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High-performance polymer solar cells with moderately reduced graphene oxide as an efficient hole transporting layer

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ABSTRACT

As an alternative to the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole transporting layer (HTL) in polymer solar cells (PSCs), moderately reduced graphene oxide (GO) films fabricated by simple and fast thermal treatment of solution processed GO were investigated. PSC with thermally treated GO at 250 °C exhibited best performance with a power conversion efficiency (PCE) of 3.98%, compared to the PSC containing conventional PEDOT:PSS HTL with a PCE of 3.85%. Furthermore, the PSC with thermally treated GO showed superior stability compared to the PSC with conventional PEDOT:PSS HTL under the atmosphere condition without any encapsulation process. Our demonstration suggests that moderately reduced GO by simple thermal treatment could be promising HTL replacing PEDOT:PSS in PSCs as well as other organic electronics.

1. Introduction

Solution-processable polymer bulk-heterojunction (BHJ) solar cells have attracted constant attention as a cost-efficient power source [1–12]. In conventional BHJ solar cells, a poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) blend layer is sandwiched between a transparent anode and a low work-function metal cathode such as Ca/Al or LiF/Al. In this case, direct electrical contacts between the interfaces of active layer and electrodes lead to recombination of carriers and current leakage. Therefore, various hole transport layers (HTL) are being used to circumvent this issue. Water-soluble poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been widely used as an appropriate HTL for more efficient hole collection via alignment of work functions of P3HT and transparent ITO anode as well as improvement of contact between active layer and transparent anode by minimizing the detrimental effects of ITO roughness [13,14]. Although this layer helps PSCs achieve an improvement in efficiency, many of research group have tried to replace PEDOT:PSS due to the several problems including highly acidic and hygroscopic properties, leading to poor long-term stability [15]. To solve these problems, wide band gap p-type like inorganic materials such as V_2O_5, MoO_3, and NiO have been reported [16–20]. However, most of the inorganic HTLs are deposited using vacuum system, which is incompatible with solution-processable and printable PSCs. For this reason, very recently interest in a thin film of graphene oxide (GO) and reduced GO as an efficient HTL for high-performance PSCs has been emerged [21–24]. GO is a graphene sheet functionalized with oxygen groups in the form of epoxy and hydroxyl groups on the basal plane and various other types at the edges [25,26]. In GO, because most of carbon atoms bonded with oxygen is sp^3 hybridized, it disrupts the sp^2 conjugation of the hexagonal graphene lattice. Hence, the substantial sp^3 fraction in GO makes it an insulating material. Therefore, when the insulating GO was used as HTL, the device performance will be highly dependent on the thickness of GO due to its insulating property [24].

Jung et al. reported that incremental removal of oxygen in GO induces transition of GO from electrical insulator to semiconductor and ultimately to a graphene-like semimetal [27]. Although the reduction of GO can be effectively performed by chemical process using a hydrazine reagent, it is inadequate for mass production due to the toxicity of chemical reducing agent and multiple-steps [24]. In addition, the dispersion concentration of the reduced GO produced using hydrazine is low, which could also be disadvantageous for practical applications to the devices. Recently, it is reported that GO can be reduced with thermal methods, which are believed to be green methods without using any hazardous reductants. There have been two kinds of thermal methods reported. One is solvothermal reduction method, which usually needs harsh solvents such as N,Ndimethylformamide or

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N-methyl-2-pyrrolidinone, high pressure, and/or long reacting time [28–30]. The other is solid heating reduction method necessarily requiring ultra-high vacuum under Ar and H_2, and/or rapid heating (>200 °C min^{-1}) up to 1050 °C under Ar gas or up to 800 °C under H_2 gas [31–32]. These complicated and high temperature processes over 500 °C are not adequate to the simple and cost-efficient production of PSCs on various substrates.

In this study, we demonstrate a facile, low-cost and fast route to fabricate highly efficient PSCs containing moderately reduced GO by thermal treatment of GO films in air. GO films were prepared via solution process on ITO anode and then annealed under the various conditions of temperature, from 100 to 350 °C in air. Effect of heat treatment of GO HTL films on the cell-performances was characterized, and stability of PSCs with moderately reduced GO was compared to conventional systems including PEDOT:PSS HTL.

2. Experiments

For the use of GO as HTL, GO was prepared according to the previous report [33]. Graphene oxide was prepared by stirring 1 g of powdered graphite (Alfar Aesar, ~325 mesh) and 3 g of potassium permanganate (Sigma-Aldrich) into 23 mL of H_2SO_4 (Sigma-Aldrich, 98%) at room temperature for 30 min. And then, the temperature of the reaction mixture was increased to 40 °C, where it was maintained for 6 h. At the end of 6 h, 50 mL of de-ionized (DI) water was slowly added into the pasty mixture. The suspension was poured over 500 g of ice containing 10 mL of H_2O_2 (35 wt%, Sigma-Aldrich), and then the resulting bright yellow suspension was filtered through the PTFE membrane (polytetrafluoroethylene). After this, the remaining gel-like GO was thoroughly washed with diluted 1 M HCl followed by acetone and DI water. Finally, GO powder was freeze dried at −60 °C for 1 day. For device fabrication, this prepared GO powder was dispersed into DI water, and then the aqueous dispersion of GO was further diluted with N,N-dimethylformamide (DMF) at a concentration of ~1.5 mg/mL for the use as a coating solution.

ITO (Samsung Corning Co, Ltd.)-coated glass substrates were cleaned with a special detergent followed by ultrasonication in acetone and isopropyl alcohol and then kept in an 100 °C oven for 30 min. Before the preparation of HTL, all substrates were treated with UV/O_3 for 20 min to increase wettability of ITO surface. First, for the conventional device structure, PEDOT:PSS (Baytron P AI 4083) HTL with a thickness of ~30 nm was spin-coated onto the UV/O_3-treated ITO/glass substrates followed by annealing at 120 °C for 10 min. To characterize the effects of thermal treatment of GO on the device performance, GO HTL was spin-coated using the prepared dispersion of GO. Spin-coated GO layer was thermally treated at 150, 250, and 350 °C. P3HT:PCBM active layers were spin-coated onto the HTL coated substrate at 700 rpm for 60 s using o-dichlorobenzene (o-DCB) solution containing a 25 mg/mL of P3HT (Rieke Metals) and a 25 mg/mL of PCBM (Nano-C). Then, to obtain highly ordered active layer, the active layer coated substrates were kept in a glass jar at room temperature to evaporate o-DCB solvent slowly for 2 h in an N_2-filled glove box, followed by annealing at 110 °C for 7 min inside the glove box. Finally, top electrodes composed of LiF (0.7 nm)/Al (80 nm) with an area of 4.14 mm^2 were deposited using a thermal evaporator in vacuum with a pressure of 10^{-6} Torr.

Cell performance was measured using a Keithley 2400 instrument under 1 sun (100 mW/cm^2) using a xenon light source and AM 1.5 global filter. A reference Si solar cell certified by the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc) was used for calibration for accurate measurement. To analysis the effect of HTL on the stability of devices, change of cell performance was recorded as a function of exposed time in air using the same instrumental setup without any encapsulation process.

The optical properties of various GO and PEDOT:PSS HTLs were investigated via. UV–vis spectrophotometer with a Varian, AU/DMS-100S. The successful formation of various GO HTLs on ITO and surface morphologies of GO and PEDOT:PSS were measured by AFM using a Veeco Dimension 3100 instrument operated in tapping mode with a silicon cantilever. Degree of reduction of GO by thermal treatment under various temperature was compared through the XPS measurements using an AXIS-NOVA (Kratos) system with a monochromatized Al Kα under a pressure of 5×10^{-8} Torr.

3. Results and discussion

As shown in the schematics of device structure in Fig. 1, to confirm the potential of solution processed GO as HTLs and characterize the effects of simple thermal treatments of solidified GO films on the electronic properties of GO and performance of PSCs containing GO based HTLs, GO HTLs with a thickness of ~3 nm are prepared by spin-coating followed by thermal annealing at 150, 250, and 350 °C for 10 min in air. As we mentioned, because usual thermal reduction of GO requires ultra-high vacuum under Ar and H_2 and high temperature of ~800 °C–1000 °C under Ar gas or under H_2 gas, these conditions are not adequate to the simple production of PSCs on transparent electrode/glass substrate, even on flexible polymer films. Hence, we tried to characterize the possibility of moderately reduced GO

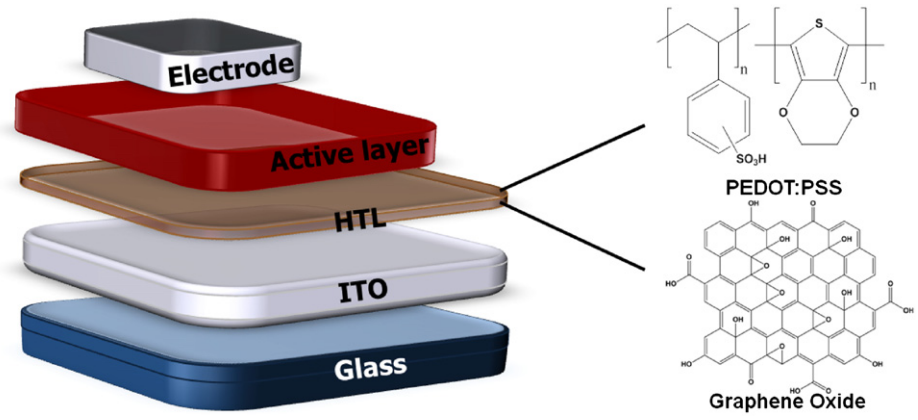

Fig. 1. Schematic of PSCs fabricated with PEDOT:PSS and GO.