The role of surfactant-treated graphene oxide in polymer solar cells: Mobility study

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ARTICLE INFO

ABSTRACT

In our previous work, the device performance of polymer solar cells (PSCs) was enhanced by blending surfactant-treated graphene oxide (GO) nanocomposites [didodecyldimethyla-mmonium bromide (DDAB):GO] as the active layer. However, its underlain mechanism is not clearly reported. In this work, therefore we measured the charge carriers mobility of the active layers before and after blending GO:DDAB nanocomposites to reveal the role of GO:DDAB in PSCs, and found that GO:DDAB can form three-dimensional network for charge carriers transport, meanwhile 'traps' for electrons can be introduced by GO:DDAB and formed in the bulk and/or at active-layer/electrode interfaces, compromising the electron mobility. Meanwhile, the hole mobility was improved due to the enhanced crystallinity of the composite films after blending GO:DDAB into P3HT:PCBM. Therefore, the transport balance between electrons and holes is enhanced and thus the device performance is improved.

1. Introduction

Polymer solar cells (PSCs) have been widely investigated in recent decades due to their special advantages of low cost, beneficial optical and mechanical properties, and ease of large-area fabrication by roll-to-roll or printing [1]. Recently, the power conversion efficiency (PCE) of polymer/fullerene blend solar cells has been enhanced significantly over the past two decades, and it exceeds 10% [2], which still lags behind those of the most efficient tandem cells, mainly due to the relatively small absorption overlap with the solar spectrum. Therefore, searching for new materials as donors and acceptors with better energy-level matching, stronger light absorption and higher charge mobility with high stability are urgent research topics, which leads to the investigation of other allotropic forms of carbon nanomaterials, including single- and/or multi-walled carbon nanotubes as acceptors. As a very recent rising star in materials science with two-dimensional structure and consisting of sp^2-hybridized carbon, graphene exhibits remarkable electronic and mechanical properties that meets its applications in future photovoltaic devices [3–6].

Two basic questions should be considered to develop polymer:graphene nanocomposites: (i) the dispersion of graphene in organic solvents, and (ii) the interfacial adhesion between the graphene and the polymers. In order to get highly dispersible graphene oxide (GO) sheets in o-dichlorobenzene, we have synthesized GO:(didodecyldimethyla-mmonium bromide, DDAB) nanocomposites by attaching DDAB onto the GO sheets via ionic interactions and mild sonication, and have obtained enhanced-performance of PSCs by blending GO:DDAB nanocomposites into the copolymer as active layer [7]. However, the detailed mechanism is not clear then and a comprehensive study in terms of electrical conductivity and crystallinity of the active layers is still needed.

Therefore, in this work we explore the underlain mechanism for the performance enhancement of PSCs by measuring the mobility of charge carriers in the active layer to explore the role of the GO:DDAB nanocomposites in PSCs. Our experimental data show the enhanced performance of PSCs by adding GO:DDAB into poly (3-hexylthiophene-2,5-diyl) (P3HT) [6,6]:-Phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$) as the active layer comes from the enhancement of transport balance between electrons and holes.

2. Experimental

2.1. Materials

GO was made from pure graphite (Alfa Aesar, 99.999% in purity) by a modified Hummers method [8]. DDAB was added into the stock solution of GO in aqueous solution to yield a mass ratio of about 1:4 for GO to DDAB. The preparation of GO and its aqueous solution, and the transfer of GO in aqueous solution into organic solution were reported in our previous work [7].

P3HT (average Mn 15,000–45,000, > 99.9%), $PC_{61}BM$ (910.88, > 99.5%) and PEDOT:PSS (Viscosity, 8 mPa s) were bought from Sigma Aldrich Chemicals without any further purifications.

2.2. Device fabrication

Firstly, ITO substrate (Xiangcheng Technology Co. LTD, Resistivity: $\leq 8\ \Omega$, Shenzhen, China) was cleaned for 15 min by ultrasonication with DI water, acetone and isopropyl alcohol (IPA), sequentially. The PEDOT:PSS layer was annealed at 150 °C for 15 min. Then the device was transferred to a nitrogen glove box, where the blend active layer of $P3HT:PC_{61}BM$ (or $P3HT:PC_{61}BM:(GO:DDAB)$) was spin-coated onto the PEDOT:PSS. Finally, Ca and Al electrodes were evaporated successively onto the active layer to complete the device ITO/PEDOT:PSS/Active-layer/Ca/Al at a pressure of ca. 3.0×10^{-4} Pa through a shadow mask.

Similarly, 'hole-only' device ITO/PEDOT:PSS/P3HT:PCBM/Au and 'electron-only' device Al/P3HT:PCBM/Al were fabricated to measure the mobility of holes (μ_h) and the mobility of electrons (μ_e), respectively.

2.3. Device characterization

The current density-voltage (J-V) characteristics were measured with a computer-controlled Keithley 236 SourceMeter. A xenon lamp coupled to AM1.5 solar spectrum filter was used as the light source, and the incident light intensity was 100 mW/cm^2. The Surface Profilometer (Tencor, ALFA-Step 500) was used to estimate the thickness of active layers. The Raman spectroscopy (RS, RM2000, Renishaw) was taken with an excitation wavelength of 532 nm. The phase identification was determined by X-ray diffraction (XRD) (Rifaku D/MAX-2004) with Cu Kα radiation ($\lambda = 1.54178$ Å) operating at 40 kV and 60 mA.

All the measurements were done in N_2-filled box at room temperature without any encapsulation.

3. Results and discussion

Firstly, we fabricated the solar cells ITO/PEDOT:PSS/$P3HT:PC_{61}BM:(GO:DDAB)$/Ca/Al (Device **A**) and the control devices ITO/PEDOT:PSS/$P3HT:PC_{61}BM$/Ca/Al (Device **B**), and found the open-circuit voltage (V_{oc}) of the device **A** is almost same as that of device **B** but the short-circuit current (J_{sc}) of device **A** is larger than that of device **B**, consequentially, the power conversion efficiency (PCE) is enhanced from 3.08% to 3.64% after blending GO:DDAB into $P3HT:PC_{61}BM$ as the active layer, as shown in Fig. 1. Also, Table 1 shows all the photovoltaic parameters obtained in the experiments, including those for the P3HT:indene-C_{60} bisadduct (ICBA) based solar cells.

In order to know the underlain mechanism for the device performance enhancement, a comprehensive study in terms of the crystallinity and electrical conductivity of the active layer should be taken. Fig. 2 shows the schematic illustration of the process by transferring GO from water to o-dichlorobenzene solution. From here, one can see that DDAB is amphiphilic material and it can carry positive charges (NR_4^+) and negative charges. The hydrophilic head of the surfactant is adsorbed on the surface of GO sheets while its hydrophobic tail is oriented towards the aqueous phase. Therefore, the surfactant-supported
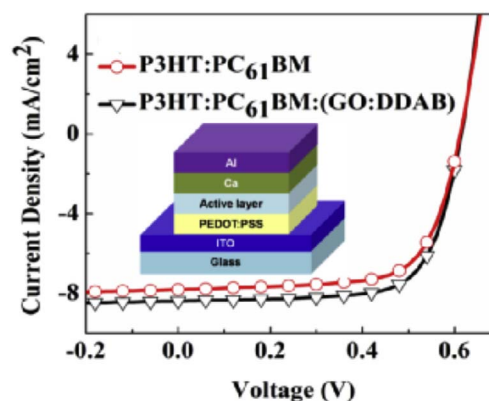

Fig. 1. J-V characteristics of the solar cells ITO/PEDOT:PSS/Active-layer/Ca/Al, in which $P3HT:PC_{61}BM$ doped with/without GO:DDAB as the active layer, respectively. The inset shows a schematic diagram of the device.

Table 1
Photovoltaic parameters obtained in our experiments for photovoltaic devices ITO/PEDOT:PSS/Active-layer/Ca/Al.

Active layer	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
$P3HT:PC_{61}BM$	0.61	7.57	66.31	3.08
$P3HT:PC_{61}BM:(GO:DDAB)$	0.61	8.39	70.73	3.64
P3HT:ICBA	0.85	9.20	63.84	5.01
P3HT:ICBA:(GO:DDAB)	0.85	9.27	68.79	5.34

functionalization of GO sheets can be realized through ionic interactions, and as a result a stable solution of GO:DDAB in o-dichlorobenzene can be obtained finally.

The XRD patterns of raw graphite, GO and GO:DDAB samples are shown in Fig. 3 (a). From here, one can see there is a strong diffraction peak at 24.4° for graphite and it corresponds to (002). After its oxidation and exfoliation processes, this peak disappears and a new peak appears at 7.4°. A broad and much lower diffraction peak appears at 23.5° after GO is attached to the surfactant DDAB. In the XRD pattern of $P3HT:PC_{61}BM$ (see Fig. 3 (b)), the diffraction of the crystallographic planes (100) appears at 5.68°. From here, one can see that the peak intensity at (100) for $P3HT:PC_{61}BM:(GO:DDAB)$ is higher than that for $P3HT:PC_{61}BM$, and it is the characteristics of the π-π stacking between benzene rings, and also it is the direct evidence for the enhanced crystallization of the nanocomposite films after blending GO:DDAB into $P3HT:PC_{61}BM$ [9].

Further, the Raman spectra of the GO and GO:DDAB are shown in Fig. 3 (c). From here, one can see three important peaks: the D peak, the G peak and the 2D peak. The appearance of D peak is due to the presence of defects, whereas the G peak is associated with the double-degenerated E_{2g} mode, and the 2D peak is due to the second-order zone boundary phonons [10]. The position and the intensity of the G band and 2D band provide us the information about the crystallinity and the number of layers [11]. Fig. 3 (d) shows the Raman spectrum of $P3HT:PC_{61}BM:(GO:DDAB)$ in o-dichlorobenzene, showing the strong G-mode of GO:DDAB but the D and 2D Raman modes of GO:DDAB are absent, and the absence of the D band implies a well ordered GO:DDAB [13] film, and theoretically the intensity of the 2D Raman mode decreases when the electron–electron collisions increase strongly for the high doping levels [14]. The inset in Fig. 3 (d) shows the Raman spectrum of $P3HT:PC_{61}BM$ and one can see many modes occurred in it. Here, we pay attention to the C-C skeletal stretch mode and the symmetric C=C stretch mode since these two stretch modes determine the electron conductivity of P3HT [12].

Usually, higher charge carrier mobility (μ) could benefit to a larger photocurrent and then a higher fill factor, and μ_h and μ_e can be derived from 'hole-only' and 'electron-only' devices, respectively, by using the