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공학석사학위논문

**Band Gap Engineering of Graphene
Oxide by Controlling Amount of
Oxygen-containing Functionality**

산소 작용기 제어를 통한
그래핀 옥사이드의 밴드 갭 조절

2019년 2월

서울대학교 대학원
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이 논문을 공학석사 학위논문으로 제출함

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Abstract

Band Gap Engineering of Graphene Oxide by Controlling Degree of Reduction and Functionality

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Graphene is a two-dimensional nanomaterial with carbon atoms arranged in a hexagonal lattice. Due to its excellent physical, optical and electrical properties, various applications have been proposed. Particularly, when graphene is applied to a transistor device, it becomes possible to integrate more transistors on a circuit than a silicon semiconductor. However, graphene is semimetal with band gap close to zero, which make it not suitable for realizing a logic circuit.

Therefore, studies for increasing the band gap of graphene have been actively conducted in various fields. Among them, the method of utilizing the oxygen functional group of graphene oxide, which is an intermediate stage of graphene synthesis, is excellent in commercial value in that the process is simple and mass production is possible. In addition, analogous effects can be obtained without introducing hetero

elements, and the hydrophilicity of the graphene is enhanced due to the oxygen functional group, which enables various applications.

However, experimental data on how various oxygen functional groups affect the band structure of each graphene are insufficient, and the application of graphene oxide to the transistor material is very limited. Therefore, in order to overcome these limitations, this study investigate the specific relationship between the oxygen functional group of graphene and the electrical properties including band gap. For the purpose, different reduction reactions were applied to graphene oxide, and the composition of the functional groups were adjusted by controlling degree of reduction. The changed band gaps were measured to analyze the quantitative relationship with the functional groups.

Analysis of the relationship between the material properties and electrical properties of graphene showed that single and double bonds of carbon and oxygen have significantly different effects on the band gap. Also, the band gap tuning effect of the hydroxyl group was figured out to be tenuous. Based on the analytical results, we suggested the synthesis direction for synthesizing graphene with specific performance. The results of this experiment can be expected to improve the usability of graphene oxide in electronic devices.

Keywords : Reduced graphene oxide, graphene, functionality, band gap, degree of reduction, transistor

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1. Introduction

1.1. Introduction to Graphene as Transistor Material

1.1.1. Properties of Graphene

Graphene is one of carbon isotopes consisted of carbon atoms arranged in hexagonal lattice, and is the first two-dimensional material found. Although the thickness of a graphene layer is only 0.2 nm, the chemical · physical stability is very high. Since its first exfoliation from graphite by “Scotch tape method” in 2004, graphene has received much attention due to its unique and excellent properties. [1, 2] Graphene is considered to be the strongest of all existing materials performing tensile strength of more than 200 times that of steel ($\sim 1.0 \text{ TPa}$). Moreover, its matchless electrical conductivity is higher than copper and its thermal conductivity is higher than diamond ($\sim 5000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). [3] Furthermore, the absorption of single layer graphene is so low in visible light that the transmittance is 97.7 % at 500 nm.

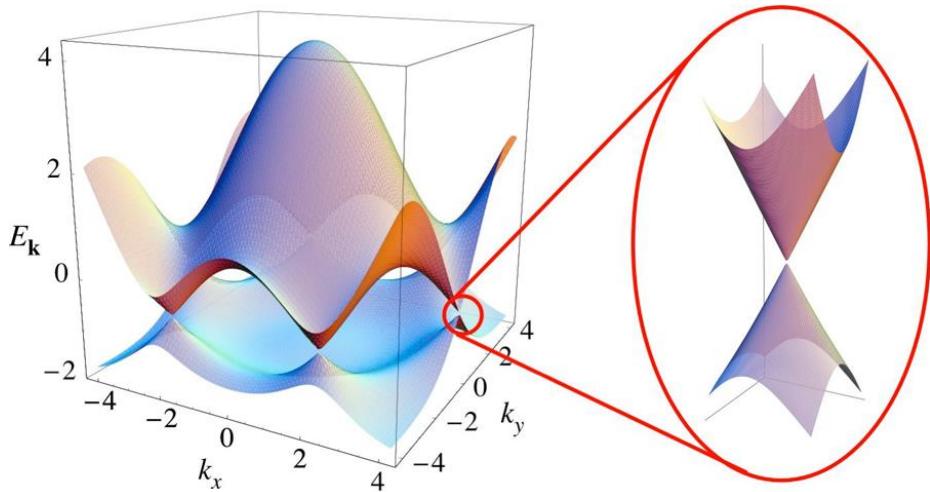


Figure 1. Electronic dispersion in the honeycomb lattice. (Figure is adapted with permission from [4]. Copyright 2009 American Phisics Society.)

Many of the unique properties of graphene are induced from the extraordinary carrier mobility. The s, p^x, p^y atomic orbitals of carbon atoms form sp² hybrid orbital, and the p^z orbital of each atom overlap those of neighboring atoms forming occupied π orbitals and unoccupied π^* orbitals. [2] These π and π^* orbits function as valence band and conduction band respectively, and form a unique band structure of two cone-shaped bands in contact with each other. As a result, graphene is a “zero band-gap semimetal” with a valence and a conduction band as observed in other semiconductors. In addition, it has a carrier effective mass close to zero at the band edge (*i.e.*, the apex of the cone-shape band), resulting in very high mobility ($\sim 10^6 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). [5]

1.1.2. Advantages of Graphene as Transistor Material

There is no doubt that the greatest advantage of graphene is its high carrier mobility. As well as the excellent theoretical upper limit, substantially more than tens of thousands of mobility is commonly measured in graphene. Transistors must react quickly to the input signal, or gate voltage, and the carrier drift rate is linearly proportional to the mobility at an electric field below the saturation value. However, the usefulness of graphene in transistor is not only of low electronic effective mass and high mobility.

Electronic devices produced in these days are a collection of modern technologies that contain billions of field effect transistors (FETs) with gate length of only a few nanometers. The semiconductor industry has become one of those with the largest initial development cost, and astronomical unit of money come and go in the development and production of devices each year. Although the trend of demanding devices with smaller size, high performance continues, it is believed that performance improvement through miniaturization and integration of gates has reached the limits. It is therefore clear that new materials and device concepts must be introduced in order to pursue performance improvements over the long term.

Graphene is promising as a next-generation major semiconductor material because of its matchless carrier transport properties and own two-dimensional structure. The FET, the majority of modern integrated circuits (ICs), consists of a gate, a channel connecting two electrodes —

source and drain, and a barrier separating the channel and the gate. When voltage (V_{GS}) is applied to the gate and the source, drain current flows through the channel region to produce ‘on signal’. The shorter the gate length, not only the more transistors in an IC, but also the faster the information processing speed. [6] For high performance of FET, *i.e.* high integration and processing speed, short channel and rapid carrier transport are essential.

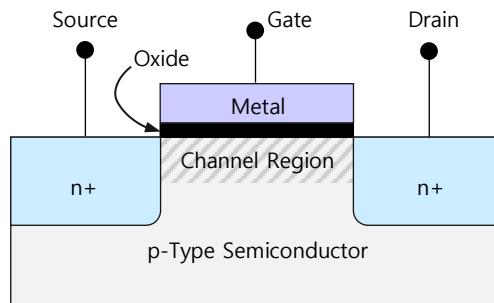


Figure 2. The structure of field effect transistor [6]

However, when the gate length is overly short, short channel effects (drain-induced barrier lowering, velocity saturation, and carrier degradation, etc.) could be induced. [7] If a typical three-dimensional material is used as a channel and is made extremely thin, scattering of charge carrier by the dangling bonds of the surface cannot be ignored. To top it all off, an undesired interface state may be created when the source and drain electrodes are deposited above, deteriorating short channel effects. [8] Graphene, on the other hand, is a 2D material that is stable even at atomic scale thickness and whose charge transfer is confined to the plane. Even in this respect, graphene has high utility as a transistor.

1.1.3. Issues on Graphene Transistor; Band Gap Opening

Despite the many advantages of increasing graphene's potential for FETs, pure graphene has a fatal flaw of zero band gap. The band gap is the core property of semiconductors, and a semiconductor channel with a band gap above a certain value is essential for proper FET operation. As mentioned above, the FET for digital logic operates by generating an on-current when the voltage is applied. The 'on' current of the FET is not directly related to the band gap, but conversely, the 'off' current when no voltage is applied appears as follows; [9]

$$I_{off} \propto \exp \frac{-E_G}{mk_B T} \quad (1)$$

E_G is the band gap, m is a factor of 2 or varies depending on the FET design, k_B is the Boltzmann constant, and T is the temperature. The ratio of on current to off current (on/off ratio) is therefore

$$\frac{I_{on}}{I_{off}} \propto \exp \frac{E_G}{mk_B T} \quad (2)$$

The off current must be sufficiently low compared to the on current in order to transmit the digital information. Unfortunately, pure graphene has zero or very low band gap so the current flows well even in the off state, and is not suitable for it. Accordingly, researches on the appliance of graphene as transistor channel are mostly focused on opening the band gap of it.

1.1.4. State-of-the-Arts of Band Gap Opening in Graphene

Modification methods for increasing the band gap of graphene have been made adopting various approaches. Such approaches can be roughly classified into chemical methods, physical methods, and hybridization according to the basic principle. There are nanoribbons and quantum dots as examples of modifying graphene to physically adjust the band gap. When the size of the graphene is reduced to an extreme, the electrons are confined to the lateral direction in the layer and behave in the way as in materials with lower dimensions — one-dimension in graphene nanoribbons (GNRs) and zero-dimension in graphene quantum dots (GQDs). The band gap increases as the width of the nanoribbons or the diameter of the quantum dots decreases. [10, 11] Otherwise, by controlling the stacking of the bilayer graphene, the band gap can be increased to some extent. However, these methods have very low yields and poor uniformity in production, and require very expensive equipment in some cases.

Hybridization of graphene with other materials has been studied more actively in recent years. Typically, 2D materials similar to graphene can form van der Waals heterogeneous structures. Many studies of hybridization with metal oxides, polymers, and other semiconductor materials have also been reported. [12-14] Graphene is intrinsically possible to have various combinations with other materials, so the spectrum of performance to be obtained through hybridization is very

wide. However, the process is complicated and the synthesis issues of some materials need to be improved.

On the other hand, chemical methods have great practical advantages such as simple process and mass production. Graphene can be modified by substituting dopants in graphene, or by combining other materials to create nanocomposites. [15] Otherwise, similar modification effects can be brought without introducing such external substances.

In Hummers' method, which is a typical method of synthesizing graphene in liquid, graphite is exfoliated in the oxidized state and become graphene oxide (GO). [16, 17] GO has a structure consisted of carbon atoms bonded with various oxygen functional groups such as hydroxyl, carboxyl, carbonyl, and epoxy groups. The molecular orbitals of some carbon atoms bonded to them are sp^3 hybridized, which make GO insulator with large band gap. In addition, due to the oxygen functional groups, dispersibility in many solvents, especially in water, becomes very excellent and enable graphene to be processed in various formula. [18]

As GO is reduced, the electron conjugation and sp^2 molecular orbital are restored and the band gap becomes gradually narrower. Thus, controlling oxidation or reduction of graphene may provide the possibility of tuning the band structure over a wide range. Application of this phenomenon can greatly simplify the synthesis of graphene with proper band gap. Moreover, because GO is synthesized in a liquid state and can maintain a chemically stable dispersion state, the advantages of

chemical modification method — scalability, economic feasibility and simplicity of process — are maximized.

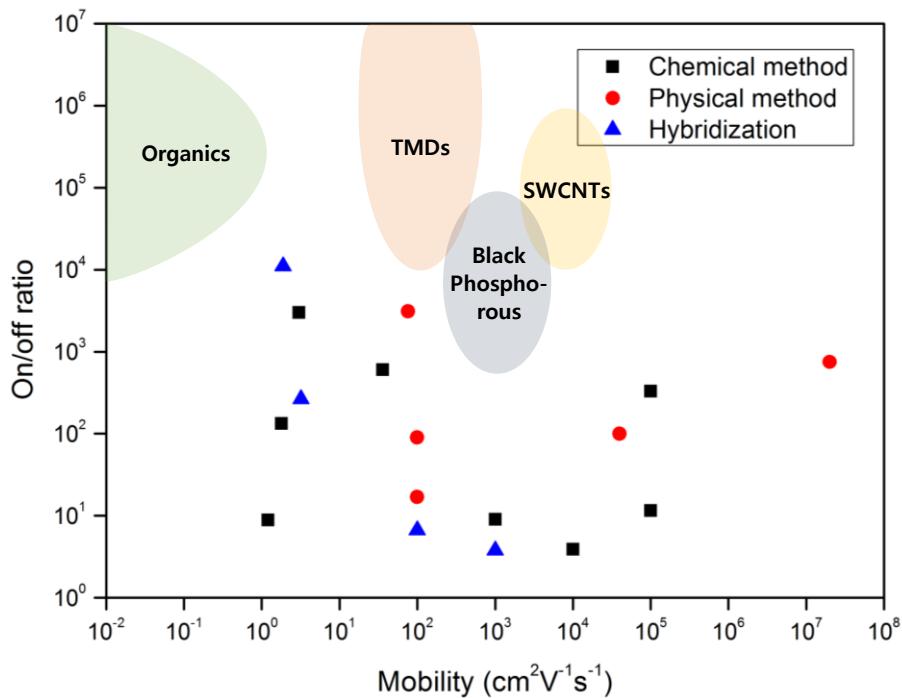


Figure 3. Mobility and on/off ratio of graphene FETs [19-35]

1.1.5. Limitations of State-of-the-arts

It has been experimentally proven that the percentage of oxygen contained in graphene is approximately proportional to the band gap of it. The doping effect of oxygen functionalities, which is similar to substituting carbon atoms into external elements such as B or N atoms, is also well-known. However, previous studies have been limited to casual observation of property variation according to oxygen content.

Even in a systematic research, since the GO was normally known as an intermediate step for making highly conducting reduced graphene oxide (rGO), it is restricted to the rGO containing very little amount of oxygen. The fact that the oxygen contained in the GO can exist in various functional groups means that the change in the properties of GO and rGO due to oxidation cannot be simply quantified. However, only a few computational studies that take this into account with considerably simplified models.

Table 1. State-of-the-arts of band gap tuning through reduction

Reference	Limitation
[36]	Lack of systematic reduction control and association with chemistry
[37]	Focused on how quickly we can achieve high levels of reduction.
[38]	Insufficient interpretation of chemistry, simple comparison of the reduction time and the resulting band gap
[39]	Low reduction levels, insufficient result data
[40]	Only analysis of reduction techniques.

Although there are many practical advantages of oxygen functional groups, there is very little empirical data on how the electronic properties of graphene affect its performance. As a result the use of GO itself as a transistor material is very limited.

1.2. The strategy and aim

1.2.1. Control of Degree of Reduction and Functionality

As described above, oxygen functional groups can induce analogous effects to substitutional doping or nanocomposite, but build of systematic and reliable data about them is primarily required to apply graphene to transistors. Therefore, the electrical properties including band gap of graphene were measured with changing the oxygen contents of graphene. The oxygen content was controlled by adjusting degree of reduction. Adjusting reduction of highly oxidized GO facilitated modification of the rGO composition without hindering the exfoliation of graphene. This procedure is even more essential as previous studies of graphene reduction are mostly focused on how high C/O ratios can be achieved.

It has been computationally proven that doping effects and degree of deformation of graphene lattice by different oxygen functional groups are different. However, it is necessary to study the performance of graphene when these are actually combined. Therefore, by adopting methods known to be different in the reduction mechanism, the relation between the oxygen bond content and the band gap is experimentally derived.

1.2.2. Identification of Relationship between Performance and Chemistry of Reduced Graphene Oxide

The band gap, a key characteristic for graphene as a transistor channel material, and the conductivity directly connected to the mobility were measured according to the degree of reduction. We assume that each oxygen functionality has different effects on these properties, and identified the specific influences of the functionality obtained through the component analysis based on that premise. The relationship between the material properties and the electrical properties of the reduced graphene oxide was analyzed, and a logical process was applied to find out the principle that the oxygen functional group electrically affects graphene oxide.

1.2.3. The Goal of the Study

In this study, control of oxygen-containing functionality composition of graphene through reduction is firstly achieved. This provides a basis for synthesizing graphene with optimal performance. Afterwards, the relationship between band gap and the functionality is synthetically analyzed. It would help to present the practical synthesis direction for graphene to perform a certain performance, and to develop the utilization of graphene in transistors as well as in other applications.

2. Experimental

2.1. Preparation of Highly Oxidized Graphene

2.1.1. Materials

The graphite precursor (flakes, natural), potassium persulfate ($\geq 99.0\%$), phosphorus pentoxide (99 %), potassium permanganate ($\geq 99.0\%$), hydroiodic acid (57 wt.%), and sodium borohydride (99 %) were purchased from Sigma-Aldrich. Sodium hydroxide (beads, $\geq 97\%$), concentrated sulfuric acid ($\geq 98\%$), hydrochloric acid ($\geq 35.0\%$) and hydrogen peroxide (30 %) were purchased from Daejung Chemicals & Metals Co. Ltd.

2.1.2. Synthesis of Graphene Oxide: Modified Hummers' Method

Graphite precursor was pre-oxidized into expanded graphite by following steps in advance. 8 g of potassium persulfate and 8 g of phosphorus pentoxide were completely dissolved in 60 mL of concentrated sulfuric acid in around-bottom flask at 80 °C, followed by adding 4 g of graphite flakes. The mixture was stirred for 24 hours, and washed by DI water repeatedly until the pH of washed water become

close to 7. The expanded graphite was completely dried in a 60 °C vacuum oven before performing modified Hummers' method.

For synthesizing GO, 2 g of expanded graphite was oxidized with 12 g of potassium permanganate in 92 mL of concentrated sulfuric acid. Reaction was performed at 35 °C for 12 hours while stirring in jacketed glass reaction vessel. The mixture was then cooled to 0 °C, and 200 mL of DI water was slowly added over one hour. To terminate the oxidation reaction, 10 mL of hydrogen peroxide was added. The aqueous mixture was centrifuged at 13,000 rpm for 30 minutes and the supernatant was decanted. The GO precipitate was mixed with 1M hydrochloric acid and centrifuged for 15 minutes in order to remove unnecessary chemicals. The same process was repeated for three times. It was then centrifuged with DI water for 15 minutes five times, and lastly dense dispersion of GO was collected.

2.2. Reduction of Graphene Oxide

2.2.1. Sodium Borohydride (NaBH_4) Reduction

Prior to reduction, master solution was prepared that prevents solvolysis of NaBH_4 based on LG. Guex's research [41]. 433 mg of NaOH and 227 mg of NaBH_4 was dissolved in DI water, and water was added to make a total solution of 12 mL. GO dispersion was diluted to 1 mg/mL, and 24 mL of it was taken and mixed with 12 mL of the master

solution for the desired time at room temperature while stirring. In order to terminate reduction reaction, 16 mL of HCl 1 M solution was added to induce solvolysis of NaBH₄ and hydrogen gas was rapidly generated.

The reacted material was neutralized by washing multiple times by vacuum filtration and centrifugation. The produced dispersion was made into a film by vacuum filtration.

2.2.2. Hydroiodic Acid (HI) Reduction

GO was first made into a freestanding film using aluminum oxide membrane filter. 15 mL of GO dispersion diluted to 1 mg / mL was completely filtered with a membrane filter to make a translucent solid film.

HI was heated to 80 °C on a hot plate, and a GO film was placed thereon to vaporize the desired time. The GO film becomes shiny black as it is reduced by HI vapor. The remaining HI after the reaction was completely evaporated by heating on a hot plate overnight. The same reduction process was applied to GO transparent film formed by spin-coating on a glass substrate.

2.2.3. Thermal Reduction

The thermal reduction of the GO was done in a box furnace under continuous nitrogen flow. GO freestanding film and transparent film on glass substrate were annealed at a heating rate of 5 °C. The GO film was maintained in isothermal condition for 1 hour after heating was completed, and cooled down slowly.

2.3. Characterization of Reduced Graphene Oxide

2.3.1. Material Properties Measurement

The content of carbon and oxygen contained in rGO were estimated by the X-Ray Photoelectron Spectroscopy (XPS; AXIS-His, KRATOS), and detailed oxygen bonding changes were analyzed by Fourier transform infrared spectroscopy (FT-IR; Nicolet iS50, Thermo Fisher Scientific). The atomic ratio (at.%) data off all the measurement was mainly used, and the relative values of oxygen and oxygen bonding atomic ratios divided by those of carbon (O/C ratio) are considered as the main parameters hereafter in this study. Raman spectroscopy (LabRAM HV Evolution, HORIBA) was used to estimate defect level of rGO films.

2.3.2. Electrical Properties Measurement

The band gap of rGO was measured by UV-vis-NIR spectrophotometer (Cary5000, Agilent Technology) and sheet resistances were measured by 4-point probe measurement. The conductivity of each film was calculated with thickness measured with field-emission scanning electron microscopy (FE-SEM; MERLIN Compact, ZEISS)

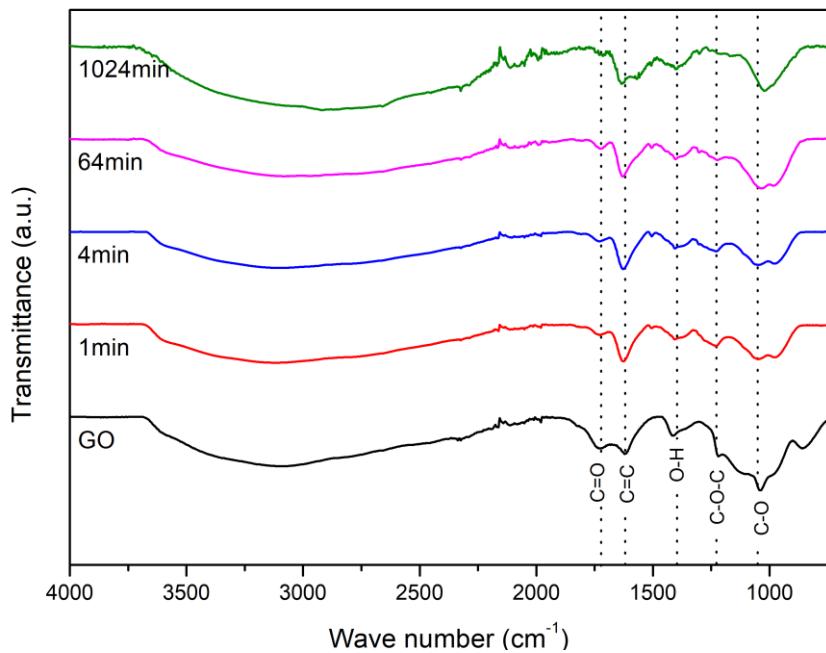
3. Results and Discussion

3.1. Chemical Characterization of rGO

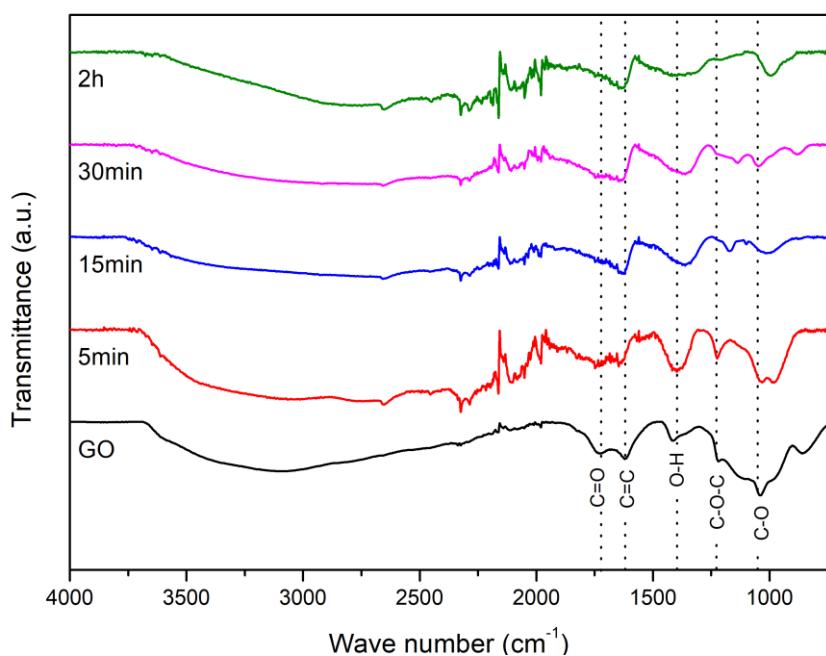
3.1.1. Variation of Oxygen-containing Functionality with Reduction; Qualitative Analysis

FT-IR is a useful tool to observe the oxygen functional group tendency of rGO. Graphene oxide typically exhibits a C-O stretching mode, which is dominated by hydroxyl and epoxy groups, at around 1045 cm^{-1} , and an epoxy stretching mode at 1226 cm^{-1} . The C=O double bond of the carboxyl and the carbonyl groups appears at 1722 cm^{-1} , and aromatic C=C bonding appears at 1620 cm^{-1} . Normalization based on the intensity of C=C absorption peak enable rough comparison of the change of oxygen functionalities. The stretching mode of O-H bonds by water or rGO hydroxyl groups is also observed at 1396 cm^{-1} and 3397 cm^{-1} . [42]

(a)



(b)



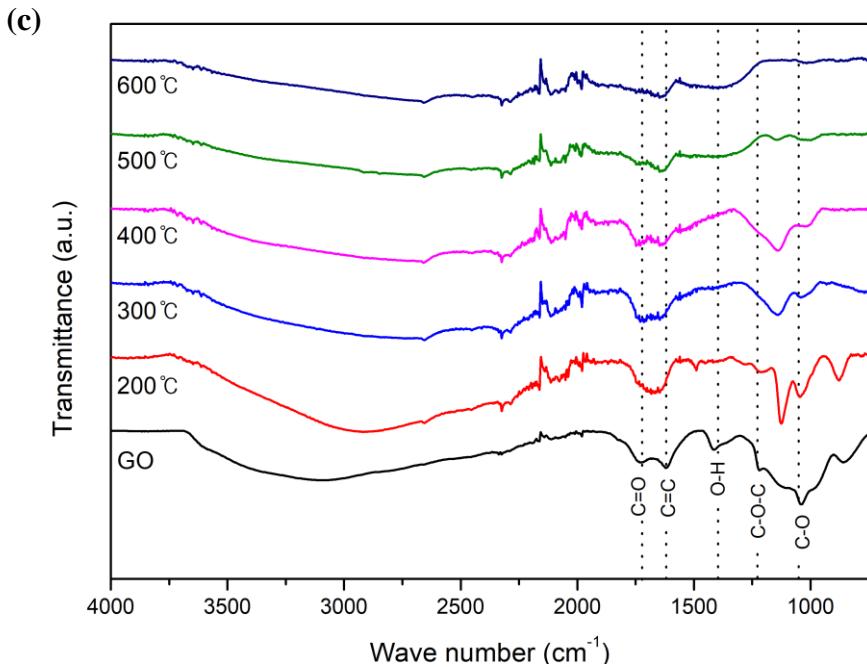


Figure 4. FT-IR spectroscopy of (a) RGO_BH, (b) RGO_HI, and (c) RGO_TH with GO

In RGO_BH, the intensities of peaks corresponding to C-O and O-H were not much reduced compared to other oxygen peaks. This is due to the reduction mechanism of NaBH₄, which matches the XPS analysis results. While every functional group was sequentially reduced in RGO_HI, RGO_TH spectra unusually showed the peak of O-H regenerated at high temperature. Many studies have reported that epoxide groups are reduced to phenolic groups above 400 °C. [43] It is also known that the resulting hydroxyl groups are difficult to pyrolyze completely even at very high temperatures because they are intercalated between conjugated regions. [43-45]

3.1.2. Variation of Oxygen-containing Functionality with Reduction; Quantitative Analysis

The XPS analysis confirmed that the oxygen content has changed as intended as the reduction progressed. The numerical value directly related to the properties of graphene is not the atomic percentage of oxygen to the total GO, but the relative amount of oxygen functional groups to the conjugated graphene sheet area. Therefore, we define oxygen content as the value of the atomic ratio of oxygen bonding divided by that of carbon, and set this as the main parameter indicating degree of reduction. According to XPS deconvolution data, oxygen content varied from a maximum of 1.16 to 0.34. In the chemical reduction reaction, the reaction was judged to have reached the saturation state, as the oxygen content did not change even though it had been reacted for a sufficiently long period.

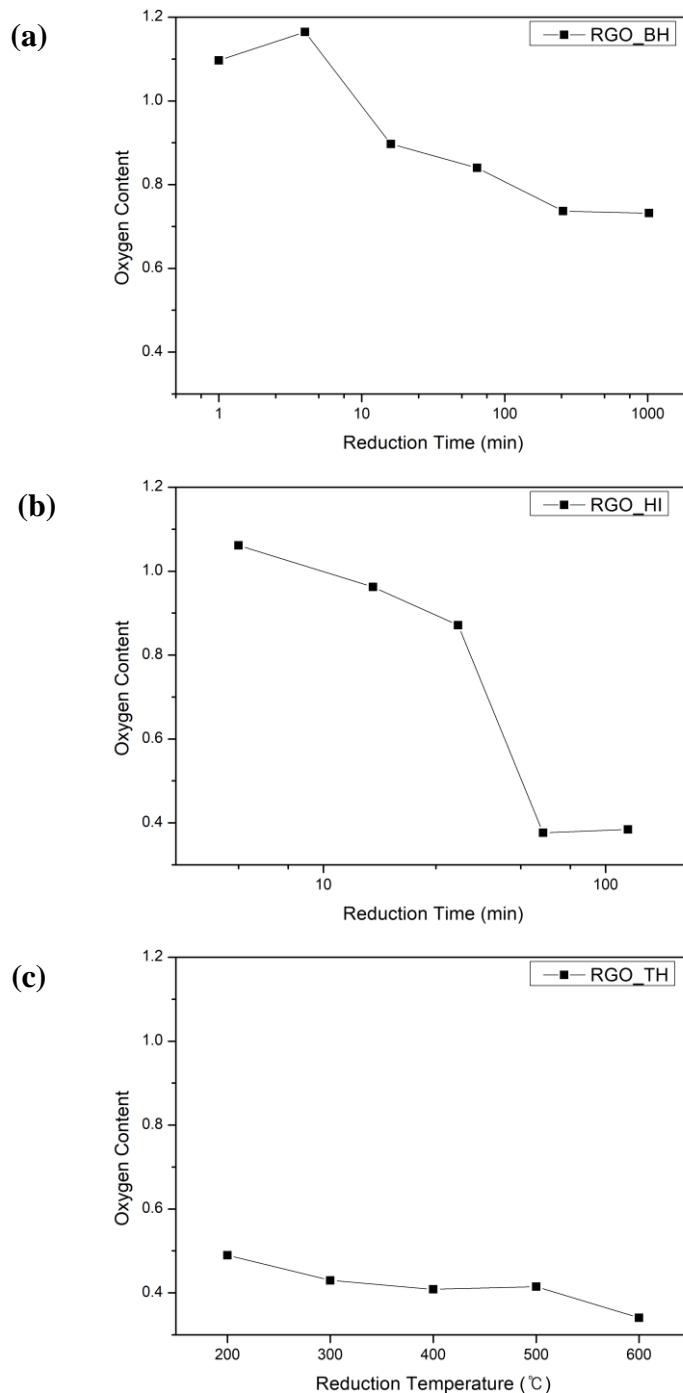


Figure 5. Oxygen content variation of (a) RGO_BH, (b) RGO_HI, and (c) RGO_TH by degree of reduction

C1s deconvolution results showed differences in the reduction pattern depending on the sample. RGO_BH showed almost no decrease in the contents of C-O bonding compared to C=O bonding, while RGO_TH showed greatly reduced fraction of both types of bonding. In RGO_HI, C-O bonding gradually decreased as reacted for a long time.

The reason why the two chemical reduction results show such a large difference is due to the reaction mechanism of the two reducing agents. NaBH₄ produces BH₄⁻ anion in aqueous solution, and the anion attacks electrophilic carbonyl carbon as a nucleophile. Ideally this reaction occurs continuously until all B-H bonds are depleted. However, the esters cannot be reduced by NaBH₄, while a few kinds of oxygen functional groups with carbonyl carbon, *e.g.* aldehydes and ketones, can be reduced leaving hydroxyl groups. [46] In contrast, HI reduces oxygen functionality through nucleophilic substitution reactions — *via S_N1* or *S_N2* pathways depending on the reactants. Hydrogen halides including HI are excellent reducing agents that can oxidize epoxy and hydroxyl groups, as well as other oxygen functionality. [47]

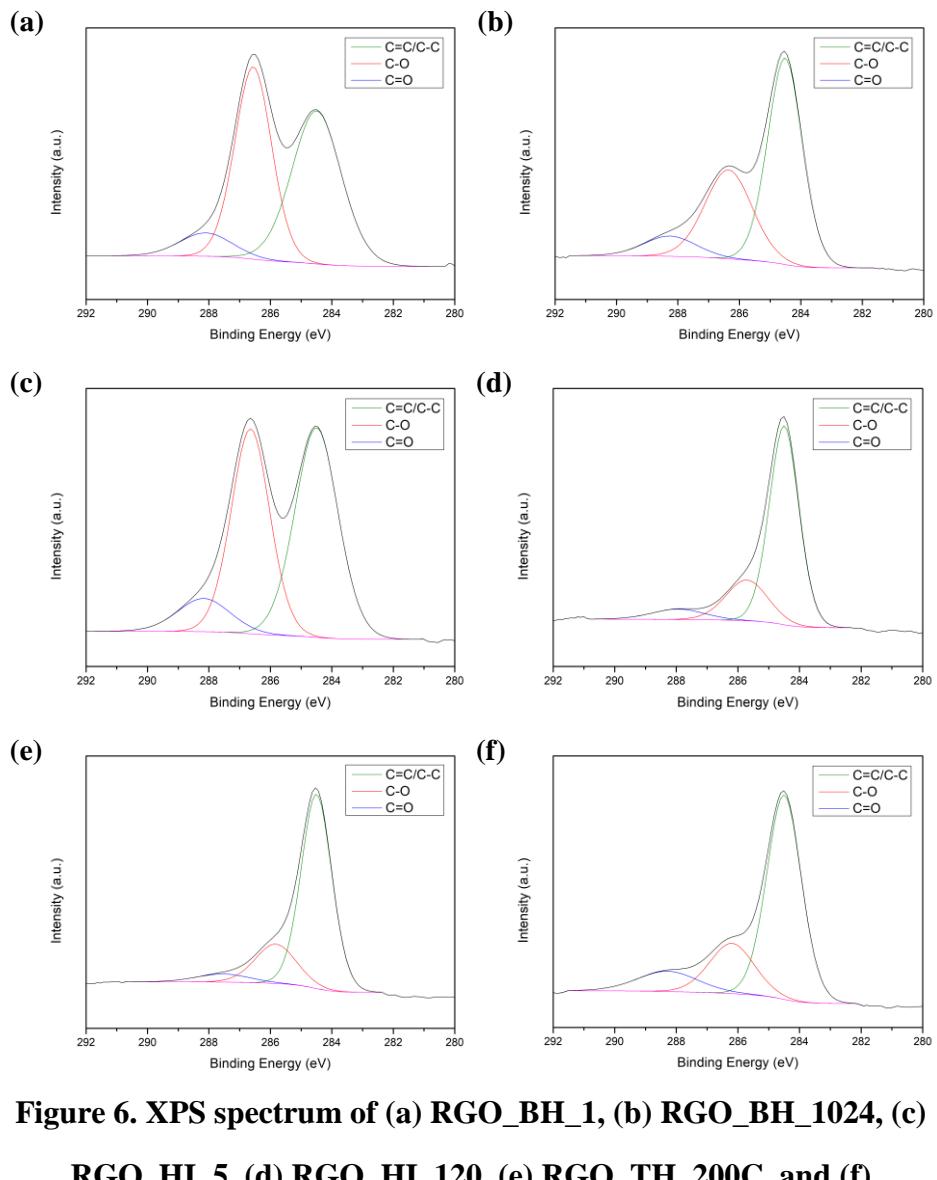


Figure 6. XPS spectrum of (a) RGO_BH_1, (b) RGO_BH_1024, (c) RGO_HI_5, (d) RGO_HI_120, (e) RGO_TH_200C, and (f) RGO_TH_600C

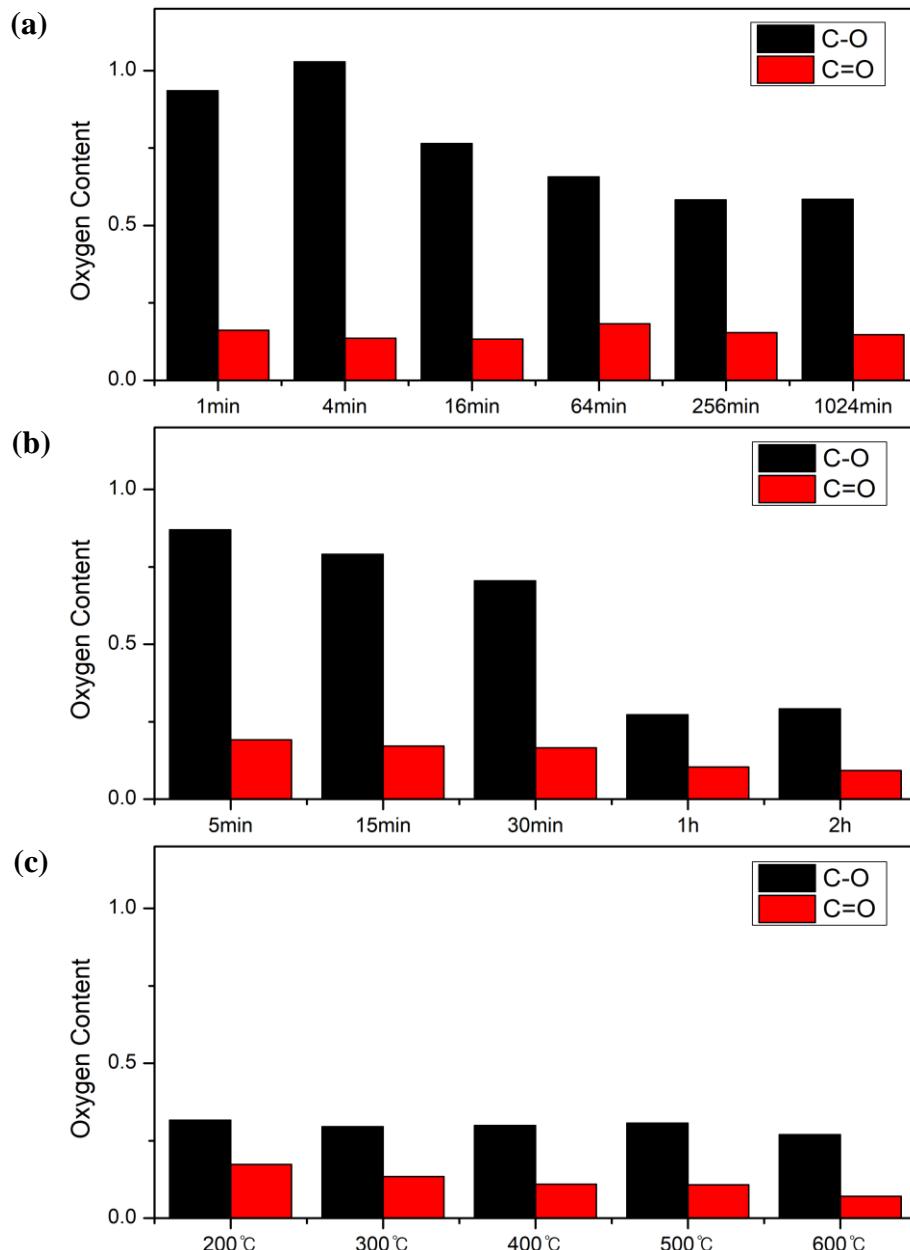


Figure 7. Reduction of each oxygen bonding content of (a)

RGO_BH, (b) RGO_HI, and (c) RGO_TH

3.1.3. Defect Level Comparison through Raman Spectroscopy of Reduced Graphene Oxide

Functionality is not the only factor that affects the various properties of graphene, of course. The Hummers' method of oxidizing and exfoliating graphite leaves a significant amount of defects on the surface, so the defect levels of rGO were measured by Raman spectroscopy. Raman spectroscopy has been widely used to investigate the properties of graphene materials and their effect on the performance of related devices. Raman spectra show spectral characteristics inherent not only to a variety of graphene-based materials but also to bulk graphite.

The G band of Raman spectrum is associated with two optical modes in the Brillouin zone center and is a characteristic peak of the graphene related material. Peak positions in the G mode (at $\sim 1588 \text{ cm}^{-1}$) are sensitive to defects, doping, strain, temperature, etc. Therefore, they have been widely used to investigate responses of graphene-based materials and devices to external factors. On the other hand, D peaks (at $\sim 1580 \text{ cm}^{-1}$) originate from intervalley phonons between two nonequivalent Dirac cones. They can be used to characterize defective carbon materials, especially graphene oxide. [48]

As a result of examining the D band and the G band in the Raman spectrum of rGO, there was little difference in the peak position of the G band, but the slightly high intensity of the D band to the G band is notable in rGO_HI. This suggests that rGO_HI has a higher defect level than

other rGO measured, even in consideration of its high degree-of-reduction.

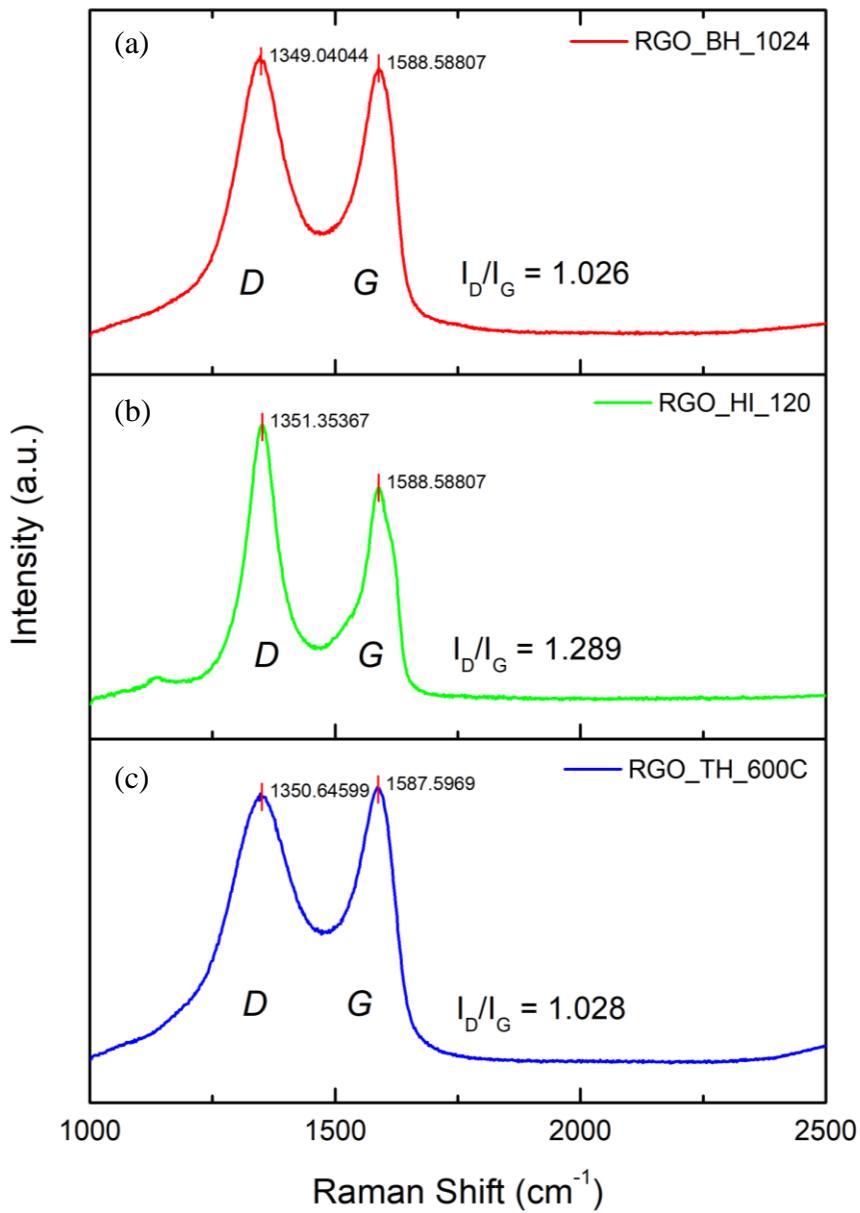


Figure 8. Raman spectroscopy of (a) RGO_BH, (b) RGO_HI, (c) RGO_TH

3.2. Electronical Characterization of rGO

3.2.1. Band Gap Changes of RGO with Oxygen-containing Functionality

Figure 9 and 10 shows the change in band gap with decreasing oxygen content. The band gap was measured to be 3.01 eV as the maximum when reduced the least, and decreased to 1.83 eV as the minimum. The band gap positively correlates with the oxygen content, and it was confirmed that depending on the oxygen content, the band gap can have a broad electrical spectrum from insulator to semiconductor.

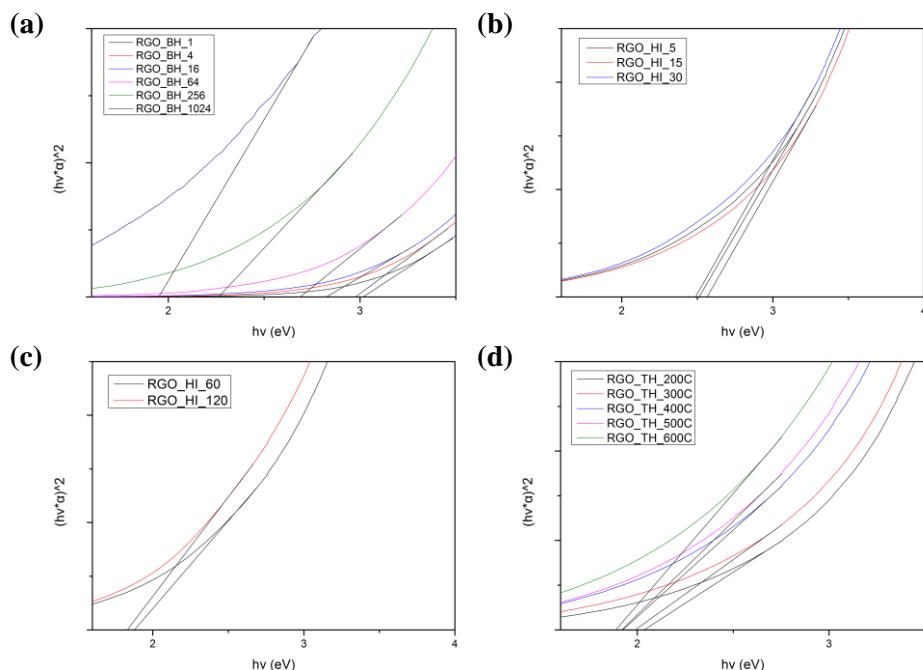


Figure 9. Representative Tauc plot for UV-Vis-NIR absorption of (a) RGO_BH, (b), (c) RGO_HI, (d) RGO_TH

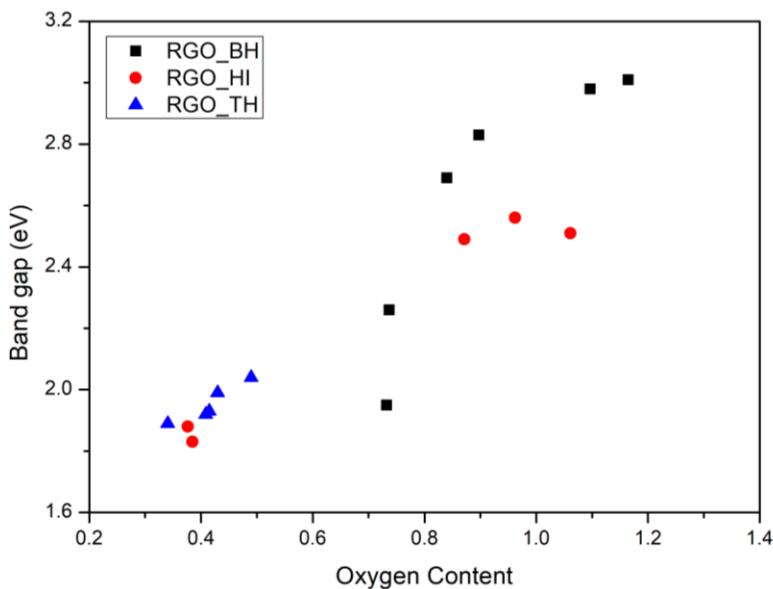


Figure 10. Band gap versus oxygen content of reduced graphene oxide

3.2.2. Conductivity of Reduced Graphene Oxide Film

The sheet resistance of rGO film was measured by 4-point probe measurement, and the conductivity of the film was calculated by applying it to the formula together with the film thickness. Conductivity is proportional to the product of mobility and carrier concentration.

$$\sigma = e(n\mu_e + p\mu_h) \quad (3)$$

Conductivity increased with decreasing oxygen content, ranging from a very low value of at least about $3.5 \times 10^{-5} \Omega^{-1} \cdot m^{-1}$ to a high value of up to about $10^4 \Omega^{-1} \cdot m^{-1}$. This indicates that as the reduction progresses, the

proportion of sp^2 hybrid orbitals of carbon becomes higher and gradually the conjugation of electrons is restored.

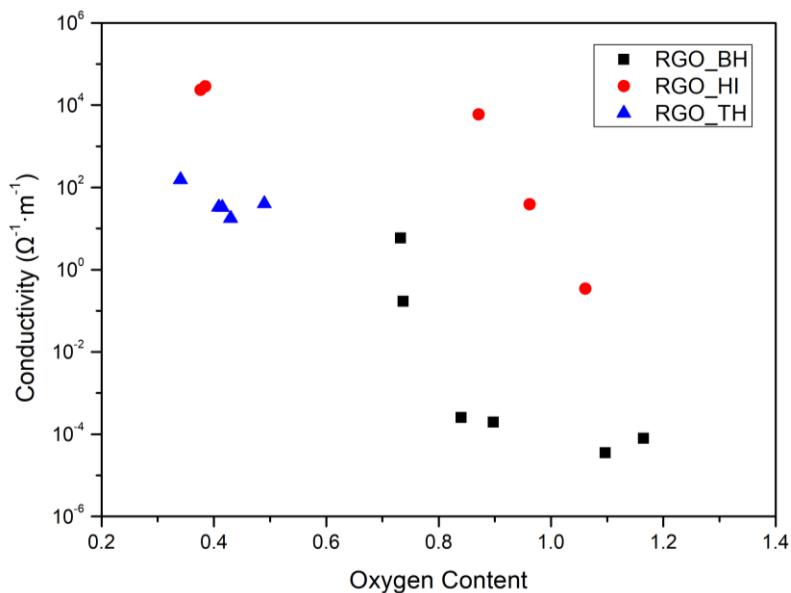


Figure 11. Conductivities of reduced graphene oxide films versus oxygen content

The result of plotting the exponential value of the conductivity against the band gap showed a roughly similar shape to the inverse graph. This is in agreement with previous studies, but RGO_HI has a relatively high value compared to other samples with similar band gaps.

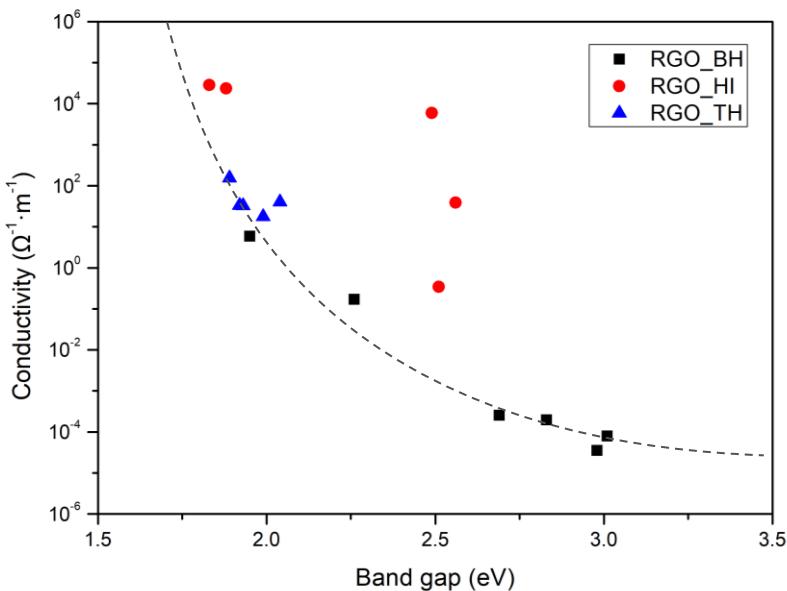


Figure 12. Conductivities of reduced graphene oxide films versus band gap

The abnormally high conductivity of RGO_HI can be explained in two ways. The first is the doping effect of the iodine ions that occurs when reduced by HI. It is well known that doping has a great influence on the conductivity of semiconductor materials. In the case of iodine, the conductivity can be enhanced by increasing the hole concentration in carbon-based materials. To prove this, we analyzed the Raman spectrum of RGO_HI in a shift range that is lower than the typical method for analyzing graphene. As a result, a remarkably strong peak appeared at about 164 cm^{-1} , which is similar to the peak indicated by I_5^- in the iodine-doped carbon nanotube. Thus, the hole supply from the iodine chain increased the charge concentration of RGO_HI, resulting in a significantly higher electrical conductivity. [49]

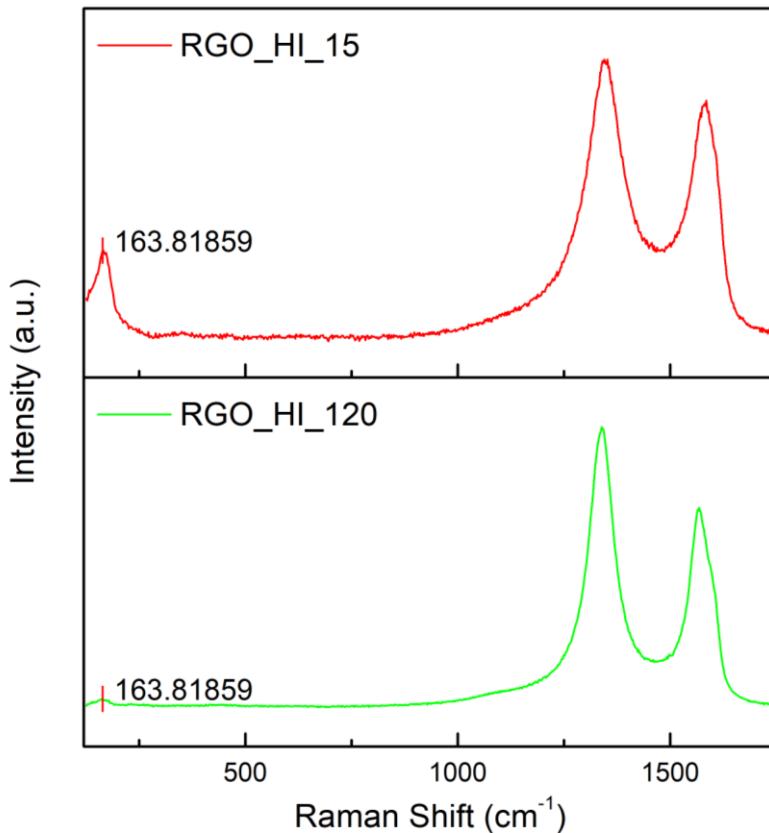


Figure 13. Raman spectrum of RGO_HI in the low shift range. HI vapor was reacted for 15 minutes and two hours, respectively.

The second is that the shrinkage of the film when the HI vapor treatment is performed. Due to shrinkage, the conductivity of the bulk film compared to the graphene sheet was less underestimated. As shown in Figure 14, the GO films of the same mass (~15 mg) were reduced by HI, but the thickness was remarkably decreased when the reduction was progressed for longer time.

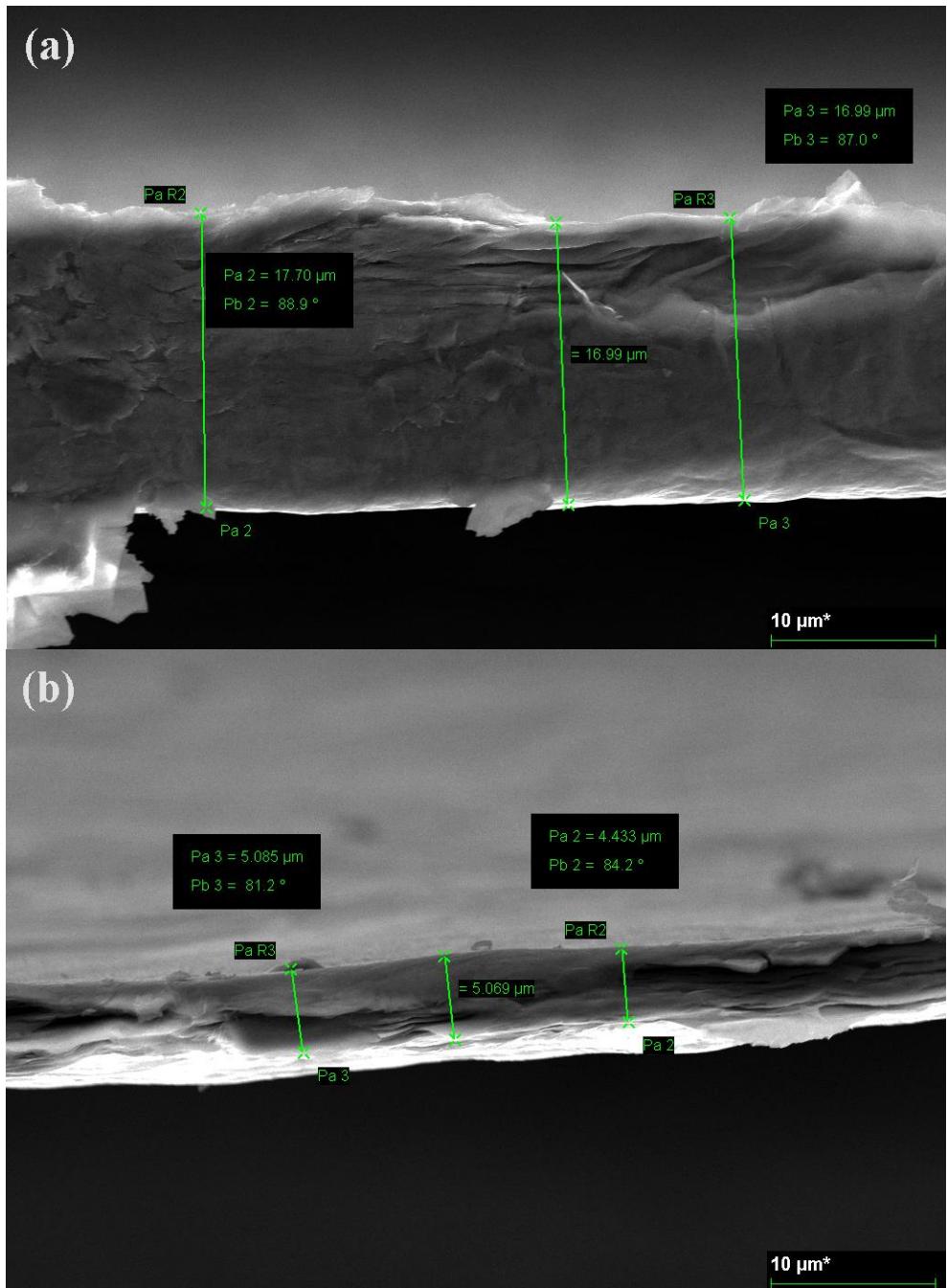


Figure 14. SEM images of RGO_HI reduced for (a) 15 minutes and (b) two hours.

3.3. Empirical Analysis on Relation between Oxygen Functionality and Band Gap of Graphene

3.3.1. Simplified Model for Determining the Effect of oxygen Functionality

Hereafter, we will comprehensively interpret the relationship between the characteristics of rGO analyzed earlier. Several assumptions were made to quantitatively analyze the band gap opening effect of the functional group attached to graphene. First, molecular orbitals pristine graphene are ideally conjugated so that charge carriers can move freely within the sheet. In other words, the electrons are free in the 2D direction and therefore have all levels of energy. Second, the carbon bonded to the functional group does not participate in the conjugation, and thus acts as a potential barrier in the transfer of electrons and holes.

In a classical particle-in-a-box model, the energy level gap an electron can have is inversely proportional to the square of the distance the electron can freely move. [50]

$$E_{n_x,n_y,n_z} = \frac{\hbar^2 k_{n_x,n_y,n_z}^2}{2m} \quad (4)$$

$$k_{n_x,n_y,n_z} = \frac{n_x \pi}{L_x} \hat{x} + \frac{n_y \pi}{L_y} \hat{y} + \frac{n_z \pi}{L_z} \hat{z} \quad (5)$$

Third, the average distance an electron travels until spontaneous migration of the non-conjugated sp^3 carbon (molecular orbitals of carbon atoms bonded to functionalities are not always sp^3 hybridized, but they are named as such for convenience) is inversely proportional to content of sp^3 carbons.

$$L \propto \frac{1}{C_{oxygen}} \quad (6)$$

This assumption can be derived through the following process. We defined the minimum electron-nucleation distance d for electrons to fall within the sp^3 atom's electrical range. While an electron moves at a speed of v for a specific time (t), it would be encountered with the sp^3 carbon in the radius d of the travel path, so that they are all affected by the sp^3 atom whose nucleus are in the area of $vt \times 2d = 2vtd$. That is, the number of times the electron encounters the 'barrier' during time t can be written as

$$n = 2vtd \times (\# \text{ of } sp^2 \text{ per area}) \quad (7)$$

The average distance an electron can move freely at a time is

$$L = \frac{vt}{n} = \frac{1}{2d(\# \text{ of } sp^2 \text{ per area})} \quad (8)$$

In practice, electrons do not move in one direction but randomly move, so the average velocity will be proportional to the real speed of the electron but smaller. The area of graphene is proportional to the number

of sp^2 carbon atoms constituting graphene, so that L is inversely proportional to the oxygen content.

$$L \propto \frac{1}{\# \text{ of } sp^2 \text{ per area}} \propto \frac{1}{C_{oxygen}} \quad (9)$$

From a very simplified model and three assumptions we can get the following short relation:

$$\sqrt{E_G} \propto C_{oxygen} \quad (10)$$

Based on the above equation for each content, the degree of contribution of two bonds to the band gap opening was simply quantified.

$$E_G = 0.59 \cdot C_{oxygen}^2 + 0.48 \cdot C_{oxygen} + 1.6 \text{ [eV]} \quad (11)$$

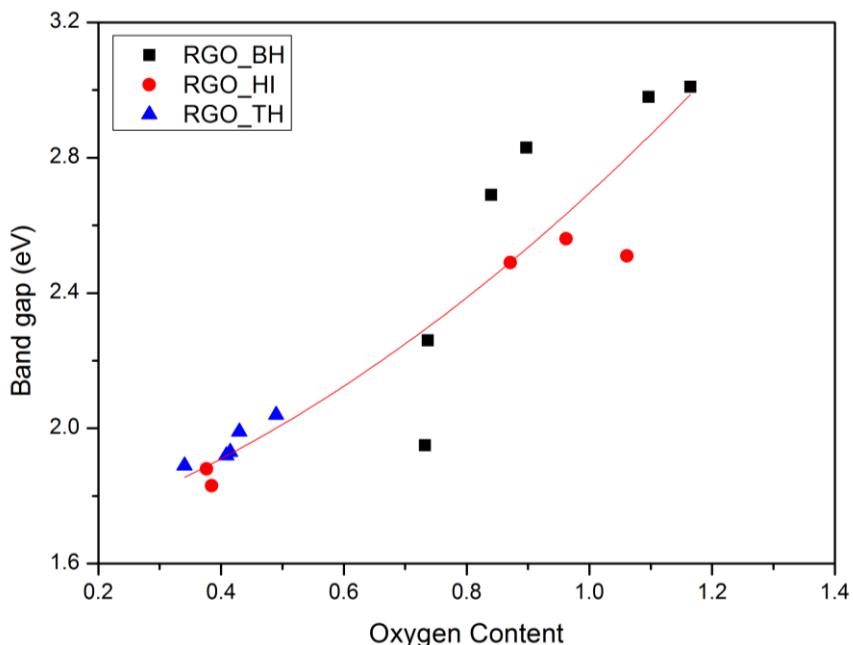


Figure 15. Band gap versus oxygen content, and the calculated value from Eq. (11) (red line)

The second order polynomial for the oxygen content was able to produce a formula that fit well into the actual measurements. Ideally, when the oxygen content is zero, it means pure graphene, so that the band gap should be zero. However, according to the equation, the band gap does not converge to 0 even when both bonding are completely reduced and a band gap of about 1.6 eV remains.

In fact, the actually synthesized graphene is somewhat different from the ideal case. The constant term of the equation can be used to reflect the gap between the actual graphene and the ideal graphene. In this study, we have investigated the effect of graphene on the formation of graphene in the Hummers' method. Graphite is oxidized, exfoliated and reduced again in the Hummers' method, resulting in a considerable number of defects in the graphene sheet and band gaps due to such defects. In other words, constant term means the size of band gap caused by factors other than oxygen functionality. It can be interpreted that the cleavage or pore generated in the oxidation and reduction process is not completely recovered. The exact origin of the constant term can be accurately identified in future studies that have controlled variables other than reduction.

Another remarkable point is that the more oxygen content the experimental and calculated values are, the more divergence arises. However, when the corresponding oxygen content is more than 0.8, approximately half of the bonds of the carbon atoms constituting the graphene oxide act as a potential barrier. This makes it impossible to assume that there are irregularly arranged potential barriers independent

of a certain potential field, as in the above model. In fact, computational studies have shown that oxygen functional groups tend not to be produced maintaining the widest spacing. [51]

3.3.2. Band Gap Variation According to sp^2 Conjugation Domain

It is conceivable that the sp^2 conjugated region is restored as the reduction progresses, rather than creating a barrier along the oxygen functional group on the planar potential surface. The sp^2 conjugation area is directly proportional to the atomic percentage of C-C / C=C bonding in XPS data, as it is proportional to the number of aromatic C-C bonds. As this value approaches 1, the number of atoms participating in the conjugation of all carbon atoms increases, which means that the conjugation region gradually recovers and becomes closer to the pristine graphene.

$$E_G = 0.56 \cdot \frac{1}{C_{carbon}^2} - 0.59 \cdot \frac{1}{C_{carbon}} + 1.6 \quad [eV] \quad (12)$$

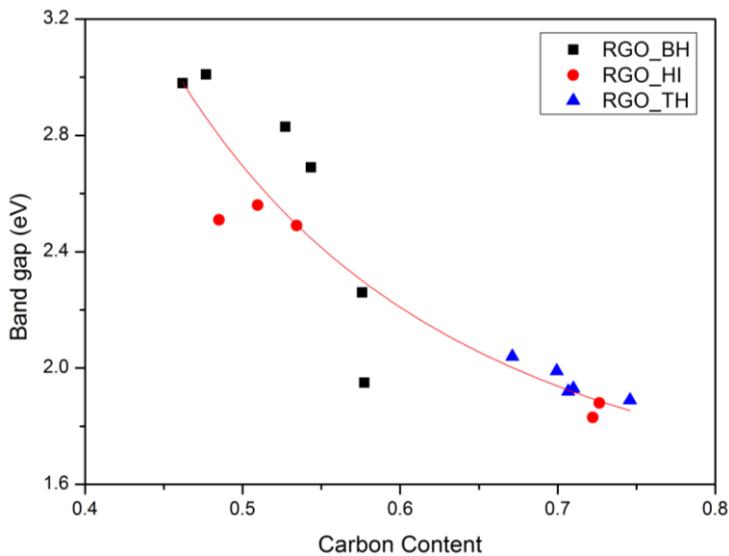


Figure 16. Band gap versus carbon content, and the calculated value from Eq. (12) (red line)

Since carbon content is inversely related to oxygen content, we have shown the reciprocal value of carbon content. Similar to Eq. (11), an inverse quadratic polynomial with a constant of about 1.6 eV was derived, which shows that the spacing between the two energy bands decreases as the pi conjugation area recovers

3.3.3. Electronical Effects of Individual Functionalities on Band Gap

In order to provide a more detailed synthesis guide, two types of carbon-oxygen bonds in graphene were classified and plotted based on Eq. (10), and the following relation was derived.

$$E_G = (0.5 \times C_{C-O} + 0.08 \times C=C_O + 1.2)^2 [eV] \quad (13)$$

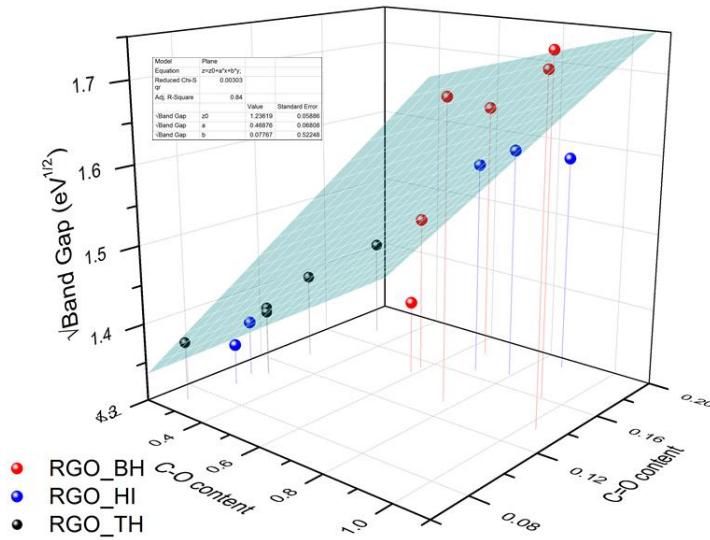


Figure 17. The square root of band gap versus C-O and C=O content. The lattice-patterned plane represents the calculated value of the band gap using the Eq. (13).

The coefficient of C-O content is about 6 times that of C=O content, which implies the band gap of rGO is more sensitive to the amount of C-O bonding. Among the various oxygen functionality, functional group containing C=O double bond is structurally different as compared with the case of non-functional group, so that C-O single bond and double bond may affect band gap differently. This is because the functionality including C=O double bond is often present on the edge of the graphene sheet, whereas in the case of C-O single bond, it is usually present in the basal plane of the graphene sheet except for the carboxyl group. As a result, C-O single bonds form different molecular orbitals from pristine

graphene and deform the crystal structure, severely hindering sp^2 conjugation. The different coefficients of the two bonds also mean that the rate at which two oxygen bonds contribute to band gap opening is different. In other words, the functionality that includes only single bonds is advantageous for modifying the band structure of graphene. The usefulness of this conclusion will be discussed later in this paper.

Although we used a very simplified structure, we can see that the measurement value and the calculated value rather coincide with each other.

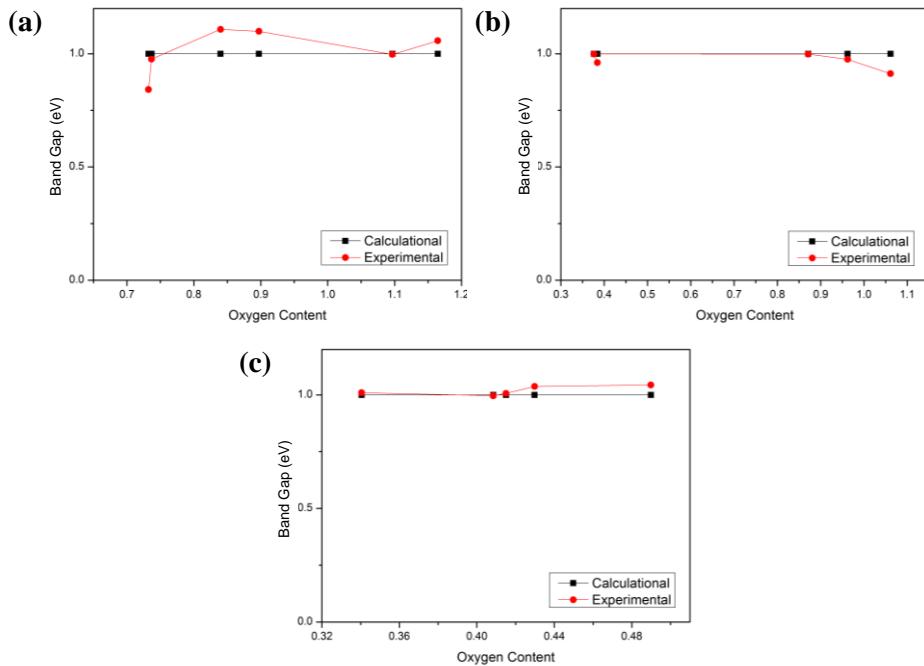


Figure 18. Comparison between calculated band gap values and actual measurement band gap values of (a) RGO_BH, (b) RGO_HI, and (c) RGO_TH obtained using the Eq. (13)

However, some RGO_BH samples with high oxygen content showed exceptionally high band gap, but as the reduction progresses, it rather decreased. Compared with other reduction methods and considering the characteristic point of functionality change when reduced by NaBH₄, these differences may be attributed to the increased hydroxyl groups in graphene oxide reduced by NaBH₄.

As described above, the reduction mechanism of NaBH₄ begins with the attack of the nucleophilic borohydride ion on the electrophilic carbonyl carbon. The resulting alkoxide is supplied with proton from the water to produce alcohol. On the other hand, HI is possible to reduce most oxygen groups leaving a small amount of carbonyl residues. This means that, unlike RGO_HI, as the degree of reduction of RGO_BH increases, the total oxygen content decreases, but the absolute amount of hydroxyl groups increases. In particular, the proportion of hydroxyl groups in the C-O bonds will be significantly increased. The fact that the proportion of the hydroxyl group was increased and the band gap is lower than the expected value can be interpreted as follows; the hydroxyl group has a particularly small band gap opening effect among all the functional groups.

A similar tendency was observed in RGO_TH samples of which FT-IR spectra showed small increases in hydroxyl groups. Although the band gap deviation is relatively small, it also demonstrates the small band gap contribution of the hydroxyl group.

3.4. Increased Efficacy of Reduced Graphene oxide and Future Research

3.4.1. Directional Suggestion to Synthesize Graphene of Desired Specification

We have clarified that among the many oxygen functional groups which make up GO and rGO, the oxygen single bond is more effective in increasing the band gap than double bond. Also, the hydroxyl group was figured out not to greatly affect the band structure of graphene than other functional groups consisted of C-O — carboxyl group, epoxy group, etc. Therefore, selective reduction of the C=O bond is useful to obtain a sufficient band gap with only a small oxygen content.

Conversely, C-O bonding, in particular the hydroxyl group, is the most effective to exploit the fine dispersibility and hydrophilicity of graphene oxide while maintaining the small band gap. Through the results of this study, rGO can be utilized for a variety of electrical applications such as transparent electrodes and flexible electrodes as well as ultra-thin channels of transistors at low cost and simple process.

As a result of applying typical carrier concentration of rGO to graphene synthesized in this study, it is predicted that the mobility will have a range of approximately minimum $1.1 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ to maximum $9.0 \times 10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. Graphene with this specification is suitable to be used for insulting layer, photocatalyst, logic transistor and the like. Using the results of this study would facilitate the synthesis of

graphene that can be applied to a wide variety of fields as well as the applications listed above.

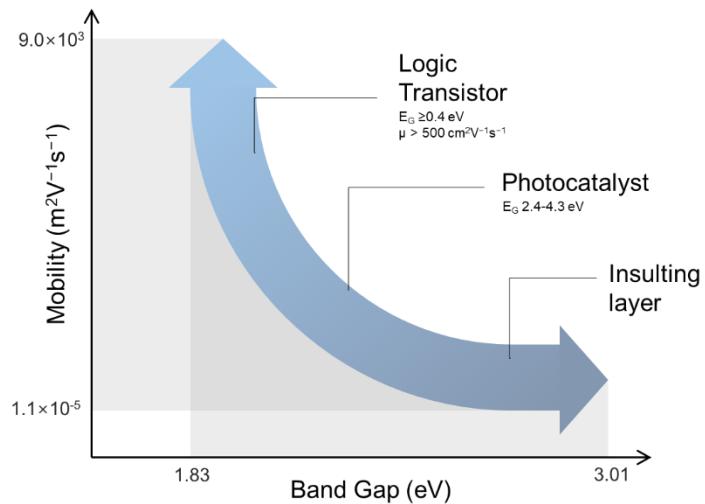


Figure 19. Possible applications of graphene synthesized in this study

3.4.2. Future Research Direction

In this study, we clarified the simplified relationship between oxygen functionality and electrical properties of graphene, and the dependence of the band gap on the oxygen bond was approximately quantified. However, even if consisted of the same kind of atomic bonds, it has been found that the magnitude of the effect of each functional group is significantly different. Therefore, it is essential to adjust the functional groups more precisely and to construct quantitative data on them.

Although the method of controlling oxygen functional groups in this study is confined to reduction, it is obvious that there are multiple methods even in the synthesis step of GO. In the relationship between the oxygen functional group and the band gap, it is also necessary to study in detail the part that is interpreted as the parameter of oxidation. Therefore, the evaluation of the characteristics of graphene when adjusting elements other than reduction should be considered as a future research subject.

In addition, we studied only oxygen functional groups that rGO itself contains as a factor determining band gap, in order to maximize advantages of chemical modification of graphene. In fact, graphene can also make composites by attaching other functional groups, *e.g.* amine, or by covalent bonding with polymers. It is a great merit of graphene that various combinations are possible, and the action of oxygen functional groups disclosed in this study is likely to be applied in other functionalities besides oxygen. Therefore, it is desirable to study on whether the relation figured out in this study works similarly for other substances as a future research direction.

4. Conclusion

Various reducing methods were applied to GO and the degree of reduction was controlled to synthesize rGO having various oxygen functional groups. The oxygen content varied from 1.16 at the minimum to 0.34 at the maximum, and XPS analysis and FT-IR analysis also confirmed the differences in oxygen functional group composition.

The band gap and electrical conductivity of rGO with the broad composition spectrum were measured and analyzed. Band gap of graphene increases with increasing oxygen content, and it responds more sensitively to C-O single bonds. In addition, even when all oxygen functional groups are reduced, the band gap does not converge to zero due to internal defects. Not only the oxygen single bond and the double bond were different, but also the degree of each of the functional groups contributing to the band gap opening was remarkable.

From the experimental results of this study, a large band gap of graphene can be achieved with only a little amount of oxygen functionality. It would also be possible to easily synthesize graphene with appropriate performance that can be utilized in a variety of electronic devices.

Bibliography

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A.J.s. Firsov, Electric field effect in atomically thin carbon films, 306(5696) (2004) 666-669.
- [2] M.J. Allen, V.C. Tung, R.B. Kaner, Honeycomb Carbon: A Review of Graphene, Chemical Reviews 110(1) (2010) 132-145.
- [3] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N.J.N.I. Lau, Superior thermal conductivity of single-layer graphene, 8(3) (2008) 902-907.
- [4] A.C. Neto, F. Guinea, N.M. Peres, K.S. Novoselov, A.K.J.R.o.m.p. Geim, The electronic properties of graphene, 81(1) (2009) 109.
- [5] A. Geim, Graphene update, APS Meeting Abstracts, 2012.
- [6] F. Schwierz, Graphene transistors, Nature Nanotechnology 5 (2010) 487.
- [7] K. Rim, J.L. Hoyt, J.F.J.I.T.o.E.D. Gibbons, Fabrication and analysis of deep submicron strained-Si n-MOSFET's, 47(7) (2000) 1406-1415.
- [8] M. Chhowalla, D. Jena, H.J.N.R.M. Zhang, Two-dimensional semiconductors for transistors, 1(11) (2016) 16052.
- [9] F. Schwierz, J. Pezoldt, R. Granzner, Two-dimensional materials and their prospects in transistor electronics, Nanoscale 7(18) (2015) 8261-8283.
- [10] M.Y. Han, B. Özyilmaz, Y. Zhang, P.J.P.r.l. Kim, Energy band-gap engineering of graphene nanoribbons, 98(20) (2007) 206805.
- [11] X. Wang, G. Sun, N. Li, P.J.C.S.R. Chen, Quantum dots derived from two-dimensional materials and their applications for catalysis and energy, 45(8) (2016) 2239-2262.
- [12] A.K. Geim, I.V.J.N. Grigorieva, Van der Waals heterostructures, 499(7459) (2013) 419.
- [13] C. Zhang, T.J.C.s.b. Liu, A review on hybridization modification of graphene and its polymer nanocomposites, 57(23) (2012) 3010-3021.
- [14] A. Jana, E. Scheer, S. Polarz, Synthesis of graphene–transition metal oxide hybrid nanoparticles and their application in various fields, Beilstein Journal of Nanotechnology 8 (2017) 688-714.
- [15] S. Lonkar, Y. Deshmukh, A. Abdala, Recent Advances in Chemical Modifications of Graphene, 2014.

- [16] L. Shahriary, A.A. Athawale, Graphene oxide synthesized by using modified hummers approach, *Int J Renew Energy Environ Eng* 2(01) (2014) 58-63.
- [17] J. Liu, J. Tang, J.J. Gooding, Strategies for chemical modification of graphene and applications of chemically modified graphene, *Journal of Materials Chemistry* 22(25) (2012) 12435-12452.
- [18] W. Gao, The chemistry of graphene oxide, *Graphene oxide*, Springer2015, pp. 61-95.
- [19] P. Jangid, D. Pathan, A. Kottantharayil, Graphene nanoribbon transistors with high ION/IOFF ratio and mobility, *Carbon* 132 (2018) 65-70.
- [20] J. Sun, T. Iwasaki, M. Muruganathan, H. Mizuta, Lateral plasma etching enhanced on/off ratio in graphene nanoribbon field-effect transistor, *Applied Physics Letters* 106(3) (2015) 033509.
- [21] R.R. Pandey, M. Fukumori, A. TermehYousefi, M. Eguchi, D. Tanaka, T. Ogawa, H. Tanaka, Tuning the electrical property of a single layer graphene nanoribbon by adsorption of planar molecular nanoparticles, *Nanotechnology* 28(17) (2017) 175704.
- [22] S.Y. Lee, D.L. Duong, Q.A. Vu, Y. Jin, P. Kim, Y.H. Lee, Chemically modulated band gap in bilayer graphene memory transistors with high on/off ratio, *ACS nano* 9(9) (2015) 9034-9042.
- [23] J.G. Son, M. Son, K.J. Moon, B.H. Lee, J.M. Myoung, M.S. Strano, M.H. Ham, C.A. Ross, Sub-10 nm Graphene Nanoribbon Array Field-Effect Transistors Fabricated by Block Copolymer Lithography, *Advanced Materials* 25(34) (2013) 4723-4728.
- [24] R. Liu, M. Peng, H. Zhang, X. Wan, M.J.M.S.i.S.P. Shen, Atomic layer deposition of ZnO on graphene for thin film transistor, 56 (2016) 324-328.
- [25] A.N. Aleshin, I.P. Shechrbakov, A.S. Komolov, V.N. Petrov, I.N.J.O.E. Trapeznikova, Poly (9-vinylcarbazole)-graphene oxide composite field-effect transistors with enhanced mobility, 16 (2015) 186-194.
- [26] C.-J. Shih, Q.H. Wang, Y. Son, Z. Jin, D. Blankschtein, M.S.J.A.n. Strano, Tuning on-off current ratio and field-effect mobility in a MoS₂-graphene heterostructure via Schottky barrier modulation, 8(6) (2014) 5790-5798.
- [27] C.-C. Lu, Y.-C. Lin, C.-H. Yeh, J.-C. Huang, P.-W.J.A.n. Chiu, High mobility flexible graphene field-effect transistors with self-healing gate dielectrics, 6(5) (2012) 4469-4474.
- [28] S. Lee, O.D. Iyore, S. Park, Y.G. Lee, S. Jandhyala, C.G. Kang, G. Mordi, Y. Kim, M. Quevedo-Lopez, B.E.J.C. Gnade, Rigid substrate process to achieve high mobility in graphene field-effect transistors on a flexible substrate, 68 (2014) 791-797.

- [29] W. Song, S.Y. Kwon, S. Myung, M.W. Jung, S.J. Kim, B.K. Min, M.-A. Kang, S.H. Kim, J. Lim, K.-S.J.S.r. An, High-mobility ambipolar ZnO-graphene hybrid thin film transistors, 4 (2014) 4064.
- [30] H.-C. Shin, Y. Jang, T.-H. Kim, J.-H. Lee, D.-H. Oh, S.J. Ahn, J.H. Lee, Y. Moon, J.-H. Park, S.J.J.J.o.t.A.C.S. Yoo, Epitaxial growth of a single-crystal hybridized boron nitride and graphene layer on a wide-band gap semiconductor, 137(21) (2015) 6897-6905.
- [31] A. Behranginia, P. Yasaei, A.K. Majee, V.K. Sangwan, F. Long, C.J. Foss, T. Foroozan, S. Fuladi, M.R. Hantehzadeh, R.J.S. Shahbazian-Yassar, Direct Growth of High Mobility and Low-Noise Lateral MoS₂-Graphene Heterostructure Electronics, 13(30) (2017) 1604301.
- [32] J. Son, S. Lee, S.J. Kim, B.C. Park, H.-K. Lee, S. Kim, J.H. Kim, B.H. Hong, J. Hong, Hydrogenated monolayer graphene with reversible and tunable wide band gap and its field-effect transistor, Nature communications 7 (2016) 13261.
- [33] K.I. Ho, M. Bouthchich, C.Y. Su, R. Moreddu, E.S.R. Marianathan, L. Montes, C.S. Lai, A Self-Aligned High-Mobility Graphene Transistor: Decoupling the Channel with Fluorographene to Reduce Scattering, Advanced Materials 27(41) (2015) 6519-6525.
- [34] W.S. Hwang, P. Zhao, K. Tahy, L.O. Nyakiti, V.D. Wheeler, R.L. Myers-Ward, C.R. Eddy Jr, D.K. Gaskill, J.A. Robinson, W. Haensch, Graphene nanoribbon field-effect transistors on wafer-scale epitaxial graphene on SiC substrates, APL materials 3(1) (2015) 011101.
- [35] S.K. Lee, H.Y. Jang, S. Jang, E. Choi, B.H. Hong, J. Lee, S. Park, J.H. Ahn, All graphene-based thin film transistors on flexible plastic substrates, Nano Lett 12(7) (2012) 3472-6.
- [36] Y. Shen, S. Yang, P. Zhou, Q. Sun, P. Wang, L. Wan, J. Li, L. Chen, X. Wang, S.J.C. Ding, Evolution of the band-gap and optical properties of graphene oxide with controllable reduction level, 62 (2013) 157-164.
- [37] M. Velasco-Soto, S. Pérez-García, J. Alvarez-Quintana, Y. Cao, L. Nyborg, L. Licea-Jiménez, Selective band gap manipulation of graphene oxide by its reduction with mild reagents, Carbon 93 (2015) 967-973.
- [38] A. Mathkar, D. Tozier, P. Cox, P. Ong, C. Galande, K. Balakrishnan, A. Leela Mohana Reddy, P.M. Ajayan, Controlled, stepwise reduction and band gap manipulation of graphene oxide, The journal of physical chemistry letters 3(8) (2012) 986-991.
- [39] Z. Hong, X. Jiao, Q. Gao, Y. Zhang, C. He, J. Yang, Y. Liu, Tuning the Band Gap of Stable and Dispersible Graphene Aqueous Solution via Hydrothermal Reduction Method, Integrated Ferroelectrics 145(1) (2013) 115-121.

- [40] S.-Y. Gu, C.-T. Hsieh, T.-W. Lin, J.-K. Chang, J. Li, Y.A. Gandomi, Tuning oxidation level, electrical conductance and band gap structure on graphene sheets by cyclic atomic layer reduction technique, *Carbon* 137 (2018) 234-241.
- [41] L.G. Guex, B. Sacchi, K.F. Peuvot, R.L. Andersson, A.M. Pourrahimi, V. Strom, S. Farris, R.T. Olsson, Experimental review: chemical reduction of graphene oxide (GO) to reduced graphene oxide (rGO) by aqueous chemistry, *Nanoscale* 9(27) (2017) 9562-9571.
- [42] Y. Shang, D. Zhang, Y. Liu, C.J.B.o.M.S. Guo, Preliminary comparison of different reduction methods of graphene oxide, *38*(1) (2015) 7-12.
- [43] T. Szabó, O. Berkesi, P. Forgó, K. Josepovits, Y. Sanakis, D. Petridis, I. Dékány, Evolution of surface functional groups in a series of progressively oxidized graphite oxides, *Chemistry of Materials* 18(11) (2006) 2740-2749.
- [44] D.W. Boukhvalov, M.I. Katsnelson, Modeling of graphite oxide, *Journal of the American Chemical Society* 130(32) (2008) 10697-10701.
- [45] A. Ganguly, S. Sharma, P. Papakonstantinou, J.J.T.J.o.P.C.C. Hamilton, Probing the thermal deoxygenation of graphene oxide using high-resolution *in situ* X-ray-based spectroscopies, *115*(34) (2011) 17009-17019.
- [46] H.J. Shin, K.K. Kim, A. Benayad, S.M. Yoon, H.K. Park, I.S. Jung, M.H. Jin, H.K. Jeong, J.M. Kim, J.Y.J.A.F.M. Choi, Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance, *19*(12) (2009) 1987-1992.
- [47] C.K. Chua, M. Pumera, Chemical reduction of graphene oxide: a synthetic chemistry viewpoint, *Chemical Society Reviews* 43(1) (2014) 291-312.
- [48] J.-B. Wu, M.-L. Lin, X. Cong, H.-N. Liu, P.-H. Tan, Raman spectroscopy of graphene-based materials and its applications in related devices, *Chemical Society Reviews* 47(5) (2018) 1822-1873.
- [49] S. Pei, J. Zhao, J. Du, W. Ren, H.-M.J.C. Cheng, Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids, *48*(15) (2010) 4466-4474.
- [50] R.H. Bube, *Electrons in Solids: An Introductory Survey*, Elsevier Science1992.
- [51] T.-T. Jia, B.Z. Sun, H.-X. Lin, Y. Li, W.-K. Chen, Bonding of Hydroxyl and Epoxy Groups on Graphene: Insights from Density Functional Calculations, 2013.

국문 초록

그래핀은 탄소 원자가 육방 격자로 배열된 2 차원 나노물질이며, 뛰어난 물리적, 광학적, 전기적 성질로 인해 다양한 응용이 제시되어 왔다. 특히 그래핀을 트랜지스터 소자에 적용하면 실리콘 반도체 이상의 집적화가 가능하게 된다. 그러나 그래핀은 밴드 갭이 0에 가까운 반금속으로, 논리 회로를 구현하는 데에는 적절하지 않다.

따라서 그래핀의 밴드 갭을 증가시키기 위한 연구가 다방면에서 활발하게 진행되어 왔다. 그 중에서도 흑연을 산화시켜 박리한 형태인 그래핀 옥사이드의 산소 작용기를 활용하는 방법은, 공정이 경제적이고 대량 생산이 가능하다는 점에서 상업적 가치가 뛰어나다. 더불어 이종 원소를 도입하지 않고도 유사한 효과를 이끌어낼 수 있고, 산소 작용기로 인해 그래핀의 친수성이 향상되어 다양한 응용이 가능하다.

그런데 다양한 종류의 산소 작용기들이 각각 그래핀의 밴드구조에 어떻게 영향을 미치는지에 대한 실험적인 자료가 미비하고, 그로 인해 그래핀 옥사이드의 트랜지스터 재료에의 적용이 매우 제한적이다. 따라서 본 연구에서는 이러한 한계점을 극복하기 위해서, 그래핀의 산소 작용기와 밴드 갭을 비롯한 전기적 성질과의 실험적 관계를 연구하였다. 이를 위해 그래핀 옥사이드에 서로 다른 종류의 환원 반응을 적용하였고, 환원 정도를 조절하여 작용기의 조성을 제어하였다. 그리고 그로써 변화한 밴드 갭을 측정하여 작용기와의 정량적 관계를 분석하였다.

이와 같이 그래핀의 재료적 성질과 전기적 성질의 관계를 분석한 결과, 그래핀 원자와 산소 원자의 서로 다른 결합이 밴드 캡에 미치는 영향이 상당히 다름을 보였다. 또한 수산기의 밴드 캡 조율 효과는 매우 미비한 것으로 나타났다. 이러한 분석 결과를 바탕으로 특정 성능을 갖는 그래핀을 합성하기 위한 합성 방향성을 제시할 수 있었다. 본 연구를 통해 전자 소자에서 그래핀 옥사이드의 활용성이 향상될 것을 기대할 수 있을 것이다.

주요어 : 환원된 그래핀 옥사이드, 그래핀, 작용기, 밴드 캡, 환원도, 트랜지스터

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