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## Preparation of conductive carbon films from polyacrylonitrile/graphene oxide composite films by thermal treatment

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### ABSTRACT

Electrically-conductive carbon films were prepared by the thermal treatment of polyacrylonitrile/graphene oxide (PAN/GO) composite films. PAN/GO composite films spin-coated on substrates were stabilized in air and then carbonized under inert atmosphere at 1000 °C to form carbon films. It was found that the cyclization of PAN and the partial reduction of GO occurred simultaneously during stabilization. The incorporation of GO was found to help to lower the energy and temperature of cyclization by an additional ionic reaction mechanism and to form large and compact crystalline structures. The electrical conductivity increased to  $5.92 \times 10^2$  S/cm with an increasing GO content.

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### Introduction

Conductive carbon films have been used as electrode materials for a variety of applications in energy conversion and storage devices, biosensors, environmental remediation, and separation and adsorption due to their outstanding electrical and electrochemical properties [1–4]. These carbon films are generally prepared by spin-coating of carbon nanomaterials, such as graphene and carbon nanotubes, and conducting polymers [5–7]. However, such materials have several disadvantages, such as high surface roughness, low thermal and chemical stability, and complex fabrication processes [8]. To overcome these disadvantages, carbon films are prepared by pyrolysis of organic materials. Saufi and Ismail [9] reported the possibility of forming carbon membranes from polymeric precursors such as polyacrylonitrile (PAN), polyimide, and phenolic resin. Among these polymeric precursors, PAN have been widely used to prepare carbon materials because PAN-derived carbon materials show good mechanical, thermal and electrical properties as well as high carbonization yield [10–15].

Recently, PAN composites containing various carbon nanomaterials, such as carbon nanotubes (CNTs), graphene (GN), and graphene oxide (GO), have been studied to further improve the

mechanical, thermal, and electrochemical properties of the final carbon materials [16–18]. However, CNTs and GN have poor miscibility with polar solvents and PAN, which limits their practical applications [19,20]. In contrast, GO is the most promising candidate to produce homogenous polymer composites on account of its easy and diverse functionalization to tailor its miscibility with various polymers, thermal reduction ability, and capability of enhancing the graphitization of organic matrices [21].

In this study, conductive carbon films were prepared from PAN/GO composite films by two thermal treatment steps: stabilization and carbonization. Thin PAN/GO composite films coated on substrates were stabilized in air and then carbonized under inert atmosphere. The final carbon films were investigated in terms of their chemical structures and compositions, carbonaceous and crystalline structures, and thermal and electrical properties.

### Materials and methods

#### Materials

A GO aqueous solution (5 mg/ml) and PAN (Mw: ~150,000) were purchased from Graphene Supermarket (Galverton, NY, USA) and Aldrich Chemical, respectively. *N,N'*-dimethylformamide (DMF) as a solvent was purchased from Duksan Company. All chemicals were used without further purification.

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### Preparation of PAN/GO films and thermal treatment

A GO aqueous solution was centrifuged at 14,000 rpm to exchange the solvent into DMF and the precipitate, GO, was then well-dispersed in DMF by ultra-sonication for 10 min. To prepare PAN/GO solutions with various GO contents (1, 3, 5, and 10 wt%), PAN powder was put into the prepared GO solution under vigorous stirring. Finally, the prepared PAN/GO solutions were mixed using a homogenizer for 10 min to produce homogenous solutions. The PAN/GO solutions were spin-coated on well-cleaned SiO<sub>2</sub>-deposited Si wafers at 3000 rpm for 40 s and then baked at 90 °C for 90 s. The PAN/GO films were stabilized in a muffle furnace at 250 °C for 3 h under air. Afterwards, the stabilized PAN/GO films were placed in a tube furnace (Yulsan, Korea), heated 1000 °C at a heating rate of 5 °C/min under nitrogen atmosphere, and then naturally cooled down to room temperature.

### Characterization

The chemical structure of the films was investigated by using an attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Nicolet iS5, Thermo Scientific Corp., USA) and an X-ray photoelectron spectrometer (XPS, MultiLab 2000, Thermo Electron Corp., England). Differential scanning calorimetry (DSC) was carried out on a DSC1 analyzer (Mettler-Tolledo, Switzerland) under an air or nitrogen atmosphere at a heating rate of 5 °C/min at temperatures ranging from 50 to 400 °C. Thermogravimetric analysis (TGA) was performed using a TGA-8000 analyzer (PerkinElmer, USA) under a nitrogen atmosphere at a heating rate of 5 °C/min at temperatures ranging from 50 to 800 °C. X-ray diffraction (XRD) patterns were obtained using an X'Pert Pro Multi-Purpose X-ray diffractometer (PANalytical, Netherlands) with a CuK $\alpha$  radiation source from 5 to 60°. The interlayer spacing ( $d_{(002)}$ ) and crystallite size ( $L_{c(002)}$ ) were calculated by using Bragg's and Scherrer's equations [22]. The sheet resistance and electrical conductivity of the films was measured by using a 4-point probe conductivity meter (CMT SR-1000N, Advanced Instrument Technology, USA). The thickness of the films was measured using an Alpha Step IQ surface profiler (KLA Tencor, USA).

### Results and discussion

The changes in the chemical structures occurring during the stabilization of PAN/GO composite films were investigated by ATR-FTIR analysis, and the results are shown in Fig. 1. In the case of

the pristine PAN (P-PAN) film, the characteristic peaks for the PAN main chains appeared at 2941 (vibrations of the aliphatic —CH/CH<sub>2</sub> groups), 2241 (stretching vibration of C $\equiv$ N bond), and 1454 cm<sup>-1</sup> (bending vibration of —CH bond in CH<sub>2</sub>) [23]. The spectrum of the pristine PAN/GO (P-PAN/GO) containing 10 wt% GO was similar to that of the P-PAN except peaks corresponding to —OH (3420 cm<sup>-1</sup>), C=O (1737 cm<sup>-1</sup>), and C=C (1656 cm<sup>-1</sup>) groups of GO [24]. Both stabilized PAN and PAN/GO (S-PAN and S-PAN/GO) spectra showed the characteristic peak for C=N at 1589 cm<sup>-1</sup>, indicating the existence of cyclized ladder-type (pre-graphitic) structures formed by stabilization [25].

XPS analysis was performed to further investigate the changes in the chemical compositions in PAN and PAN/GO during the sequential thermal stabilization and carbonization, and the results are shown in Fig. 2. As seen in Fig. 2, the P-PAN showed two typical peaks for elemental carbon (C) and nitrogen (N) at 285 eV (75.78 at.%) and 398 eV (24.12 at.%), respectively. In the P-PAN/GO spectrum, a new peak for oxygen (O), in addition to peaks for C (74.98 at.%) and N (13.79 at.%), appeared at 532 eV (11.23 at.%), indicating the presence of GO. After stabilization, in the spectrum of the S-PAN, the C content had decreased to 69.37 at.%, the O content had increased to 17.44 at.%, and the N content had decreased to 13.19 at.%, indicating that oxidation occurred during thermal stabilization. Likewise, the S-PAN/GO spectrum exhibited a similar tendency towards changes in the C, N, and O contents, but its O content (14.02 at.%) was lower than that of S-PAN (17.44 at.%) probably due to the partial deoxygenation of GO. After carbonization, in the case of the C-PAN, the N and O contents had decreased to 2.85 at.% and 10.31 at.% in comparison to those of S-PAN, while the C contents had increased to 86.84 at.%. Similarly, the C-PAN/GO exhibited such a tendency towards changes in the C, N, and O contents. However, its C and N contents were higher than those of C-PAN whereas the O content was much lower. This elemental change in the C-PAN/GO could be attributed to the reduction of GO.

As shown in the C1s deconvolution peaks Fig. 3(a), the C—C and C—N peaks of P-PAN were observed at 285.3 and 286.2 eV, respectively [8]. In the case of P-PAN/GO (Fig. 3(d)), the C=C, C—O, and C=O peaks in addition to the C—C and C $\equiv$ N peaks appeared at 284.5 eV, 286.2 eV, and 287.6 eV, which originated from the oxygen-containing groups of GO [26]. In the cases of the S-PAN and S-PAN/GO (Fig. 3(b) and (e)), new peaks corresponding to C—N/O and C=O appeared at 286.1 and 287.6 eV, respectively, indicating that effective cyclization and oxidation reactions occurred during stabilization [27]. On the other hand, as shown in Fig. 3(c) and (f),

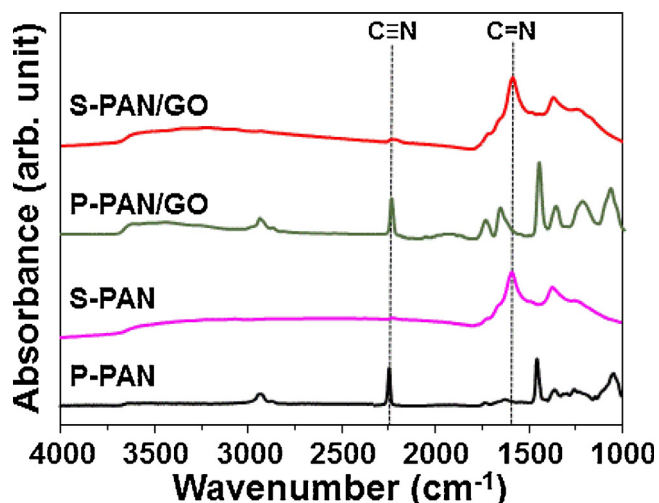


Fig. 1. ATR-FTIR spectra of pristine and stabilized PAN and PAN/GO films.

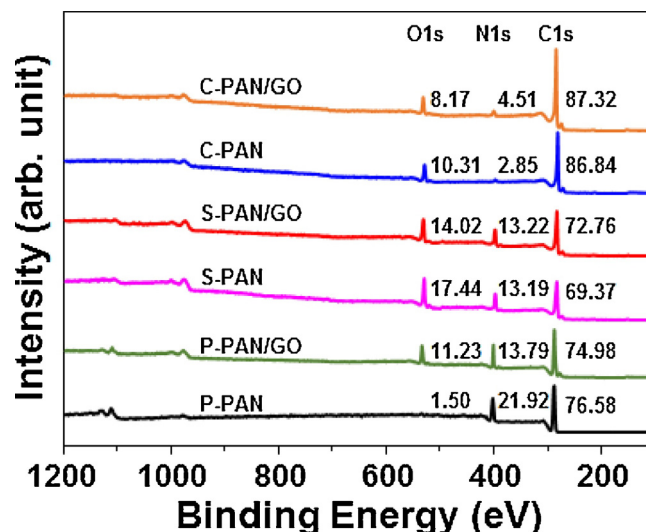


Fig. 2. XPS survey spectra of pristine, stabilized, and carbonized PAN and PAN/GO.

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