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# High-quality graphene thin films synthesized by H<sub>2</sub> ambient-annealing of reduced graphene oxide sheets

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Highly conductive low-oxygen graphene thin films were produced by thermal annealing of chemically reduced graphene oxide (RGO) sheets under  $H_2$  ambient. X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy measurements showed that the thermal annealing efficiently removed residual oxygen-containing functional groups on the surface of the chemically reduced RGO sheets and simultaneously recovered  $sp^2$  carbon networks in the graphene sheets. Consequently, the electrical conductivity of the graphene films was greatly improved, from 24 S/cm for RGO films to 200 S/cm after the thermal annealing process. In addition, we have studied the NO<sub>2</sub> gas sensing characteristics of the prepared graphene films.

Key words: Graphene, Gas sensors, Annealing.

## Introduction

With the various nanostructures and thin films opening a new era [1-29], graphene, a single layer of sp<sup>2</sup>-hybridized carbon atoms in a hexagonal twodimensional lattice, has attracted tremendous attention due to its unique physical and chemical properties and potential applications in many fields, including nanoelectronics, a sensor for biomolecules, transistors, solar cell and catalysts [30-33]. Up to now, some major methods have been developed to synthesize graphene, including mechanical exfoliation, epitaxial growth, bottom-up synthesis and the chemical reduction of graphene oxide suspension. Among them, the last method is considered to an efficient approach to produce graphene sheets in bulk quantity at a relatively low cost.

Currently, the Hummers' method is the most widely used technique for preparing graphene oxide (GO) [34], and involves the oxidation of graphite in the presence of strong acids and oxidants. When oxidized, GO still possesses a layered structure, being composed of unoxidized aromatic regions and aliphatic regions, which contain many oxygen functional groups [35, 36]. The  $\pi$ -conjugated system in graphene is disrupted by these oxygen-containing functional groups, producing separated nanocrystalline graphene. Since the asprepared GO is an electrical insulator, various reduction methods have been developed to efficiently recover its electrical property [37-40]. Chemical reduction of graphene oxide is one of the most promising methods to realize the low-cost and high-throughput preparation of converted graphene with excellent processability [41]. However, the chemically reduced graphene oxide (RGO) sheets still exhibit much lower conductivity than pristine graphene, mainly due to the presence of irreversible defects, disorder and residual functional groups. Recently, it was demonstrated that thermal annealing is the most effective method to remove oxygen from GO films, where the reduction is accomplished by decomposition of oxygen containing groups and the simultaneous restoration of sp<sup>2</sup> carbon networks [42]. Hence, high-temperature annealing is required to repair the defects and further remove the residual functional groups in RGO sheets to improve its electrical properties.

Because the prepared graphene film possesses nanometric thickness, high electrical conductivity, high aspect ratio, and good mechanical property, it has been regarded as a promising material for gas sensor devices. Recent studies on the interaction of graphene with gas molecules have indicated that it can act as a good sensor [43-50]. Schedin and co-workers [48] have shown that the increase in the charge carrier concentration induced by gas molecules adsorbed on the surface of graphene can be used to fabricate sensitive gas sensors. Based on theoretical investigations on the adsorption of gas molecules on single-layer graphene as well as on graphene nanoribbons, it has been predicted that doping in carbon nanostructures may improve their sensitivity [51-54]. Ao and co-workers have applied density functional theory to show that aluminum-doped graphene can be used as a good detector for carbon monoxide [55]. Functionalized graphite nanostructures

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are able to sense traces of pollutant gases such as NO<sub>2</sub> [56]. Water vapor sensing characteristics of RGOs have been studied [57]. RGO is also shown to be good sensor for toxic vapors [58]. Spin-coated hydrazine functionalized graphene dispersions are able to detect NO<sub>2</sub>, NH<sub>3</sub>, and 2,4-dinitrotoluene [59]. However, very little work has been reported about a NO<sub>2</sub> gas sensor based on graphene film prepared through thermal reduction of RGO films.

In this study, we employed a simple method for preparation of highly conductive graphene films through the thermal annealing of RGO in H<sub>2</sub> ambient at 1100 °C. We have studied the relation between the structure and electrical conductivity of the graphene films. Moreover, we introduced a graphene gas sensor fabricated on a Pt electrode. We have studied the sensing behavior of the above graphene films in terms of NO<sub>2</sub> gas.

#### **Experimental**

We have synthesized GO by the same procedure described in previous literature [60]. At first, 5 g of graphite, 60 mL of H<sub>3</sub>PO<sub>4</sub> (98%), and 180 mL of H<sub>2</sub>SO<sub>4</sub> (98%) were stirred in an ice bath and 60 g of KMnO<sub>4</sub> (98%) was subsequently added at 0 °C. The solution was transformed to a thick paste. Next, after distilled water (450 mL) was slowly dropped into the resulting paste, distilled water and H<sub>2</sub>O<sub>2</sub> (30 wt %) were sequentially added. By means of high-speed centrifugation of the GO suspension, the GO deposit was obtained, being subsequently washed with HCl (5%) and distilled water. To obtain uniform GO, a centrifugation was used to remove thick multilayer sheets and small GO pieces. The final sediment was redispersed in 500 ml of N,N-Dimethylformamide (DMF, 99.8%) with mild sonication, producing a solution of exfoliated GO. The exfoliated GO nanosheets were transformed to reduced graphene oxide (RGO) by adding hydrazine monohydrate and subsequently heating at  $150 \pm 5$  °C in an oil bath. The RGO was redispersed in DMF, and then the subsequent mild sonication helped to form a homogenous RGO suspension. Following this, the RGO suspension was coated on quartz substrates. The RGO film was annealed at 1100 °C under a mixture of argon (Ar) and hydrogen (H<sub>2</sub>) gas. To avoid burning the GO films at high temperature due to the self-released oxygen from GO sheets, the quartz tube was evacuated to about  $10^{-2}$ torr using a rotary vacuum pump. Next, the system was first heated for 180 min at 250 °C to remove all the moisture with  $(Ar + H_2)$  gas flowing at a rate of 100 sccm. Subsequently, the temperature was raised to 1100 °C in 60 min. The annealing reaction was carried out for 30 min. Finally, the system was naturally cooled down to room temperature at a constant  $(Ar + H_2)$  flow rate of 100 sccm.

GO, RGO and as-synthesized films were characterized by a scanning electron microscope (SEM, JEOL, JSM 5900 LV, Japan). X-ray diffraction (XRD, Cu Ka radiation at a wavelength at 1.54 Å, 40 kv, 30 mA, Rigaku, Japan) was carried out. Atomic force microscope (AFM, AFM XE-100, Park system) images also were acquired. High-resolution transmittance electron microscopy (HR-TEM) was performed with a TECNAI 20 microscope operated at 200 kV. The Fourier transform infrared (FT-IR) spectra (500-4000 cm<sup>-1</sup>) were measured using a spectrometer (Nicolet IR100 FT-IR) with KBr (99%) as background. The Raman spectroscopy measurements were conducted using a Jasco Laser Raman Spectrophotometer NRS-3000 Series, with an excitation laser wavelength of 532 nm, at a power density of  $2.9 \text{ mW} \cdot \text{cm}^{-2}$ . X-ray photoelectron spectroscopy (XPS, VG Multilab ESCA 2000 system, UK) analysis using a monochromatized Al K $\alpha$  x-ray source (hv = 1486.6 eV) was carried out to analyze the elemental compositions and the assignments of the carbon peaks of the samples at Korean Basic Science Institute (KBSI). The current-voltage (I-V) characteristics were examined by using four point probes with a Keithley 2400 Source-meter. Preliminary current mea-surements in a gas sensors characterization system (GSCS) were performed exposing the device.

In sensing measurements, Ni/Au double-layer electrodes were used. The electrical conductivity was measured with changing nitrogen dioxide (NO<sub>2</sub>) environments at 473 K, inside the vacuum chamber, in which the base pressure was set to be about  $5 \times 10^{-6}$  torr. This configuration is the same as the experimental setup used previously by our research group [41-44].

## **Results and Discussion**

Fig. 1a shows a SEM image of graphite powders used as starting material with a wide size range of the flake-shaped particles, where the dimensions are about 3-7 µm in width and several hundred nanometers in thickness. Fig. 1(b) is a SEM image of GO nanosheets. The result indicates that the average particle size dramatically decreases after the oxidation process. During the oxidation reaction of graphite powder with concentrated sulfuric acid and phosphoric acid, H<sub>2</sub>O molecules, and cations were inserted into the graphene layers and expanded the interlayer spacing in the graphite crystal structure [36]. The graphite oxide can be effectively exfoliated via ultrasonic vibration to create GO nanosheets. Further observation of the morphology has been achieved though TEM. As shown in Fig. 1(c), the transparent GO nanosheets exit in the form of thin few-layer graphene with folds and wrinkles. The edges of the GO nanosheets are distinguishable, and are observed to contain a bi-layer (inset of Fig. 1(c)). Wrinkles and folds are very clearly observed on the surface of the GO nanosheets; these are characteristic of thin and two-dimensional (2D) GO. The AFM image (Fig. 1(d)) also shows a 2D GO nanosheet with wrinkle-like features, and the apparent



**Fig. 1.** SEM images of (a) graphite powders and (b) GO, (c) TEM image and (d) AFM image of GO (right inset: height profile in a selected location).

thickness is ca. 1.2 nm, which is comparable to the data of previous literature (1.25 nm) for the bi-layer GO nanosheet [65]. Theoretically, the single-layer graphene sheet is atomically flat with a well-known van der Waals thickness of 0.34 nm, while GO sheets are expected to be 'thicker' due to the presence of covalently bound oxygen and the displacement of the sp<sup>3</sup>-hybridized carbon atoms slightly above and below the original graphene plane. In fact, some studies [66] have pointed out that the heights of 'dry' and hydrated GO were about 0.65-0.75 nm and 1.2 nm, respectively. Thus, the GO nanosheets in this research may be composed of a single or bi-layer of GO sheets, being consistent with the TEM result.

Fig. 2(a) shows a high-resolution TEM image of RGO sheets. It can be seen that the sheet is made of 3-4 layers. The increase in number of layers of RGO compared to GO can be due to an aggregation of graphene sheets after the chemical reduction process. The crystallographic structure of the RGO was determined by using the selected area electron diffraction (SAED) technique, as shown in the inset of Fig. 2(a). The SAED yields a ring-shaped pattern consisting of many diffraction spots for each order of diffraction. These spots make regular hexagons with different rotational angles, indicating the presence of a few layers in the RGO assembly. Furthermore, this result confirms that the typical six-fold symmetry of the pattern comes from the crystallographic structure of the graphene, composed by carbon atoms arranged in a strictly two-dimensional honeycomb in real space. Figs. 2(a) and 2(c) show 2D and three-dimensional (3D) AFM images of 1100 °C-annealed RGO films, respectively, revealing that the 1100 °C-annealed RGO sheets with sizes of a few microns were randomly deposited and overlapped one another to create a continuous thin film with long, broad wrinkles or folds. In spite of the formation of the wrinkles and folds



Fig. 2. (a) TEM image of RGO nanosheets (upper-right inset: corresponding SAED pattern), and (b) 2D and (c) 3D AFM images of 1100 °C-annealed RGO films.



Fig. 3. (a) XRD pattern, (b) FTIR spectrum, and (c) Raman spectrum of 1100 °C-annealed RGO films.

across the film surface, the surface root mean square roughness  $(R_q)$  was estimated to be about 1.18 nm, which is comparable to that of the reduced GO film.

The structural changes of GO were studied by using XRD. Fig. 3(a) shows the pattern of 1100°C-annealed

RGO films. In a previous study, the raw graphite showed a very strong (002) peak at 26.40°, corresponding to an interlayer distance (d-spacing) of about 3.36 Å [54]. However, after the oxidation process, the (002) peak shifted to a lower angle of around 11.92°, corresponding to the d-spacing of 7.47 Å. Such d-spacing is significantly larger than that of single-layer graphene ( $\sim 3.36$  Å), indicating that GO contains large numbers of oxygen-containing functional groups on both sides of the graphene sheets. For the RGO sample (not shown here), the peak disappeared in a region of low angle, and another broad peak at 22.0° corresponding to d-spacing of 4.03 Å appeared. This indicated that a large number of functional groups on the surface of GO was removed during the chemical reduction process. As the RGO films were annealed at 1100 °C, the (002) peak became sharper and shifted to a higher angle of 25.14° (Fig. 3(a)). The d-spacing of 1100 °C-annealed RGO films was decreased to 3.53 Å, which is smaller than that of RGO, suggesting that thermal annealing further removed the residual oxygencontaining functional group on the surface of RGO sheets. The XRD results clearly indicated that thermal annealing enables a better ordering of the 2D sheets. Note that d-spacing of the 1100 °C-annealed RGO film is slightly greater than, but quite close to, that of graphene layers in graphite, indicating that 1100 °Cannealed RGO sheets are similar to the pristine sheets. The slightly increased d-spacing of 1100 °C-annealed RGO films can be attributed to the presence of a small amount of residual oxygen-containing functional groups or other structural defects.

Fig. 3(b) shows the FT-IR spectrum of 1100 °Cannealed RGO films. In our preliminary experiment, the FT-IR spectrum of GO exhibited a strong and broad band at 3400 cm<sup>-1</sup>, which is due to the O-H stretching vibration [60]. The band at  $1724 \text{ cm}^{-1}$  is related to the C = O stretching motions of COOH groups at the edges of the sheets [60, 67]. The band at  $1622 \text{ cm}^{-1}$  can be due to the O-H bending vibration of absorbed water [60]. The peak at 1384 cm<sup>-1</sup> can be attributed to OH deformation vibration mode [67]. The spectrum also shows two peaks at 1233 and 1074 cm<sup>-1</sup>, being originated from the C-O stretching vibrations of epoxy and alkoxy, respectively [67, 68]. In the FT-IR spectrum of the RGO (not shown here), the peaks at 1724, 1834 and 1233  $\text{cm}^{-1}$ disappeared. The intensity of the peak at 1089 cm<sup>-1</sup> (C-O) and the broad peak at 3400 cm<sup>-1</sup> was markedly reduced, indicating the removal of the hydroxyl and carboxylic acid groups. It did not completely disappear because of the mild reaction conditions. In addition, three new bands at 1557, 1433 and 1198 cm<sup>-1</sup> appeared in the spectrum of RGO. The band at 1557 corresponds to aromatic C = Cbonds [67]. The two bands at 1433 and 1198 are attributed to sp<sup>3</sup> C-N [69] and C-N [70] stretching modes, respectively. After thermal annealing, the spectrum of 1100 °C-annealed RGO showed only two bands at 1543



**Fig. 4.** (a) Wide-scan XPS and (b) high-resolution C1 XPS spectra of 1100 °C-annealed RGO films.

(C = C) and 1213 (C-N stretching) cm<sup>-1</sup>, suggesting the effectiveness of thermal annealing in removing the residual oxygen functional groups on the surface of RGO sheets.

Raman spectroscopy is usually used to characterize carbon materials. Fig. 3(c) shows a Raman spectrum of 1100 °C-annealed RGO films. It was commonly observed that graphite had a prominent G band at 1582.2 cm<sup>-1</sup> which is assigned to the first-order scattering of the  $E_{2g}$ mode observed for sp<sup>2</sup> carbon domains, and the broad D band at 1358.8 cm<sup>-1</sup> is caused by sp<sup>3</sup>-hybridized carbon, structural defects, carbon amorphous or edge planes that can break the symmetry and selection rule [60, 71]. In the Raman spectrum of GO (not shown here), the G band is broadened and shifted to 1602 cm<sup>-1</sup>, while the D band at 1352 cm<sup>-1</sup> becomes prominent, indicating the destruction of conjugated system in graphite. After GO was chemically reduced, the D band became narrower and more prominent whilst the G band shifted from 1602 cm<sup>-1</sup> to 1596 cm<sup>-1</sup> [60], possibly due to an increase of the number of sp<sup>2</sup> carbon in the graphene sheets. Moreover, after the subsequent thermal reduction at 1100 °C, the G band was further shifted to 1588 cm<sup>-1</sup>, suggesting that annealing removed the residual oxygen functional groups from the RGO sheets and more  $sp^2$  carbon networks were generated in the graphene sheet. The intensity ratio of D band to G band  $(I_D/I_G)$  is usually used to measure the degree of disordered carbon, as expressed by the sp<sup>3</sup>/sp<sup>2</sup> carbon ratio [72] and an increase of  $I_D/I_G$  means the degradation of crystallinity of graphitic materials. The  $I_D/I_G$  ratios of graphite, GO, RGO and 1100 °C-annealed RGO was estimated to be 0.10, 0.85, 1.10 and 1.58, respectively.

Sample	C (%)	N (%)	O (%)
Graphite	96.5		3.5
GO-dried	69.0		31.0
RGO	77.4	2.3	20.3
RGO-1100 °C	94.0	1.2	4.3

**Table 1.** Atomic concentration of C, N, and O of Graphite, GO, RGO and 1100 °C-annealed RGO films.

The increase of  $I_D/I_G$  can be attributed to a decrease in the average size but an increase in the number of sp<sup>2</sup> domain upon reduction [73], but this effect obviously cannot be considered as the healing or repairing of defects in GO.

An important factor determining the quality of graphene is the degree of oxidation and the presence of other hetero-atoms, which affects the electrical and electronic properties of the material. XPS is a powerful tool to identify elemental composition in bulk materials. Furthermore, by analysis of binding energy (BE) values, we can detect the presence of any oxygenated groups. Figs. 4a and 4b show the wide-scan XPS survey and high-resolution spectra of 1100°Cannealed RGO films, respectively. Only carbon, oxygen and nitrogen species are detected, the atomic percentage (at %) of each element was calculated from the widescan spectra (XPS spectra of graphite, GO and RGO were shown here) and the result is summarized in Table 1. In the survey scan XPS spectra, the peaks at around 285.5, 399.8 and 534.0 eV correspond to C1s, N1s and O1s core-level, respectively. The effective reduction is clear because the content of oxygen atoms of RGO and 1100 °C-annealed RGO are significantly reduced compared with GO. The oxygen content decreased in the order of GO > RGO > 1100 °C-annealed RGO.

High resolution XPS was further performed to analyze the change of individual groups during the reduction process; the relative composition of individual groups was estimated by the percentage of the certain group (the area of peak divided by the total area of all peaks). In a previous study, we presented a detailed analysis of the C1s XPS spectra of graphite, GO and RGO [60], in which it was shown that oxygen functional groups (such as C-OH, C-O-C, C = O and COOH groups) of GO were considerably reduced after chemical reduction, while the composition of C = C bonds increased from 65% for GO, to 74% for RGO. Furthermore, after thermal reduction, it was clearly found that the residual oxygen functional groups (C-OH and C-O-C) on the surface of the RGO sheets were further reduced and some of them even disappeared (C = O, COOH). Meanwhile, the composition of C = C bonds was increased up to 84.0%, clearly indicating the effectiveness of thermal annealing in removing oxygen functional groups from GO and the restoration of sp<sup>2</sup> carbon networks.

To study the effect of the reduction processes on the



Fig. 5. Current-voltage characteristics of GO, RGO and 1100 °Cannealed RGO films.

electrical conductivity of the as-made samples, we investigated the current-voltage (I-V) characteristics using a four point probe with Keithley 2400 Sourcemeter. Fig. 5 shows the I-V characteristics of GO, RGO and 1100 °C-annealed RGO samples. It was observed that all the samples exhibited a linear I-V relation with the voltage in the range of -1.0 to +1.0 V. The I-V slope of GO is close to zero. Before reduction, the GO behaved as a close-to-insulating material [74], which can be attributed to the high oxygen content in the form of functional groups contained by GO. It is widely known that the GO structure is predominantly amorphous due to distortions from the high fraction of sp<sup>3</sup>-O. Moreover, due to the random distribution, the sp<sup>2</sup>-hybridized benzene rings are separated by sp<sup>3</sup>hybridized rings, thus leading to the insulating GO [75]. However, the I-V slope of RGO significantly increased after chemical reduction, indicating that the electrical conductivity of RGO was considerably enhanced. The enhanced electrical conductivity of RGO can be due to chemical removal of oxygen functional groups and the simultaneous restoration of sp<sup>2</sup> carbon networks during chemical reduction. However, the electrical conductivity of RGO is still low. This indicates that the structure of GO cannot be completely restored to graphitization by hydrazine monohydrate. To be suitable for practical applications, the conductivity of RGO needs to be improved. As a consequence of better ordering and additional deoxygenation by thermal annealing at



Fig. 6. Reversibility of the 1100 °C-annealed RGO films-based sensor for detection of different concentrations of NO<sub>2</sub> at 200 °C in air.

1100 °C in H<sub>2</sub> ambient, the electrical conductively of RGO is found to further increase. The graphitization temperature of carbon materials is known to be 1100 °C [76], at which the residual oxygen functional groups in RGO will be completely eliminated [77], contributing to the improvement of electrical conductivity. From the linear I-V curves the conductivity of GO, RGO and 1100 °C-annealed RGO was estimated to be  $4.2 \times 10^{-4}$ , 24 and 200 S/cm, corresponding to GO, RGO and RGO-1100 °C, respectively, which is comparable to that presented by Geng et al [78]. The I-V measurement data, in conjunction with XPS and Raman results, reveal that the conductivity of GO increased with increasing sp<sup>2</sup> carbon content and with increasing  $I_D/I_G$ A similar result was reported by Lopez at al. [79], in which it was observed that the CVD-GO exhibited an approximately linear rise of electrical conductively with increasing I<sub>D</sub>/I<sub>G</sub>. The improved electrical conductivity of GO by heating has been studied intensively [80, 81].

One of the most important issues of gas detector is reproducibility. Therefore, the 1100 °C-annealed RGObased gas detector developed in this research was exposed to a repeated cycling of the ambient gas with different NO<sub>2</sub> concentrations. Fig. 6 shows the normalized change of current in the 1100°C-annealed RGO sample as a function of time for different concentrations of NO<sub>2</sub>, ranging from a 10 ppm increase to 50 ppm. NO<sub>2</sub> appeared to act as a p-type dopant [82] for the 1100 °C-annealed RGO film, resulting in a decrease in resistance. The current of 1100 °C-annealed RGO device increased with the increasing flow of NO<sub>2</sub>. Similar results were found in the previous studies [83, 84]. Based on this result, it can be concluded that the 1100°C-annealed RGO films have great potential as an ultra-sensitive gas detector by optimization of the device structure. The detection of a single gas molecule can be achieved by using an 1100 °C-annealed RGO-based gas detector since the change in the electrical conductivity of the graphene is quantized in response to the  $NO_2$  molecule [48]. Moreover, the sensitivity can be further enhanced by adding noble metals [85].

## Conclusions

Few layered graphene (RGO) nanosheets were synthesized by the chemical reduction of GO in the presence of hydrazine monohydrate. This technique is simple, low cost and adaptable for the production of large quantities of material. Furthermore, highly conductive graphene films were prepared by spray deposition of RGO dispersions, followed by thermal treatment. By using XPS, Raman, XRD and FTIR techniques, it was shown that the structure of GO was greatly changed upon reduction. The thermal reduction of RGO sheets resulted in a further increase of sp<sup>2</sup> carbon content, though the average size of  $sp^2$  domains decreased ( $I_D/I_G$  increased). As a result, the electrical conductivity of 1100 °C-annealed RGO films (200 S/ cm) was significantly improved compared to that of RGO (24 S/cm) and GO ( $4.2 \times 10^{-4}$  S/cm). Moreover, we show that these 1100 °C-annealed RGO films can be used to detect NO<sub>2</sub> gas. The simple, low-cost sensors described here could be developed for a variety of applications, such as environmental monitoring, sensing in chemical processing plants, and gas detection for counter-terrorism.

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