



Simple synthesis of solution-processable oxygen-enriched graphene as anode buffer layer for efficient organic solar cells



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ARTICLE INFO

Article history:

Received 20 April 2015

Received in revised form

6 August 2015

Accepted 12 September 2015

Available online xxx

Keywords:

Organic solar cells

Anode buffer layer

Solution processed graphene

Functionalization

Stability

ABSTRACT

Interface material is a must for highly efficient and stable organic solar cells (OSCs) and has become a significant part of OSC research today. Here, low-cost and oxygen functionalized graphene (FG) was synthesized via a simple two-step method for applications in OSCs as anode buffer layer. The FG shows excellent dispersion in aqueous solution and great process compatibility with spin coating process. The introduction of work-function-tunable FG can effectively improve short current density of the devices. The power conversion efficiency of FG-based devices (4.13%, 4.49%, and 7.11% for P3HT:PC₆₁BM, P3HT:PC₇₁BM and PBDTTT-C:PC₇₁BM, respectively) outperforms PEDOT:PSS-based devices (3.67%, 4.17%, and 6.46%, respectively). Moreover, the stability of the devices was improved with FG as anode buffer layer compared to PEDOT:PSS. The results indicate that simple synthesized FG is a promising solution-processed anode buffer layer material for high-efficiency and stable OSCs.

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1. Introduction

In the past few years, organic solar cells (OSCs), as an alternative to their inorganic counterparts, have been studied extensively because of many competitive advantages including their versatility for large-scale fabrication through roll-to-roll printing technique, flexibility, portability, lightweight, and low cost [1,2]. In spite of those advantages, the efficiency and lifetime of OSCs are still largely limited by, among other factors, poor charge extraction from active layer to electrodes. Thus, interface layer is required to maximize the device efficiency. An ideal anode buffer layer (ABL) in conventional structure should have good optical transmission and proper energy level to improve hole extraction and block electron to diminish electron–hole recombination. Moreover, the ABL should also have good solution processability and excellent film-forming property for low-cost device fabrication [3,4]. Poly(styrenesulfonate)-doped poly(ethylenedioxythiophene) (PEDOT:PSS) is the widely used buffer layer on an indium tin oxide (ITO) electrode. However,

PEDOT:PSS has a side effect on the stability of OSCs due to its high acidity and hygroscopic nature [5]. Transition metal oxide, such as nickel oxide (NiO), molybdenum oxide (MoO₃), vanadium oxide (V₂O₅), need to be vacuum deposited with high manufacturing cost [6–9]. As a result, low cost, long lifetime, air-stable, solution processable, and inert ABL materials are being investigated.

Graphene, a highly conducting material, has attracted considerable interest due to its physical, chemical, and electrical properties [10,11]. Different fabrication methods of graphene-based materials and devices have been developed, such as adhesive tape method [11], chemical vapor deposition (CVD) [12,13] and epitaxial growth [14]. However, producing high quality graphene over large areas is much difficult and requires high temperature and vacuum conditions. Additionally graphene without functionalization are insoluble and infusible. Poor processability has precluded pristine graphene materials for various potential applications. Recently, chemically derived graphene oxide (GO) was used in OSCs as the ABL [15–24]. However GO, derived from graphite, demonstrated poor device performance owing to its non-uniform size and shape with a scale of several hundred nanometers and even micrometers [25,26]. Dai et al. [27] reported a solution processable graphene oxide nanoribbon (GOR) with proper energy level alignment for optoelectronic applications. Using the GOR as hole-extraction material could significantly improve the performance of OSCs.

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Unfortunately, the purification process for GOR was quite cumbersome due to high content of residual single-walled carbon nanotubes (SWCNTs). Moreover, the size of SWCNTs is prohibitively large as the starting material.

In this work, motivated by the need to overcome the limitations of application of carbon material in OSCs, a much facile two-step method for functionalizing graphene (FG, which contains 40.17 at.% of oxygen) with an effectively tuned band gap was reported. The FG exhibited good solubility, excellent film-forming capability, high transparency and comparable work-function with indium tin oxide (ITO) coated glass. The photovoltaic performance of buffer layers was investigated by fabricating OSCs based on poly(3-hexylthiophene) (P3HT) or poly(4,8-bis-alkoxy-benzo [1,2-b:4,5-b'] dithiophene-alt-alkylcarbonyl-thieno [3,4-b] thiophene) (PBDDTT-C) as a donor and (6,6)-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or (6,6)-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as an acceptor. The OSCs with the FG as ABL show enhanced photovoltaic performance in comparison with the devices with PEDOT:PSS as the ABL. The power conversion efficiency (PCE) of 7.11% was achieved using PBDDTT-C:PC₇₁BM as active layer and FG as ABL, higher than that of 6.46% with PEDOT:PSS as ABL.

2. Experimental section

2.1. Materials

ITO coated glass with a sheet resistance of 15 Ω/sq was supplied by Shenzhen Display Co., LTD (China). PEDOT:PSS (Clevious PVP AI 4083) was supplied by H. C. Stark company. P3HT and PBDDTT-C were bought from FEM. Inc. and Solarmer, respectively. PC₆₁BM and PC₇₁BM were purchased from American Dye Sources (ADS). 1,8-Diiodooctane (DIO) was purchased from Sigma Aldrich. All materials were used directly without any further purification.

2.2. Synthesis and purification of pristine graphene (PG)

PG was prepared according to our previously published procedure [28]. By the reaction of tetrachloromethane (CCl₄, 3.0 mL) with potassium (K, 4.0 g) at 200 °C for 15 h in an autoclave, the product was achieved and washed subsequently by 18 wt.% hydrochloric acid (HCl), de-ionized water, acetone and de-ionized water. After dried at 100 °C for 12 h, about 0.3 g of PG was collected.

2.3. Functionalized graphene (FG)

Briefly, a mixture of PG (100 mg) and 98% H₂SO₄ (100 mL) was ultrasonicated in a water bath for 30 min and stirred overnight at room temperature. Then, potassium permanganate (KMnO₄, 300 mg) was added into the solution above and stirred for 2 h at room temperature. After the mixture solution was stirred at 70 °C for 2 h, extra KMnO₄ (200 mg) was added. Upon cooling down to room temperature, the obtained mixture was carefully poured into a mixture of ice (200 g), water (200 g), and hydrogen peroxide (H₂O₂, 4 mL) under stirring. Centrifugation (10000 rpm, 20 min) was then performed to remove surplus sulfuric acid. The resulted aqueous solution was centrifuged to remove black precipitate (large size graphene). The supernatant was further loaded in dialysis bag (3500 Da) to remove impurities in ionized state. After the pH of solution showed neutral, the FG solution was collected as final product.

The solubility of functionalized graphene (FG) in water was tested by a simple gravimetric method [29,30]. Gravimetric measurements of solubility were conducted by filtering a certain volume of saturated solution and drying graphene residue to measure the mass of graphene. This method gave a solubility value of

600 mg/L for FG. Figure S1 in the supporting information shows FG is well-dispersed in water, resulting in clear and homogeneous aqueous solution with a concentration of 600 mg/L.

2.4. Device fabrication

ITO glass substrates were cleaned sequentially with detergent, de-ionized water, acetone, and isopropanol, followed by drying with N₂ flow and UV-ozone treatment for 5 min. Then, the ABL was formed via spin coating. FG aqueous solution with the concentration of 300 mg/L was spin coated at 6000 rpm for 40 s. PEDOT:PSS aqueous solution was spin coated at 4000 rpm for 40 s, followed by heating at 160 °C for 10 min. The substrate was then transferred to a N₂ filled glove box. Then, the active layer was spin coated from the solution of P3HT:PCBM (1:1) in *o*-dichlorobenzene (36 mg mL⁻¹) at 600 rpm for 30 s, followed by thermal annealing at 150 °C for 10 min. PBDDTT-C:PC₇₁BM was prepared by spin coating (1300 rpm) its *o*-dichlorobenzene solution of 1:1.5 w/w, polymer concentration of 12.5 mg/mL with 3% volume ratio of DIO additive on the ITO/ABL electrode. Finally, the sample was transferred to a vacuum chamber and a 10 nm of Ca layer was thermally deposited on the photo active layer under a base pressure of 5 × 10⁻⁴ Pa. A 100 nm Al layer was thermally deposited on the top of Ca in vacuum. The active area of the device is 0.1 cm².

2.5. Characterization and measurement

Scanning electron microscope (SEM, JEOL JSM-6700F) and transmission electron microscope (TEM, H-7650) were performed to characterize the morphology and structure of graphene. Phase composition of graphene was studied by X-ray diffraction (XRD) with a Rigaku Mini Flex II system. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a VG ESCALab220i-XL electron spectrometer with 300 W Al K α radiation. UV–vis spectra were recorded from 300 nm to 900 nm on a Hitachi U-4100. Raman spectroscopy was conducted on the DXR Raman microscope (Thermo Scientific) using a 532 nm laser as the excitation source. The thickness of films was measured by Veeco Dektak150 surface profiler. The measurements on water contact angles were obtained on a homemade JY-82 contact angle system (China). The deionized water was obtained from Millipore ultrapure water system. Current density–voltage (J–V) characteristics of the devices were measured in N₂-filled glove box with a Keithley 2420 source measurement unit under simulated 100 mW/cm² (AM 1.5G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQEs) of solar cells were analyzed by using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

3. Results and discussion

PG powder was synthesized by solvothermal method as previously reported [28]. Solution-processable FG was prepared from oxidizing PG with KMnO₄ in concentrated H₂SO₄, slightly different from the published procedure [27,31]. As described in the literature [32], oxygen-containing functionalities such as carbonyl, carboxyl and hydroxyl existed at the edge and surface of the products to form oxygen-enriched graphene. The mechanism of functionalization of graphene appears to be similar to ‘unzipping’ of carbon nanotubes (CNTs) [31]. As depicted in Scheme 1, graphene opening could occur in a linear cut. The manganate ester formation is proposed as the first step under attacking of potassium permanganate, and further oxidation is possible to afford the dione in the dehydrating medium. Juxtaposition of the ketones distorts partial graphene backbone, making it more prone to next attack by

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