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Efficient modification of transparent graphene electrodes by electron beam irradiation for organic solar cells

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ABSTRACT

A simple, solvent-free, and efficient electron beam (EB)-irradiation based modification of graphene and its use as a transparent electrode in organic solar cells (OSCs) were described in this research. A chemical vapor deposition (CVD)-prepared graphene was irradiated by an energetic EB for various irradiation times to modify its chemical and electrical properties. The analytical results revealed that the graphene was successfully modified by EB irradiation-induced oxidation and amorphization, and thereby resulting in the increase in its sheet resistance and work function. Moreover, on the basis of the results of the OSC-performance test, the OSCs with the graphene electrode modified at the irradiation time of 5 s exhibited the highest power conversion efficiency of 2.76%, which is much better than that with a non-irradiated graphene electrode. Therefore, it can be confirmed that the EB irradiation could be used in effectively tuning the graphene's properties and the resulting EB-treated graphene can be directly applicable as a transparent electrode and beneficial for high-performance organic electronics.

Introduction

Graphene that is a two dimensional and sp^2-bonded carbon-atomic monolayer with honeycomb lattice has drawn a significant attention owing to its outstanding optical transmittance, electrical and thermal conductivity, and mechanical properties, which are highly beneficial for various applications such as transparent electrodes, transistors, nanosensors, and photovoltaics [1–5].

In general, for graphene analyses and graphene-device fabrication, the use of the scanning microscopy, transmission electron microscopy, and electron beam lithography was usually required [6–8]. This electron beam irradiation on graphene can have influence on graphene structure and properties, resulting from lattice defects or oxidation by breaking the carbon bond in graphene [6–10]. However, no detailed studies of the electron-beam effects on graphene under a wide range of electron-beam irradiation have been investigated so far, which could be highly needed for fully understanding the overall structural and electrical properties of graphene. More importantly, it was recently known that the functionalization of graphene by controlling the graphene-surface structure could be highly beneficial for its practical device application as transparent electrodes and charge transporting layers [11,12]. Thus, controlling intrinsic properties of the graphene through irradiation with UV, electron beam, and ion beam has been explored, and its feasibility has been reported [13,14]. However, approaches on the electron-beam based graphene functionalization have hardly been studied, and no researches on practical applications of electron-beam-treated graphene as a transparent electrode in organic solar cells have been studied so far.

In this study, the simple, solvent-free, and ambient temperature electron beam (EB)-based modification of graphene for its use as a transparent electrode in organic solar cells (OSCs) was described. The graphene was irradiated under various EB-exposure times to modify its properties. Furthermore, the modified graphene was practically applied as a transparent electrode of OSCs to investigate the effectiveness of the electron-beam-based modification.

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Experimental

The chemical vapor deposition (CVD)-prepared graphene on a quartz with a sheet resistance of 600–800 $\Omega/\square$ was supplied from Graphene Square (Seoul, Korea). The CVD-graphene electrodes were irradiated at room temperature in the air with the electron beam (EB) from the 0.2 MeV electron beam source and the 0.5 mA beam current (max. beam current, 1 mA) installed at Korea Atomic Energy Research Institute (KAERI). Its window size exposed by electron beam irradiation was 2 cm × 12 cm. E-beam was irradiated on the sample with the normal incidence angle. Because the e-beam dosage is related to the energy, time, and the electron beam flux, we changed the expose time to control the e-beam dosage. To avoid thermal damage on the samples during the irradiation, the cooling plate of a sample stage where the samples were placed was kept as 5 °C, and the uncertainty of the given doses reported by the operator at the KAERI was less than 5%. At the same electron beam flux, current, and energy, we changed the EB-exposure time to control the absorbed dose density; the EB irradiation times were 1, 5, 10, 100, and 500 s, and precisely controlled absorbed dose density of $\sim$1.3 e^{-}/nm^{2} was applied on each graphene sample.

The modified CVD-graphene layers were used as transparent electrodes in organic solar cells. The device structure of the organic solar cells was EB treated CVD-graphene/poly(3, 4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS)/poly(3-hexylthiophene) (P3HT, Rieke Metals): [6,6]-phenyl-C61 butyric acid methyl ester (PCBM, Nano-C)/Ca/Al. For the fabrication of devices, PEDOT:PSS (Clevios PH 1000, H. C. Starck) as a hole transporting layer was spin-coated on the graphene electrodes prepared with different EB-exposure times at 5000 rpm for 40 s. The resulting samples were baked at 120 °C for 10 min. A blend solution with 50 mg of P3HT and 50 mg of PCBM in 2 ml of 1,2-dichlorobenzene (DCB) was spin-coated on the top of the PEDOT:PSS-coated samples at 700 rpm for 60 s, followed by a solvent-annealing treatment in a petri dish to remove DCB solvent slowly for 90 min and a thermal treatment at 110 °C for 10 min inside N_2-filled glove box. Lastly, a Ca (20 nm)/Al (100 nm) metal was deposited as top electrodes by thermal evaporation in a vacuum at 10^{-6} torr through a shadow mask (4.64 mm^2) to produce a device-active area. To investigate cell-performances of devices, current density–voltage (*J*–*V*) curves of graphene-based OSCs were measured using a Keithley 2400 source meter unit under 100 mW/cm^2 solar illumination and AM 1.5 G conditions. A precisely calibrated reference Si solar cell certified by the National Renewable Energy Laboratory (NREL) was used for accurate device-measurement.

The X-ray photoelectron spectroscopy (XPS) analysis was performed using X-ray photoelectron spectroscope (XPS, AXIS-NOVA, Kratos Inc.) with a monochromatized Al $K\alpha$ radiation under a vacuum of 5×10^{-8} torr. Static contact angle (CA) was measured using a Phoenix 300 contact angle analyzer (Surface Electro Optics Co., Ltd., Korea). Raman spectra were collected on Raman spectrometer (Jobin Yvon LabRAM system) with an Ar-ion laser at an excitation wavelength of 514.5 nm. The work function was measured using an ultraviolet photoelectron spectroscope (UPS, Kratos Inc., AXIN-NOVA) with a He *I* discharge lamp ($h\nu$ = 21.2 eV). The work function was determined from the secondary electron cutoff of the UPS spectra using metallic gold as a reference. The position of the Fermi level was calibrated by measuring the Fermi edge of the gold. The sheet resistance was measured using a four-point-probe (FPP-RS8, Dasol Eng.).

Results and discussion

To investigate the EB irradiation-induced changes in the chemical composition of graphene, XPS analysis was performed, and the results are shown in Fig. 1. The O–C=O, C=O, C–O, and C=C peaks of the non-irradiated graphene were observed at 289, 287, 286.5, and 284.5 eV, respectively. For the EB-irradiated graphene in Fig. 1, the intensities of the oxygen-containing functionalities were continuously increased with increasing EB-exposure times, and beyond 100 s, they were increased dramatically. This result suggests that the electron beam irradiation predominantly induces the oxidation of graphene.

For better comparison, the changes in the atomic percentage of carbon and oxygen atoms of graphene by EB-irradiation times were recorded as shown in Fig. 1. With increasing EB-exposure times, the carbon atomic percentage was continuously decreased, while the oxygen atomic percentage was gradually increased; in comparison to the unirradiated CG spectrum, the atomic percentages (at%) of the oxygen-containing functionalities (O–C=O, O–C=O, C=O, and C–O) in the C1s spectra of the irradiated graphenes gradually increased up to 93.11 at% with an increasing irradiation time, while that of the graphitic carbon (C=C) decreased up to 2.06 at%. These results verify that the carbon bonds of graphene were gradually broken and also support that electron beam irradiation induces oxidation [11].

To investigate the changes in the wettability of graphene by EB irradiation times, the static contact angle (CA) was measured, and the results are presented in Fig. 2. In comparison to the non-irradiated one with a CA of ~76°, the CA of the irradiated graphene was evidently decreased to ~48° with increasing irradiation times. This result indicates that the EB irradiation-induced oxidation caused the significant enhancement in the wettability of the graphene and considering that the well-known, hydrophobic property of graphene can present to have the uniform coating of PEDOT: PSS widely used for a hole transporting layer, and thus leading to poor device-performances, the improved hydrophilicity of graphene by EB irradiation could be highly desirable for better coating of PEDOT:PSS for better-performance devices [15].

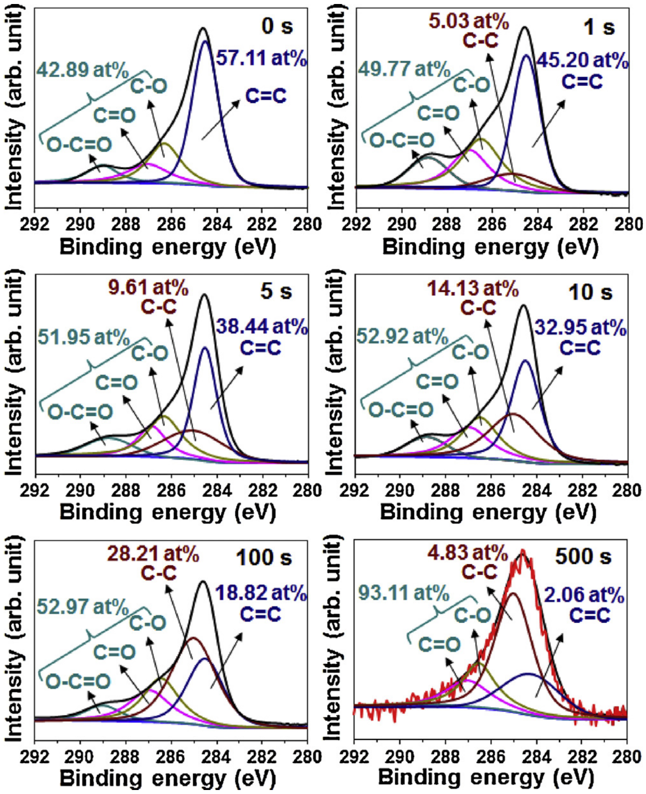

Fig. 1. C1s XPS spectra of graphene prepared at different exposed dosages of 0 s, 1 s, 5 s, 10 s, 100 s, and 500 s.