



# Effect of fluorine plasma treatment with chemically reduced graphene oxide thin films as hole transport layer in organic solar cells



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## ABSTRACT

The inorganic materials such as  $V_2O_5$ ,  $MoO_3$  and  $WO_3$  were investigated to replace PEDOT:PSS as hole transport layer (HTL) in organic electronic devices such as organic solar cells (OSCs) and organic lighting emission diodes. However, these methods require vacuum techniques that are long time process and complex. Here, we report about plasma treatment with  $SF_6$  and  $CF_4$  using reactive ion etching on reduced graphene oxide (rGO) thin films that are obtained using an eco-friendly method with vitamin C. The plasma treated rGO thin films have dipoles since they consist of covalent bonds with fluorine on the surface of rGO. This means it is possible to increase the electrostatic potential energy than bare rGO. Increased potential energy on the surface of rGO films is worth applying organic electronic devices as HTL such as OSCs. Consequently, the power conversion efficiency of OSCs increased more than the rGO films without plasma treatment.

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## 1. Introduction

Graphene oxides (GO) have been used as a way to obtain graphene when the solution-based chemical reduction of GO to graphene [1,2] has previously been developed. The GO was easily obtained by exfoliation of graphite oxide using ultrasonication in a bath. The chemical reduction which changes to reduced graphene oxide (rGO) from GO was conducted using vitamin C as a reducing agent. Moreover, vitamin C, having a mild reductive ability and nontoxic property, is used in nature as a reducing agent in many living organisms. The rGO have some advantages that solution based chemical rGO include low cost, bulk scale production ability, a single layer graphene can simply be obtained by sonicating at room temperature, and the rGO can be made of thin films with a solution technique using dip-coating, [3] spin-coating, [4] spray coating, [5] and Langmuir–Blodgett assembly [6] at room temperature. The rGO-based films can be used as transparent conductors, [7] ultracapacitors, [8] field emitters, [9] and gas barriers [10]. Applied graphene-based materials have also been studied for various functional parts such as additives [11] and electrode [12] in energy conversion and storage devices [13–15]. The use of functional graphene should lead to additional improvements in organic solar cells (OSCs). Recently, graphene oxide thin films were investigated for their use as a hole transport layer (HTL) in

organic electronic devices such as OSCs [16–23] and organic light-emission diodes (OLED) [24]. The power conversion efficiency (PCE) value of a conventional device with GO thin layer (2 nm thickness) as an efficient HTL was increased to 3.50% more than device without graphene (only ITO) [25]. The advantages of rGO are that it serves to minimize the detrimental effects of indium tin oxide (ITO) roughness as well as to align the work function of either Poly (3-hexylthiophene-2,5-diyl) (P3HT) in OSCs or 1,4-bis[(1-naphthylphenyl)amino]biphenyl in OLED and ITO for more efficient collection and emission of holes as HTL. To obtain the high performance of OSCs, rGO films require a change of work function such as p-doping with gold nanoparticles [26,27]. However, this is not only expensive but is also inefficient for devices and causes an electrical short between the ITO and the active layer due to many large particles.

In this paper, we report for the first time simply treated rGO thin films with sulfur hexafluoride ( $SF_6$ ) and tetrafluoromethane ( $CF_4$ ) as a new type of HTL that can be readily fabricated using reactive ion etching (RIE). Its treatment has the C–F covalent bonds. Firstly, our method starts with the synthesis of rGO by vitamin C from graphite powder followed by modified Hummer's method with sodium dodecyl benzene sulfonate (SDBS) for protection from hazardous materials and the plasma is then treated on the surface of rGO. rGO thin films as HTL increase PCE more dramatically and efficiently than bare ITO. Moreover, the  $SF_6$  and  $CF_4$  plasma treated rGO films increase the short circuit current density ( $J_{SC}$ ) and fill factor (FF), resulting in a greater PCE increase than with rGO thin films because the effect of plasma.

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## 2. Experimental

### 2.1. Materials

Graphite oxide was prepared from natural graphite powder (99.9999%, –200 mesh, Alfa Aesar), Potassium peroxodisulfate, Phosphorus pentoxide, Sulfuric acid, Hydrochloric acid, hydrogen peroxide (30 wt% aqueous solution), vitamin C, and Potassium permanganate (Sigma–Aldrich) and was used as an oxidizing agent. SDBS was purchased from TCI, while P3HT and Phenyl-C61-butiric acid methyl ester (PCBM) were purchased from Rieke metals and Nano-C, respectively.

### 2.2. Preparation of reduced graphene oxide

Graphite powder was preferentially oxidized using the modified Hummer method to form graphite oxide. Typically, graphite powder (1.2 g) was added to a prepared solution of concentrated  $\text{H}_2\text{SO}_4$  (5 mL),  $\text{K}_2\text{S}_2\text{O}_8$  (1 g), and  $\text{P}_2\text{O}_5$  (1 g). The solution was kept at  $80^\circ\text{C}$  for 4.5 h, and was then diluted with deionized (DI) water (200 mL). The mixture was filtered, washed, and dried to remove any residual acid. The pretreated graphite powder (2 g) was dispersed in concentrated  $\text{H}_2\text{SO}_4$  (46 mL) in an ice bath. The mixture was kept at  $0^\circ\text{C}$  with the gradual addition of  $\text{KMnO}_4$  (6 g) while stirring. The mixture was reacted at  $35^\circ\text{C}$  for 2 h, and was then diluted with DI water (92 mL) and reacted at  $35^\circ\text{C}$  for 2 h. The mixture was diluted with DI water (280 mL), followed by the addition of  $\text{H}_2\text{O}_2$  (30 wt%), and was left for several seconds whereby the color changed to brilliant yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution and DI water and was dialyzed for two weeks. The washed solution was dried on a Petri dish in a vacuum oven at  $60^\circ\text{C}$  for one day to obtain a powder form. The presence of surfactant SDBS facilitated the exfoliation of the graphite oxide to GO and a larger size of GO sheet can be obtained in the ultrasonication process. The GO was exfoliated by sonicating  $1.5\text{ mg mL}^{-1}$  graphite oxide solution for 2 h in the presence of SDBS. The aqueous solution was reduced by vitamin C at  $80^\circ\text{C}$  for one day.

### 2.3. Fabrication of devices

The ITO coated glass substrates were cleaned with ultrasonication, acetone, methanol, and DI water for 30 min each, sequentially, and then dried in an oven at  $120^\circ\text{C}$  for 10 min. All substrates were treated with  $\text{O}_2$  plasma for 4 m. The GO films as interfacial layers such as rGO were spin-coated onto the  $\text{O}_2$  plasma treated ITO/glass substrate at 1000 rpm followed by annealing of the resulting film at  $120^\circ\text{C}$  for 10 min. To remove impurities such as vitamin C, the products were prepared by rinsing with ethanol followed by annealing at  $120^\circ\text{C}$  for 10 min. The plasma treatment was carried out using a RIE system. The chamber was evacuated to less than  $5 \times 10^{-5}$  Torr at fixed parameters including work pressure, gas flow rate, and RF power that were 20 mTorr, 20 sccm, and 20 W, respectively. The etch times were performed from 10 to 60 s in a  $\text{SF}_6$  and  $\text{CF}_6$  environment. For the active layer, P3HT and PCBM were dissolved in mono-chlorobenzene (CB, 40 mg/ml) and blended using a mixing ratio of 10:15 for 16 h. The active layer films using blended P3HT/PCBM were spin-coated at 900 rpm for 30 s, and thermal pre-annealing was then performed at  $140^\circ\text{C}$  for 10 min in a glove box in an argon atmosphere. Finally, the Al cathode (100 nm) and the interlayer (LiF 0.8 nm) were thermally evaporated in a vacuum greater than  $9 \times 10^{-8}$  Torr.

### 2.4. Characterization

Atomic force microscopy (AFM) images were taken using a XE-100 operated in tapping mode with a silicon cantilever on a silicon

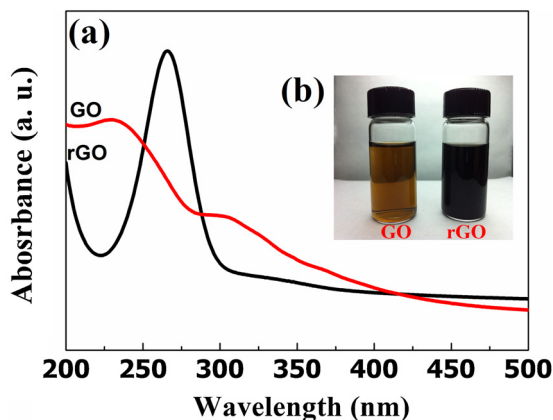


Fig. 1. UV-visible spectroscopy of GO aqueous dispersions before and after being reduced with vitamin C. Inset: optical images of GO and rGO.

dioxide wafer. The silicon dioxide wafer was cleaned in prepared piranha solution (a mixture of 7:3 (v/v) 98%  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$ ) at  $80^\circ\text{C}$  for about ten minutes then washed in methanol and ethanol. Because piranha solution reacts violently with almost any organic material, it was handled with extreme care. The UV-vis/NIR spectra were obtained using a Carry 5000 in a quartz cell (Agilent). The Raman spectroscopy measurements were conducted using a micro-Raman system (Jobin Yvon LabRAM HR 800 UV) with excitation energy of 2.41 eV (514 nm). The X-ray photoelectron spectroscopy (XPS) measurements were performed using K-alpha (thermo electron) with monochromatized Al  $\text{K}\alpha$  under a pressure of  $5 \times 10^{-9}$  Torr on the ITO substrate. The photovoltaic characteristics were measured using a Keithley 2400 source meter and simulated AM 1.5 global solar irradiation with an incident powder density of  $100\text{ mW/cm}^2$  using a 300 W Xe lamp (Oriental Instrument). The work function was measured by AC-2 photoelectron spectrometer in the air (Ren Keiki Co., Ltd.).

## 3. Results and discussion

The aqueous dispersion of GO sheets was prepared using the modified Hummer's method [28]. The graphite powders were oxidized to graphite oxide using  $\text{KMnO}_4/\text{H}_2\text{SO}_4$ . The van der Waals forces were weak when generating GO sheets by sonication in the water because of the increased interlayer distance between the graphite oxide sheets since the graphite oxide sheets are strongly hydrophilic, such that intercalation of water molecules between the layers readily occurs. To improve the electrical conductivity of GO, we conducted a reduction of sheets from GO to rGO solutions by adding SDBS as a surfactant in the water. The reduction of GO is typically carried out using hydrazine or sodium borohydride, each of which is highly poisonous and explosive. Thus, in this study, the reduction of GO was carried out using vitamin C in the water with SDBS. The vitamin C has a mild reductive ability and nontoxic property. The results of reduction were monitored by measuring the position of the UV-visible spectra absorption peak of the aqueous rGO solution.

As shown in Fig. 1, the peak was located at 229 nm as previously reported for GO by  $\pi \rightarrow \pi^*$  transitions (conjugation), but gradually red-shifts from deoxygenating occurred so that the aromatic structure was restored. A shoulder peak located at around 300 nm can be attributed to the  $n \rightarrow \pi^*$  transitions of the carbonyl group [29]. Furthermore, the optical image of GO shows a transition of reduction that changed color from light brown to black aqueous suspension (see Fig. 1. inset). The AFM image shows the height profile and surface rms roughness ( $R_q$ ) of the rGO sheets, which are about  $\sim 1.2$  and  $0.67\text{ nm}$ , indicating the single layer graphene [30] (see Fig. 2). This

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