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Efficient ITO-free polymer solar cells with pitch-converted carbon nanosheets as novel solution-processable transparent electrodes

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ABSTRACT

We demonstrate that pitch-converted carbon nanosheet (CNS) films can efficiently function as transparent conducting electrodes for polymer solar cells (PSCs). The solution-processed CNS film was prepared with spin-coating of a cost-effective pitch solution dissolved in dimethylformamide on quartz substrates, followed by stabilization and carbonization treatments to convert the pitch into CNS. The pitch-converted CNS films prepared by the successive heat-treatment process were examined as a novel transparent anode in solar cells, and as a result, PSCs fabricated directly on such CNS electrodes exhibited a high power conversion efficiency of ~1.7% under 100 mWcm^{-2} illumination and AM 1.5 G conditions. This approach could be highly desirable for advancing the realization of fully printable and flexible low-cost transparent electrodes for indium tin oxide (ITO)-free polymer solar cells.

1. Introduction

Polymer based bulk-heterojunction solar cells (PSCs) have drawn a great attention due to their unique features such as low-cost large-area compatibility, lightweight portable and printable properties, and mechanical flexibility [1–3]. However, currently, such ideal devices are highly limited due to the use of indium tin oxide (ITO) that has a high-cost indium component and inherent mechanical brittleness [4,5]. To solve such drawbacks of ITO electrodes, various transparent conducting materials, such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [5–7], metal grids or nanowires [4,8], and carbon nanotubes [4,9], have been continuously investigated as ITO-alternative materials.

Among these materials, graphene that is a single and two-dimensional (2D) carbon sheet composed of sp^2-hybridized carbon has also attracted a significant interest as a promising ITO-replacement because of its outstanding optical, electrical, and mechanical properties [10–12]. Among the general methods to produce graphene thin films such as micromechanical exfoliation, epitaxial growth, reduction of graphene oxide (GO), and chemical vapor deposition (CVD), the last two methods have been widely used to obtain graphene materials for trasnparent electrode applications [11]. The chemically reduced graphene oxide (r-GO) has been considered as a cost-effective conducting material due to its advantages of high throughput preparation, low-cost process, and the simplicity of the fabrication technique. However, the high sheet resistance and poor conductivity induced by many oxygen functional groups in the r-GO films made it rather hard to obtain a high solar cell-efficiency; the r-GO electrodes showed cell-efficiencies in the range of 0.1–1.01% [11–15]. On the other hand, the CVD-grown graphene electrodes, prepared using vaporized carbon sources on catalytic Ni or Cu under a H_2/Ar or other inert atmospheres, showed relatively high power-conversion-efficiencies in the range of 1.23–1.97%, and after a doping treatment, the cell-efficiency was increased up to ~2.6% [11,12]. However, to obtain such high-quality graphene films to be useful in practical device applications, additional physical graphene transfer processes to a reciever substrate, metal-catalyst elemination processes, and special care during the processes are essentially required.

For these reasons, several research groups have explored various methods to fabricate novel graphene based carbon material films [16–20]. For example, graphene quantum dots derived from pitch, one of the cheapest precusor used for carbon fiber production, and microwave extration of graphene from

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polyacrylonitrile (PAN)-based carbon fibers having graphene sheets with turbostratic structures have been recently introduced [19,20]. In particular, Byun et al. reported a scalable and sustainable process to form few-layer graphene films from common polymers such as polystyrene (PS), PAN, and polymethylmetacrylate (PMMA) on a SiO_2/Si substrate by capping the films with a metallic layer, followed by a heat-treatment at 1000 °C under low vaccum in an Ar/H_2 atmosphere [16]. Although they still used a metallic capping layer as a catalyst, the polymer-converted carbon nanosheet films that were created using an inexpensive polymer and a simple solution-based process could be highly desirable for the realization of low-cost and printable transparent electrodes. However, although most of the above-mentioned studies have been succesfully demonstrated as attractive methods to produce carbon-based materials, they did not provide atomically thin carbon sheets with tunable electrical and optical properties, which is highly benefical for the incoporation of such two-dimensional carbon sheets in composite materials and devices as a transparent electrode [21]. Therefore, there is a great need for novel paths to two-dimensional carbon allotropes that can have a solution-processability, a catalyst- and transfer-free process, and a tunable film property.

In this work, we demonstrate that pitch-converted carbon nanosheet (CNS) films can efficiently function as transparent conducting electrodes for polymer solar cells (PSCs). The pitch-converted CNS film was prepared with spin-coating of a cost-effective pitch-solution dissolved in dimethylformamide (DMF) on quartz substrates, followed by stabilization and carbonization treatments to convert the pitch into CNS. This stabilization and carbonization process was recently introduced to convert PAN into CNS in our group and showed the possibility of a facile and cost-effective method to produce atomically thin carbon sheets without using any transfer or catalyst processes [22]. Here, as a new CNS production material, we investigated a pitch, which is well known as one of the cheapest precursors to fabricate carbon materials such as carbon fibers can be simply obtained by the catalytic or thermal polymerization of petroleum residual oil or coal tar [23,24]. The pitch materials could be a promising candidate as cost-efficient materials, because they are inexpensive, safe to handle, and soluble in specific solvent unlike a CVD-grown graphene film [16]. The pitch-converted CNS films prepared by the successive heat-treatment process were intensively investigated for the feasibility of the use as a novel transparent electrode in polymer solar cells.

2. Experimental

Fig. 1 presents the device structure of ITO-free cells and the fabrication sequence for ITO-free solar cells with a pitch-converted CNS anode film. To prepare pitch solutions, pitches were obtained by reforming naphtha cracking bottom (NCB) oil (SK Co.), and then the pitch was dissolved in DMF to fabricate 1, 3, 5, and 6 wt% pitch solutions. As shown in Fig. 1, the pitch-based films were obtained by spin-coating of pitch solutions on quartz substrates, followed by stabilization and carbonization treatments to convert the pitch into carbon nanosheet films. The stabilization process were performed at 300 °C for 2 h under an air atmosphere in a tubular oven, and the carbonization was performed with a heating rate of 5 °C/min up to ~1200 °C under a H_2/Ar mixture. Then, the PEDOT:PSS (Clevios PH1000) buffer layer was spin-coated on top of the CNS films, followed by drying at 120 °C for 10 min. The photoactive layer was then prepared by spin-coating a blend solution with 50 mg of a poly(3-hexylthiophene) (P3HT, Rieke Metals) and 50 mg of [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM, Nano-C) in 2 ml of 1,2-dichlorobenzene, followed by a solvent-annealing treatment for 120 min and thermal annealing treatment at 110 °C for 10 min in N_2. Finally, Ca (20 nm)/Al (100 nm) cathodes were thermally evaporated in a vacuum at 10^{-6} Torr. For comparison, conventional ITO-based solar cells were also fabricated under identical procedures with ITO-free OSCs with pitch-converted CNS anodes. Raman spectroscopy was measured using the LabRAM HR system (Horiba Jobin Yvon, France) with 16 mW and 514.54 nm laser, and X-ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Inc.) was measured to investigate the chemical components of CNS films. The surface morphology of the CNS films was measured using atomic force microscopy (AFM, Veeco Dimension 3100). The UV–vis transmission and sheet resistance of CNS films were investigated using a Jasco V-570 UV-vis/NIR spectrophotometer and a four-point-probe system (FPP-RS8, Dasol Eng.). Device-performances of solar cells were investigated using a Keithley 1200 instrument under 100 mW/cm^2 solar illumination and AM 1.5 G conditions, and for a more accurate measurement, 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 of the light intensity.

3. Results and discussion

To confirm a successful CNS fabrication from the pitch solution, Raman and XPS studies were performed as shown in Fig. 2. The CNS synthesis mechanism derived using pitch solutions can be highly linked to the formation mechanism of the pitch-based carbon fibers [23–26]. As is well-known, pitch has poly-nuclear aromatic hydrocarbon molecules with some aliphatic side chains, and a stabilization process allows these molecules to be infusible pitch fibers [23–25]. Then, a carbonization process up to 1000 °C removes most of gases such as CO, CO_2, CH_4, H_2, and N_2 generated from fibers, and with further heat-treatment at 2600 °C, high-quality graphene layers with more ordered structures can be obtained [25–27]. In fact, as shown in Fig. 2(a) and (b), the pitch-based CNS films prepared through stabilization and carbonization treatments showed prominent D (1351 cm^{-1}) and G (1584 cm^{-1}) peaks with a somewhat weak and broad band that contains four components (D″+D (2467 cm^{-1}), 2D (2703 cm^{-1}),

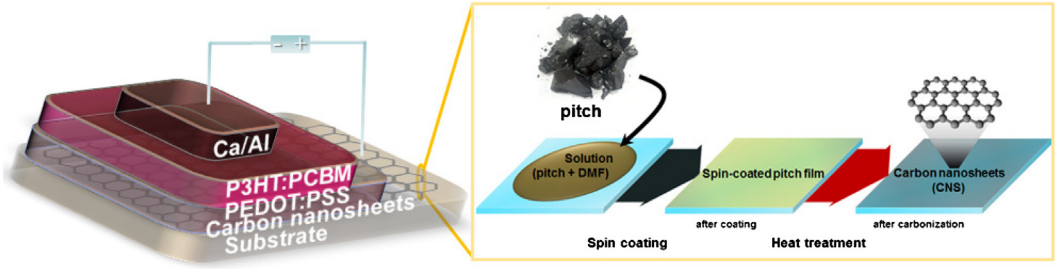

Fig. 1. Schematic representation of the fabrication sequence for ITO-free solar cells with a pitch-converted CNS anode film (left part), fabricated using a spin-coated pitch and stabilization and carbonization processes (right part).