



# Hole extraction layer utilizing well defined graphene oxide with multiple functionalities for high-performance bulk heterojunction solar cells

Chao Li, Xiaoming Yang, Yue Zhao, Pan Zhang, Yingfeng Tu<sup>\*</sup>, Yaowen Li<sup>\*</sup>

*Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China*

## ARTICLE INFO

### Article history:

Received 28 May 2014

Received in revised form 25 July 2014

Accepted 3 August 2014

### Keywords:

Graphene oxide

Hole extraction layer

Energy level alignment

Interfacial dipole

Organic solar cell

## ABSTRACT

A simple method for synthesizing a series of graphene oxide with precise oxidation (pr-GO) (mild oxidation, moderate oxidation and severe oxidation) by strictly controlling pre-oxidation steps, oxidant content and oxidation time has been successfully developed. The well defined pr-GO as hole extraction layer (HEL) presented multiple functionalities, like modulation of work function, enhanced interfacial dipole, and excellent film-forming properties, which had significantly improved the efficiency and stability of organic solar cells. The P3HT:PC<sub>61</sub>BM system device based on pr-GO-3 HEL, which possessing well defined electronic structure and moderate oxidation, exhibited an improved 3.74% in power conversion efficiency and better air-stability compared to that of other pr-GOs and conventional PEDOT:PSS based devices. The well defined electronic structure pr-GO (i.e., suitable work function, larger interfacial dipole, and high repeatability) will provide better understanding in utilizing pr-GO film as HEL in future solar cell applications.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Organic solar cells (OSCs) with a bulk heterojunction (BHJ) active layer have been widely investigated due to their potential as a low cost renewable energy source [1,2]. The significant advantages of BHJ OSCs such as light weight, flexible, and large scale manufacture through roll to roll process techniques [3], and the competitive power conversion efficiency (PCE) by using new donor/acceptor photovoltaic materials and optimizing device structures [4–7], exhibit great application prospects. In order to realize its commercial applications, the major challenges for BHJ OSCs are the achievement of competitive PCEs and the

demonstration of long-term air stability [8], which are still largely limited by the poor charge extraction from the active layer to electrodes.

A hole/electron extraction layer is often required to maximize the device efficiency. An ideal hole extraction material should have a proper energy level alignment for improving hole extraction and selectively blocking electrons to diminish electron–hole recombination on anode. Moreover, the hole extraction material should also have solution processability and good film-forming property for low-cost device fabrication [9,10], and neutral chemical property for benefiting device lifetime. However, the widely used hole extraction layer (HEL), poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS), suffers from poor device lifetime due to its acidic and hygroscopic nature while other HELs, such as semiconducting metal oxides (e.g., NiOx, MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>) [11], always need to be vacuum-deposited with a high manufacturing cost [12–14].

<sup>\*</sup> Corresponding authors. Tel.: +86 512 65884930; fax: +86 512 65882130.

E-mail addresses: [tuyingfeng@suda.edu.cn](mailto:tuyingfeng@suda.edu.cn) (Y. Tu), [ywli@suda.edu.cn](mailto:ywli@suda.edu.cn) (Y. Li).

Graphene oxide (GO) is an oxidized derivative of graphene, which can be readily synthesized by chemical oxidation of naturally abundant graphite to yield stable aqueous dispersion of single layer sheet with the thickness of around 1 nm [15]. The widely accepted structure of GO consists of two region: an aromatic region with  $sp^2$ -hybridized carbon and an oxidized region that contains carbon with oxygenated functional groups such as hydroxyl, epoxy, carboxylic, and carbonyl groups. The GO with oxygen-rich groups shows a synergistic effect to have the solution processability, band-gap, high transparency and conductivity. Recently, GO based HEL materials have been widely studied due to the no obvious detrimental effect on the device life time and large band gap which can help block electron flow towards the anode and effectively suppressing the carrier recombination, where the GO HEL with thickness of several nanometers [16–21]. However, it suffers from relatively low and huge variations in device efficiencies owing to its uncontrollable energy level alignment and insulating property [16–23]. Although some researchers have proved that the modulation of work function and conductivity of GO can be achieved by changing oxygen concentration, which can be realized by reduction of GO and adjusting the thickness of GO film [24–26], the complexity of oxidation–reduction process, oxygen defects during reduction and uncontrollable thickness lead to the limitation of the above methods. Meanwhile, the existence of two kinds of regions in GO ( $sp^2$ -hybridized carbon and an oxidized region) can make  $\pi$  electrons to produce surface  $C^{\delta+}-O^{\delta-}$  dipoles, which will have effect on the built-in potential of the device in certain extent, consequently the performance of OSCs. Therefore, achievement of perfectly defined electronic structure of GO by a simple method is especially important. It remains a big challenge to design GO-based materials with controlled electronic properties as HEL for high-performance device applications.

Here, we developed a simple method for synthesizing a series of graphene oxides with precise oxidation (pr-GOs) (mild oxidation, moderate oxidation and severe oxidation) by strictly controlling pre-oxidation steps, oxidant content and oxidation time using modified Hummers' Method [27]. A homogeneous and smooth ultrathin-film with  $\sim 3$  nm thickness could be obtained by spin-coating from aqueous solution due to the uniform dispersion of pr-GOs single layer flakes in water. The well defined pr-GO films with varied oxidation showed the excellent transparency and controllable work functions. Unlike the undefined GO, the well defined electronic structure of pr-GO films as HELs can be highly repeatable when applied in the poly(3-hexylthiophene): [6,6]-phenyl  $C_{61}$  butyric acid methyl ester (P3HT:PC<sub>61</sub>BM) based OSCs. They can efficiently promote the formation of interfacial dipole and ideal Ohmic contact between anode and P3HT, consequently increasing the charge transportation by the enhanced built-in potential and hole collection on anode, respectively. As demonstrated in this study, the pr-GO-3 with moderate oxidation surpasses the other pr-GOs and most existing hole extraction materials, in terms of the device efficiency, stability, and repeatability, to facilitate the development of high air-stable and performance OSCs.

## 2. Experimental

### 2.1. Materials and synthesis

Graphite was purchased from Uni-Chem. All reagents and chemicals were purchased from commercial sources (Aldrich, Across) and used without further purification unless stated otherwise. P3HT and Phenyl- $C_{61}$ -butyric acid methyl ester (PC<sub>61</sub>BM) were purchased from Rieke metals and Luminescence Technology Corp, respectively. PTB7 and Phenyl- $C_{71}$ -butyric acid methyl ester (PC<sub>71</sub>BM) was purchased from Organic Nano Electronic material and American Dye Source, respectively.

The precise control of oxidation was simply processed by carrying out pre-oxidation ( $H_2SO_4$ ,  $K_2S_2O_8$ , and  $P_2O_5$ ) or not, the amount of oxygenant ( $NaNO_3$  and  $KMnO_4$ ) and reaction time. All pr-GOs were synthesized by the modified Hummers' method. For pr-GO-4, 2 g of graphite powder were put into a solution of  $H_2SO_4$  (98%, 8 mL),  $K_2S_2O_8$  (1.6 g), and  $P_2O_5$  (1.6 g) with continuous stirring for 4.5 h at 80 °C. After that, the mixture was cooled to room temperature and diluted with 0.5 L water and left overnight. The mixture was filtered using a 0.2  $\mu m$  filter to remove the residual acid and washed thoroughly with water. After drying at room temperature overnight, this pre-oxidized graphite was stirred with 2 g of  $NaNO_3$  and 100 mL of concentrated  $H_2SO_4$  for 1 day in an ice water bath. Afterwards, 12 g of  $KMnO_4$  was gradually added. Once it was mixed well, the ice bath was removed and the solution was stirred at 35 °C until a highly viscous liquid was obtained. After adding 100 mL of pure water, the suspension was heated in a water bath at 98 °C for 15 min. Then, it was further treated with warm water and  $H_2O_2$  in sequence. The mixture was centrifuged at 6000 rpm and washed with HCl and water. The centrifuging and washing processes were repeated a few times. Finally, pr-GO-4 was dried at 50 °C for 24 h in a vacuum oven. For pr-GO-1, pre-oxidation procedure was removed, and the oxidant content and reaction time were half of pr-GO-4, other procedures were the same as pr-GO-4. While for pr-GO-2, the oxidant content and reaction time were half of pr-GO-4, the following procedure is same. For pr-GO-3, just the reaction time was half of pr-GO-4, then using modified Hummers' method. Finally, all graphite oxide dispersions were exfoliated by water-bath ultrasonication (300 W) for 1 h.

### 2.2. Measurements and characterization

X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 (Thermo-VV Scientific) instrument, and element analysis were recorded on Vario micro cube. UV–visible absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. SKPM measurements were carried out under ambient conditions, using a Park XE-120 microscope (Park Systems Corp., Suwon, Korea) operating in the tapping mode regime, using Ti-Pt coated conducting atomic force microscopy (AFM) tips (NSC19, Mikromasch, Tallinn, Estonia). The samples were prepared by spin-coating onto ITO at 2000 rpm from sample solutions. Typical scan line frequency was 0.3 Hz and each image contained 512 pixels (512 pixels). In standard SKPM

Download English Version:

<https://daneshyari.com/en/article/10565889>

Download Persian Version:

<https://daneshyari.com/article/10565889>

[Daneshyari.com](https://daneshyari.com)