.
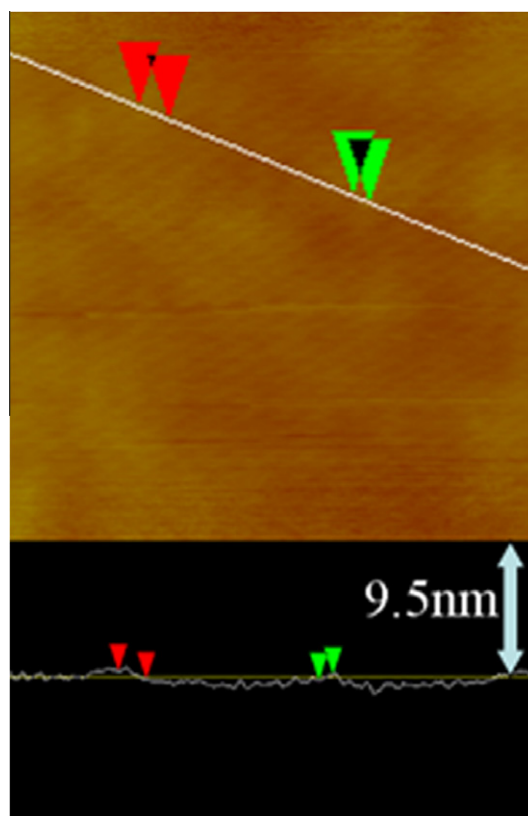

Fig. 3 – Surface morphology of graphene films (hydrazine + 700 °C). AFM height images (2.4 * 2.4 μm^2) of ~25 nm thick graphene surfaces. The surface roughness of the as-prepared graphene film over a 2.4 * 2.4 μm^2 area is ca. 0.55 nm.

acteristics of the as-prepared ~25 nm graphene films were evaluated (Table 1). Under our conditions, the reduced graphene films could have a sheet resistance of 17.9 kΩ/sq (transmittances of 69% at 550 nm) and a conductivity of 22.3 S/cm. The conductivity is comparable with that obtained using the more complicated graphene composites [9].

The average surface roughness of the as-prepared graphene film (hydrazine + 700 °C) over a $2.4 * 2.4\ \mu m^2$ area is ca. 0.55 nm (Fig. 3). It is widely accepted that the surface roughness of the electrodes is crucial for optoelectronic device performance [12]. In contrast to the rough fluorine tin oxide (FTO)

surface [13], which might short-circuit cells, an ultrasmooth surface is a prominent characteristic of the graphene films.

To demonstrate how the pure graphene films performed as the transparent anode in OPV devices, polymer OPVs were fabricated (Supplementary material). Fig. 4a shows the device structure and its energy diagram with the structure of quartz/graphene(hydrazine + 700 °C)/poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/P3HT:PCBM/LiF/Al. It can be seen that there is no current response in darkness for the OPVs, and the high dark current under forward bias indicates a distinct diode behavior. The current density–
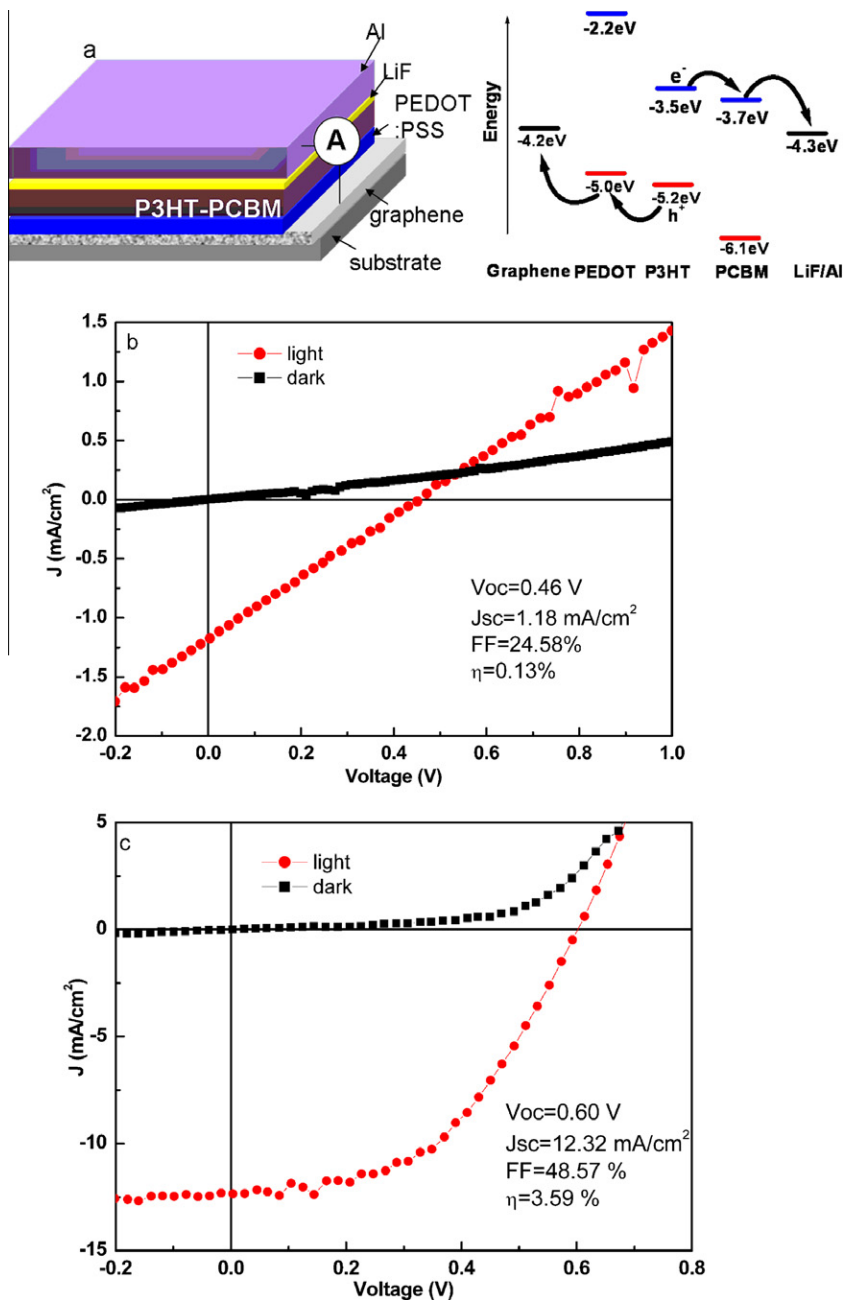

Fig. 4 – (a) Device structure and energy diagram of the fabricated device with structure quartz/graphene/PEDOT:PSS/P3HT:PCBM/LiF/Al. (b) Current density–voltage (J–V) curves of P3HT:PCBM bulk heterojunction solar cells with ~25 nm thick graphene films as the transparent anode. (c) Current density–voltage (J–V) curves of P3HT:PCBM bulk heterojunction OPVs with ITO as anode.

voltage (*J*–*V*) characteristic of the device under illumination of simulated solar light shows a short-circuit photocurrent density (J_{sc}) of 1.18 mA/cm^2 with an open-circuit voltage (V_{oc}) of 0.46 V, a calculated filling factor (FF) of 24.58%, and an overall power-conversion efficiency (PCE) of 0.13% (Fig. 4b). The low PCE is likely due to several reasons. First, the sheet resistance of graphene films needs much more improvement than ITO. Second, the reduced graphene film surface is hydrophobic, which makes it rather hard to get uniform PEDOT:PSS layer at this stage [7]. So it is highly possible that with optimized graphene-electrode conductivity and graphene film surface wetting property, the performance of these graphene-electrodes OPVs should be improved significantly. But compared with literatures, the PCE of our simple solution-processed graphene OPVs is still higher than or comparable to that of analogous cells fabricated using more complex process graphene anodes [8]. For the purpose of comparison, under the same conditions, our own testing using ITO as the electrode for the control OPVs gave V_{oc} = 0.60 V, J_{sc} = 12.32 mA/cm^2, FF = 48.57%, and PCE = 3.59% (Fig. 4c).

In conclusion, we demonstrated a solution process for fabricating conductive, transparent, ultrasmooth graphene films to replace conventional ITO electrodes in polymer OPVs. The advantages of our approach include a cost-effective, simple solution process using graphene solutions, which makes these graphene-based window electrodes versatile for applications not only in polymer solar cells described in this work, but also in other optoelectronic devices, such as flat-panel displays, and organic light-emitting devices.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.05.017.

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