



이학박사 학위논문

Studies on the Synthesis of Graphene by Chemical Vapor Deposition and Its Applications to Heterogeneous Catalysts

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Abstract of dissertation

Studies on the Synthesis of Graphene by Chemical Vapor Deposition and Its Applications to Heterogeneous Catalysts

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After graphene was introduced, it has been spotlighted as its extraordinary properties. There have been many studies to narrow the gap between theoretical and realistic properties. Still, however, there are many hurdles to overcome. Most of all, understanding surface of graphene is essential to utilize graphene for applications because all reactions are started from surface where chemicals were collided. Surface of graphene was influenced by several factors like substrate, pressure, temperature, electromagnetic wave etc. all of them were controlled to research its relationship. Some reports said modified graphene showed semiconductor and conductor properties by manipulating surrounding atmosphere. And it was revealed that graphene can have role of catalyst by charge transfer. In this dissertation, phenomenon on the surface of graphene have been investigated exhaustively. This book includes exhaustive results. Especially, charge transfer was interesting to lead study of advanced oxidation process (AOP) which is final step of wastewater treatment. Charge transfer occurred on graphene activated reactive oxygen species (ROS) that give rise to radicals. These radicals decomposed soluble phenolic compound. Reasonable study of charge transfer was also considered by controlling experimental system. Furthermore, analysis of interactions between the surface of graphene and specific molecules was explored by heating graphene for activation. Through high temperature, chemical reactions including oxidation, reduction and absorption were observed inducing spectroscopic changes.

In chapter 1, history of graphene and synthetic methods were briefly introduced. Moreover, it had summary about properties of single, double and few layer graphene as well as modifications of graphene and its applications. In chapter 2, graphene was made use of wastewater treatment because charge transfer on its surface enables to generate radicals from ROS. It was utilized for AOP where small contaminants were decomposed. It is final process among wastewater treatment. Using graphene brought several advantages to AOP. Especially, it was recyclable without reduction process unlike metal catalysts. And it was able to be activated on mild conditions.

In chapter 3, as an extension of chapter 2, column was produced by graphene for continuous degradation during AOP. Because catalytic effect depends on surface area, large area of graphene increases AOP efficiency by generating quantities of radicals. To maximize reaction, ultra violet (UV) irradiation was applied. Namely using photocatalytic effect, phenolic compounds were reduced in short time. Consequently, useful experimental result was proposed including commercial scale.

In chapter 4, interaction between bilayer graphene (BLG) and oxygen molecules (g) was analyzed following increasing temperature for reactivity in quartz tube. As BLG have attracted a lot of attention to replace existing semi-conductors, understanding of oxidation is necessary. Previous papers mainly reported irreversible oxidation of graphene but, this chapter showed reversible oxidation was possible under specific oxidative and reductive conditions and its redox reaction was reproduced repeatedly.

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Chapter 1

Introduction to extraordinary properties of graphene and its

applications

1.1. Introduction of graphene

1.1.1. Graphene and synthetic methods

Graphene have garnered considerable attention after it was discovered using exfoliated method simply peeling off from graphite in 2004.¹ As it showed unique physical and chemical properties, both academic and industrial fields dug into the

characteristics of graphene and its application. Due to its intensive studies²⁻⁵, Andre Geim and his research team received Nobel prize in 2010. Based on this honor, Researchers diligently delved into graphene through co-working each other. So far, many studies have concentrated to accomplish ideal performance of graphene reducing realistic difficulties.

Graphene have been usually prepared by two approaches, one is top-down and the other is bottom-up method. Graphite are peeled off layer by layer to prepare graphene through top-down method. For examples, Hammer's method is well known as chemical exfoliation process to make graphene.⁶ Besides, the other top-down methods have been developed for flawless preparations.⁷⁻⁹ Although graphene derived top-down, especially mechanical exfoliation have excellent intrinsic properties, it has limitation on controlling size.¹⁰ Through bottom-up methods graphene were synthesized on metallic catalyst using carbon sources such as methane and acetylene.¹¹⁻¹⁸ This method has great potential to produce large area graphene but, having lack of crystallinity for perfect hexagonal lattice over all surface. In results, it is necessary to develop methodological improvements to produce impeccable graphene.¹⁹⁻²⁶

1.1.2. Physical and Chemical properties

Graphene is a two-dimensional honey comb structure consisting of sp² bonded carbon atoms. Its height is about 0.3 nm and distance between nearest carbon atoms is about 0.142 nm.²⁷ To estimate electronic state of graphene, it was calculated via reciprocal lattice which shows Dirac cone shape where band gap is ideally zero.²⁸⁻³⁰ The band structure causes extraordinary physical and chemical properties. For instance, as electrons in graphene behave massless relativistic particle, it gives rise to quantum Hall effect.³¹ In addition, Graphene show high electron mobility^{4,5}, exceptional thermal conductivity³² and notable mechanical properties.^{33,34}

Actually, those characteristics of graphene are easily affected by manufacturing methods. Graphene made of the top-down method show exceptional electrical properties reaching at theoretical values. In 2007, Phillip Kim and his researchers measured electrical conductivity and reported carrier mobility value was 200,000 cm²/Vs.³⁵ As the mobility is higher than silicon wafer, it is well known as next generation semi-conductor to replace current materials.³⁶ On the other hand, Graphene from the bottom up have mainly focused on industrial applications as new technology. Due to resistance of graphene on PET was measured by nearly ~220 Ω /sq.¹⁸ It is comparable value with ITO on PET. Therefore, graphene would be suitable for transparent electrode and display as well. These two approaches have been developed complementarily helping each other.

1.1.3. Thermal properties

Aforementioned graphene has high thermal conductivity. The reasons are carbons have strong covalent bonding each other and show phonon scattering.³² Therefore, it is also expected as a good material in semi-conductor device. While a device is operating, it generates considerable heat. So, heat dissipation is important to keep device safe. Moreover, recently graphene has been utilized in electrodes and the relative battery materials for thermal management because battery's temperature affects its efficiency.³⁷ Table 1-1. shows relative values of thermal conductivities from various methods^{32,38-40}. illustrates schematic experimental setup for measurement of thermal conductivity.

Method	Materials	Thermal
		conductivity
Confocal micro-Raman	Single layer graphene	4840-5300 W/mK at
spectroscopy		R.T.
Confocal micro-Raman	Suspended graphene flake	4100-4800 W/mK at
spectroscopy		R.T.
Thermal measurement method	Single layer (suspended)	3000-5000 W/mK at
		R.T.
Thermal measurement method	Single layer (on SiO ₂ support)	600 W/mK at R.T.
Electrical four-point measurement	Reduced graphene oxide flake	0.14-0.87 W/mK

Table 1-1. Thermal properties of graphene and graphene oxide-based materials.^{32,38-40}

1.1.4. Optical and Mechanical properties

Previous reports show graphene has great transparency. Its transmittance decreases about 2.3% by adding a layer.¹⁸ It means the absorption of light is linearly determined by increasing the number of layers (until stacked at four layers).⁴¹ The absorption of graphene is nearly even from 300 to 2500 nm and the peak near 250 nm is related with inter-band electronic transition from the unoccupied π^* states.^{42,43} Moreover, optical transition of graphene can be changed by controlling values of Fermi energy. These tunability have been used for unique optoelectronic devices including detectors, modulators and emitters.⁴⁴

In addition, graphene derivatives like graphene oxide (GO) or graphene quantum dots (GQD) have photoluminescence (PL). Due to production method, those have inevitably size distributions which give different band gaps. So, various size gives broad range of PL spectrum.⁴⁵ In addition, if we modulate PL easily by controlling electrical field, it is opportunity to utilize numerous applications such as photodetector, light emitting devices, transparent conductors etc.⁴⁶

Mechanical strength is crucial property in devices. Because when devices would be encountered by unexpected external stimulation, it should be protected minimizing changes of intrinsic properties. On this purpose, graphene derived device may satisfy its qualifications. Research teams reported Young's modulus of suspended graphene was measured 1 TPa and spring constant was 1~5 N/m.³³ Also strain capability was measured by ~1.3% in tension and ~0.7% in compression.^{47,48} Moreover, constants related with flexibility and stretchability were measured by small changes in resistance.

Method	Material	Mechanical properties
AFM	Mono-layer graphene	$E = 1 \pm 0.1 \text{ TPa}$
		σ_{int} = 130 \pm 10 GPa at ϵ_{int} = 0.25
AFM	Mono-layer graphene	E = 1.02 TPa; σ = 130 GPa
	Bi-layer graphene	E = 1.04 TPa; σ = 126 GPa
	Tri-layer graphene	E = 0.98 TPa; σ = 101 GPa
Raman	Graphene	Strain ~1.3% in tension
		Strain ~0.7% in compression

Table 1-2. Mechanical properties of graphene.^{33,47,48}

Above studies can be also analyzed using phonon frequencies. Usually, Raman spectroscopy is well known technique detecting graphene's vibrational mode under certain external stress.⁴⁹⁻⁵¹ Moreover, when graphene was applied by controlled stress or strain, its electronic band structure was changed where energy values of band gap can be adjusted.⁵² Table 1-2 gives us positive message to utilize breakthrough modern devices. Consequently, graphene will be fabricated as organic electronics in future because it would satisfy industrial needs comparing with inorganics which have weakness and stiffness.

1.2. Properties of bilayer graphene

1.2.1. Structure and preparation of bilayer graphene

BLG is composed by two types of structure. AB stacked BLG also known as Bernal stacked BLG is tilted at 30 degrees between top and bottom layer usually observed in nature. And AA stacked BLG, non-Bernal stacked BLG, is regarded as translationally moved upper layer compared with lower layer. Specifically said, AA` stacked BLG means all of BLG except AB stacked BLG. In addition, Other notations are the one is symmetric and the other is asymmetric double layer.⁵³ BLG were also prepared by two approaches which are top-down and bottom-up. Initially, mechanical exfoliation of graphite was introduced to research its properties. However, this method has critical weakness that is limitation of size control.⁵⁴ Not long after that CVD synthesis was utilized to scale-up graphene. Due to these efforts, CVD mediated BLG domain size can be also manipulated up to our needs.⁵⁵

1.2.2. Chemical properties

BLG have different reactivities according to stacking angles. Each of tilted BLG is regarded as distinct materials.⁵⁶ Especially, different stacked BLG could be conductor, semi-conductor and even insulator under certain condition. Other works have shown that various stacking angled BLG led to different reactions though it reacted with same molecules.^{57,58} With two tilted layers, increased surface area gives rise to enhanced chemical reactivity because its surface can have behavior of charge transfer. Therefore, various composites including inorganics and metals have been combined

with BLG.59

1.2.3. Electrical properties

BLG have peculiar electronic states described as parabolic band structure which is different from single layer graphene. Most of all, as charge carriers on BLG are distinguished from finite mass (mass Dirac fermions), certain BLG would be metallic materials at neutrality points.⁶⁰ Many researchers have modified charge concentration by controlling external stimulations to prove BLG as compelling challenger of silicon.⁶¹⁻ ⁶⁴ On top of that, Recent studies have demonstrated that certain angle between two layers makes BLG superconductor internally.⁶⁵ Thanks to these advantages, BLG have been regarded as promising materials.

Although many researches about BLG have come out, there are still existing unknown regions to explain BLG's properties. Particularly, BLG with chemical dopants induce geometrical distortion of BLG structure such as replacement of carbon atoms so it gives rise to change of electronic states and other properties anonymously. It makes us struggling to understand doped BLG. Therefore, intensive exploration should be required to reveal well-defined doped BLG. For achieving this purpose, experts in various fields including spectroscopy, theory, synthesis should willingly take part in with co-working.

1.3. Applications of graphene

1.3.1. Surface modifications of graphene

Graphene have intrinsically hydrophobic surface. But, many studies about surface modification have been reported using doping methods. There are chemical and physical approaches providing doping methods. First, chemical methods include adatom doping by carrier injection where B or N atom is added, resulting in atomic bonding with sp² carbon.⁶⁶ The chemisorption enables dopants to bind carbon atoms composing sp² structure. Moreover, there are doping methods including dipping, spin coating, vapor-phase doping and construction of self-assembled monolayers with chemical dopants.⁶⁷⁻⁷¹ Physical methods can adjust Fermi level by applying electromagnetic field. Giving gate dielectric voltage is one of them.^{61,72} With top or bottom gate voltages, it deformed electronic state of charge carriers. Therefore, surface of graphene was indirectly modified. In addition, external stimulations such as light or force also enable to make doped graphene.^{52,73-76} If graphene is irradiated by certain wavelength light or LASER, its atoms or electrons are instantly excited which induce change of electronic states during the exposure. In other studies, specific directional forces such as uni- or bi-axial stress and strain, compression, tension were used to regulate electronic states of graphene.

1.3.2. Related applications

Graphene can be variously applicable to sensors, display, battery and semi-conductor fields.^{18,62,77-78} Here, two kinds of topics would be introduced. First is application of wastewater treatment. Graphene oxide (GO) have been usually used as materials in desalination or filtration because of its efficient surface area.⁷⁹⁻⁸¹ Additionally, GO have been easily treated to mix with other materials like metal oxides and polymers due to its solution phase. For this reason, GO have been used by making new composites for acquiring unique reactivities. On the contrary, CVD graphene have innate drawbacks, one of them is constrained by substrate due to its manufacturing methods. It makes difficulty to mix graphene with reactive materials. However, recently CVD graphene have been introduced as organic catalyst to decompose phenolic compounds.^{82,83} Advanced oxidation process (AOP) is oxidative destruction process of the major industrial pollutants in wastewater treatment after filtering macro-scaled substances.⁸⁴ As its performance depends on charge transfer from CVD graphene surface, suitable substrate for graphene is necessary to enhance catalytic effects. If researchers develop more efficient AOP using CVD graphene, 'Whole graphene made wastewater treatment column' will be shown up in the future.⁸⁵

Studies in sensors have been carried out because property of changes in conductivity is observed by colliding or reacting with other chemicals. Moreover, spectroscopic changes are also followed along with showing different optical conductivity. These changes will be practically utilized for developments of gas or bio-sensors. Unfortunately, previous studies are mainly results using GO as well. As mentioned, it is same reason of easy handling. But, because GO cannot be prepared wanted size and layers, utilization of CVD graphene for developing graphene sensor is needed.^{78,86-88} Furthermore, as performance of sensor depends on graphene's uniformity and well-defined atomic structure, synthetic studies of CVD graphene should be required. Ultimately, for deeper understanding of CVD graphene, researchers have to investigate relationships between structures of graphene and its characteristics though it would be hard time to solve the complexity.

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Chapter 2

Catalytic degradation of phenols by recyclable CVD graphene

film

2.1. Introduction

Phenol and its derivatives are important materials in many industries, but are also hazardous and potentially mutagenic and/or carcinogenic.^{1–3} For such reasons, destroying organic pollutants in an aquatic environment has been one of the major foci in the field of wastewater treatment. To date, oxidative destruction of phenolic compounds has been carried out mostly through advanced oxidation processes (AOPs), which exploit the generated secondary radicals as powerful oxidants under aqueous conditions.^{4–6} To facilitate the processes while minimizing disadvantages, a number of different catalysts including ferrous ion-based Fenton's reagents have been widely employed. However, these agents necessitate further steps to remove residual salts and are optimized under relatively harsh conditions such as low pH. In addition,

other candidates without ferrous ions predominantly demand external energies including UV light and electricity, which complicates their universal applications.^{7–10}

In this communication, we propose the application of a monolayer graphene film as a novel catalyst to degrade phenols through the AOP. Graphene has gained much attention in diverse fields of study due to many of its outstanding physical, chemical and electrical properties, as well as its exceptional ability to donate or withdraw electrons.^{11–14} We have thus inferred that a graphene film can be utilized to generate hydroxyl radicals from hydrogen peroxide (H₂O₂) through immediate redox reactions, where the generated radicals can be exploited to oxidatively destroy phenols without any additional treatments.

2.2. Results and discussion

For the study, a high quality monolayer graphene film was synthesized through the chemical vapor deposition (CVD) method, and transferred onto a silicon substrate (Gr/SiO_2) .^{15,16} Ideally, graphene facilitates the AOP-mediated destruction of phenols in an analogous manner to the conventional ferrous ion-based catalysts, but this would be more advantageous in multiple aspects: (i) further steps for salt removal would not be necessary, (ii) the optimal activity is not restricted to low pH, (iii) no input of external energy is required and (iv) the film is recyclable as long as graphene is not severely damaged and H_2O_2 can be replenished (Figure. 2-1a).



Figure. 2-1. Preliminary experiments to validate CVD graphene's catalytic activity with 1 cm² Gr/SiO₂. (a) Schematic representation of the conventional phenol degradation method using Fe²⁺-based Fenton's reagent (top) and the novel method with a recyclable graphene film (bottom). (b) Representative DCFH-DA fluorescence intensity (2 μ M) with respect to increasing H₂O₂ concentrations in the presence of 1 cm² Gr/SiO₂ (blue), 1 cm² SiO₂ only (red), and non-treated (black). (c) Preliminary surface adsorption test of phenols (1 mM) in the presence (black) and absence (red) of 1 cm² graphene film. (d) Representative DCFH-DA fluorescence intensity (2 μ M) in the presence of 1 cm² Gr/PET (red line), Gr/SiO₂ (blue line), PET only (red dot), SiO₂ only (black dot), and non-treated (blue dot) and (e) mono- (red), bilayer Gr/SiO₂ (black) and SiO₂ only (blue) with the respective Raman spectra. (f) Time-dependent pH (black) and temperature (blue) changes in the presence of 1 cm² graphene film, H₂O₂ (100 mM), and phenols (1 mM).

To investigate the ability of the graphene film to generate hydroxyl radicals from H_2O_2 , the fluorescence intensity of 2',7'- dichlorofluorescin diacetate (DCFH-DA, 2 μ M) was measured at different H_2O_2 concentrations. DCFH-DA is one of the most common fluorescent probes for the detection of reactive oxygen species (ROS),^{17,18} where its fluorescence intensity corresponds to the levels of ROS, Gr/SiO₂ and bare SiO₂, changes in the fluorescence intensity were monitored. While the non-treated and SiO₂ only groups respectively resulted in a 12-fold and 27-fold increase in the fluorescence intensity, Gr/SiO₂ elicited a 102-fold increase with 100 mM H₂O₂ (Figure. 2-1b).

The difference in the fluorescence intensity solely arose from the presence of a 1 cm² monolayer graphene sheet, which apparently took part in generating secondary radicals (i.e. hydroxyl radicals, \cdot OH) from H₂O₂; the radicals' strong oxidizing potential is reflected by the dramatic fluorescence intensity increment. Indeed, previous reports including density functional theory (DFT) studies have explored the H₂O₂ reduction reaction (HPRR) on graphene, through which powerful secondary radicals can be generated en route to its complete reduction to water.^{19,20} More specifically, ambient H₂O₂ molecules are transiently adsorbed onto the surface of the graphene film mainly through the van der Waals force. Upon the spontaneous physisorption, breakage of the O–O bond is replaced by the formation of the C–O bond with graphene, where the adsorbed \cdot OH on graphene plays the role of a strong oxidant against the surrounding targets like DCFH-DA.^{21,22} Unlike the temporary adsorption of H_2O_2 molecules, the molecular adsorption of phenols on the graphene film may hinder their degradation process as these ring compounds are known to interact with graphene through hydrophobic interactions.²² On account of this potential issue, the adsorption of phenols on graphene was preliminarily tested by incubating 1 cm² graphene in a 1 mM phenol solution (Figure. 2-1c). As shown from the results, practically no phenol molecules were adsorbed onto the graphene films. It can thus be inferred that the π - π interactions between phenols and graphene are either only transient or negligible, which can be supported by the previous literature that re-discussed the π -stacking in general.²³

To investigate the effects of the underlying substrate and the number of graphene sheets on the catalytic performance, monolayer graphene on flexible polyethylene terephthalate (PET) and bilayer graphene on SiO₂ were prepared (Figure. 2-1d and e). As shown in Figure. 2-1d, the substrate change resulted in only insignificant differences in the catalytic effect, as assessed by DCFH-DA fluorescence assay. Thus, Gr/SiO₂ was exploited for all following assessments to facilitate relevant analyses including Raman and XPS. In like manner, mono- and bilayer graphene, which exhibited characteristic Raman 2D/G ratios of 4.27 and 1.15, did not show critical changes in the catalytic effects (Figure. 2-1e).²⁴ The result is in accordance with a previous study on the electron transfer of mono- and bilayer graphene, which practically show no clear distinction.²⁵

In addition, the time-dependent pH and temperature changes were monitored by incubating 1 cm² Gr/SiO₂ and 1 mM phenols with 100 mM H₂O₂ under ambient conditions (Figure. 2-1f). Notably, the pH started at 6.06 and gradually increased with time, and saturated at 7.06 after 24 hours of incubation. The gradual pH increment can be attributed to the progressive consumption of phenols and H₂O₂, which are both weakly acidic, during the generation of hydroxyl radicals.^{26,27} H₂O₂ is exploited for the production of hydroxyl radicals and phenols are degraded as a result of the process. Collectively, the final pH of this graphene-catalyzed process reaches that of water, which is far more advantageous than ferrous ion-based catalysts that are optimally activated in the pH range of 3–4.5. It should also be noted that there were no significant changes in the temperature during the course of phenol degradation except for the changes caused by the surrounding temperature.



Figure. 2-2. Time-resolved high-performance liquid chromatography analysis of degraded products. (a) Time-resolved HPLC analysis with the designated peaks representing the substances detected in the midst of the pathway. (b) Standard HPLC signals of phenol and maleic acid. (c) UV absorption spectra of the labelled intermediate compounds. (d) Schematic representation of the observed degradation pathway from phenol to maleic acid.

The effect of graphene-induced radicals on the degradation of phenols was subsequently investigated. Note that the concentration of H₂O₂ was adjusted to 100 mM in all following assessments as the fluorescence intensity for the Gr/SiO₂ group was practically saturated from 100 mM onwards. After incubating 1 mM phenols with 1 cm² Gr/SiO₂ for 24 hours, the sample was analyzed by time-resolved ion-exchange high performance liquid chromatography (HPLC) (Figure. 2-2a). Besides the standard HPLC signal of phenol, which displays its characteristic peak at 68.56 minutes (Figure. 2-2b), four other distinct signals were newly observed. To identify the substances designated by the emerged peaks, a HPLC-coupled organic acid analyzer with a proton column and ultraviolet (UV) absorption spectroscopy were exploited. Foremost, we sought to characterize the three substances separated at 16.65, 41.99, and 44.25

minutes post injection, as they are likely to manifest less oxidized structures than the substance appearing at 9.74 minutes (Figure. 2-2c). Based on the reference UV spectra, we could verify that the obtained absorption spectra represent *p*-benzoquinone, hydroquinone, and catechol, respectively, for the HPLC signals at 16.65, 41.99, and 44.25 minutes.²⁸⁻³⁰ As expected, these compounds are the oxidative derivatives of phenol, with different degrees of oxidation. Although H_2O_2 signals peaking at 7.43 and 8.65 minutes overlapped with the peaks at 9.74 and 16.65 minutes (Figure. 2-S1a), they did not interfere with the identification process.

The major substance appearing at 9.74 minutes post injection was subsequently characterized with the HPLC coupled organic acid analyzer. According to the standard HPLC signals, the peak matches with that of maleic acid (Figure. 2-2b), which features a biodegradable linear structure with four carbons. Previous studies discussing the potential pathway for oxidative destruction of phenol also report maleic acid as a dominant product through the complete oxidation of phenol to carbon dioxide and water.⁴ The report also classifies *p*-benzoquinone, hydroquinone, and catechol as the major intermediate products prior to the ring opening process to maleic acid, while these substances are not deemed to be biodegradable yet (Figure. 2-2d).



Figure. 2-3. Area-dependent catalytic activity and recycle test. (a) Schematic representation of multiple 1 cm^2 graphene arrays to improve the catalytic performance. (b) Representative graphene area dependent DCFH-DA fluorescence intensity (2 μ M) with 100 mM H₂O₂. (c) Time-dependent changes in phenols and (d) maleic acid using graphene films with different unit areas. (e) Time-dependent changes

in the amount of phenols through HPLC analysis of the recycled 9 cm² graphene films with normalized phenolic levels. (f) Representative optical microscopy (OM) images and Raman spectra after performing the first, second, third and fifth incubation cycles.

As 1 cm² Gr/SiO₂ could only elicit 25% reduction of the initial concentration of phenols (1 mM), we sought to improve the catalytic efficiency by exploiting an array of multiple graphene films (Figure. 2-3a). Preliminarily, the relative DCFH-DA fluorescence intensity for graphene films with different areas – 1, 2, 4, and 9 cm² – was measured to validate that the amount of generated radicals increases with respect to the area of the graphene film. Intriguingly, the fluorescence intensity markedly increased as a function of graphene area by exhibiting a 131, 208, and 913-fold increase in the fluorescence intensity respectively with 2, 4, and 9 cm² Gr/SiO₂ (Figure. 2-3b).

The same test groups were subsequently employed in time dependent phenol degradation analysis with HPLC. In accordance with the results from DCFH-DA measurements, the oxidative destruction of phenols occurs in a time-dependent manner with a strong dependency on the area of the graphene film. After 24 hours of incubation, the initial concentration of phenol was reduced by 54%, 60%, and 92% respectively with 2, 4, and 9 cm² Gr/SiO₂ (Figure. 2-3c).

It should also be noted that the total amount of non-biodegradable ring structures – phenol, hydroquinone and catechol – decreased gradually with time. Likewise, time-dependent maleic acid concentrations were monitored by using the HPLC-coupled organic acid analyzer (Figure. 2-3d). Interestingly for 9 cm² Gr/SiO₂, which exhibited the highest phenol reduction ratio, the concentration of maleic acid sharply increased after 3 hours of incubation. However, it shows a slight decline after 6 hours and becomes saturated until the end of the incubation period. Such inconsistent trends between the maleic acid increments and the phenol decrements can be attributed to the complete oxidation of maleic acid to carbon dioxide and water, which was supported by the generation of bubbles in the test batches.

Finally, the recyclability of the graphene film was investigated by carrying out

repetitive phenol destruction tests using a single 9 cm² Gr/SiO₂ sample (Figure. 2-3e). After each cycle, the levels of phenols and oxidized intermediates were analyzed. Remarkably, graphene films elicited the same catalytic effects after a series of recycling processes; four distinct time-resolved HPLC spectra for phenol degradation by the first, second, third, and fifth recycled 9 cm² Gr/SiO₂ display practically the same results (Figure. 2-3e). On average, the concentration of the remaining phenol was 6.5 \pm 2.3% in each tested cycle. This is nearly equivalent to the 92% reduction achieved with pristine 9 cm² Gr/SiO₂.

For the analysis of the intrinsic properties of graphene, any damage or changes on the surface were evaluated through optical microscopy (OM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses (Figure. 2-3f and Figure. 2-S2). The representative OM images clearly display that the graphene film was not damaged even after the fifth round of incubation cycle, and only a minimal part of stained spots was observed. The respective Raman spectra also supported that the original condition and quality of graphene were preserved over the fifth round of degradation cycle, by showing the respective 2D/G ratios of 3.72, 3.43, 4.30, and 3.84 for the graphene film respectively after the first, second, third, and fifth recycling (2D peak at 2680 cm⁻¹ and G peak at 1580 cm⁻¹). In general, the 2D/G ratio that exceeds 2 represents monolayer graphene, and a high 2D/G ratio typically corresponds to high intrinsic crystallinity. In addition, XPS analyses on the chemical composition of graphene pre- and post-phenol degradation exhibited essentially the same results, which corroborated that graphene was not severely oxidized by the surrounding hydrogen peroxide or organic molecules (Figure. 2-S2).

2.3. Conclusions

In summary, we have successfully demonstrated the potential application of a CVD graphene film for the oxidative destruction of phenols through a novel AOP method. Although the catalytic activity of the graphene film-based AOP system is relatively lower and thus requires a longer incubation time than the conventional metal-based

catalysts, it overcomes the inevitable drawbacks of the previous methods including the need for pH adjustment, input of external energies, and further steps for residual salt removal. In addition, it is important to note that the graphene film's catalytic efficiency is markedly improved by enlarging the dimension of the film – which can be as large as 30 inches, produced by the roll-to-roll method – which is expected to be utilized as a recyclable catalyst with considerable catalytic effects for industrial applications. As graphene can also be transferred onto flexible substrates, the range of potential applications can be even more broadened to different areas that demand the use of powerful secondary radicals generated by the environment-friendly film catalyst.

2.4. Experimental

Materials and Methods

Preparation of CVD Graphene Film. Graphene was synthesized by the chemical vapour deposition (CVD) method on a highly pure copper foil (Alfa Aesar, 99.95 %) according to the previous work.¹³ The growth was performed with flowing 40 sccm H₂ and 5 sccm CH₄ gas at 1000 °C. After coating a poly methyl methacrylate (PMMA) layer on a single side of as-grown graphene on Cu foil, the uncoated graphene was removed by oxygen plasma. The Cu foil was subsequently etched in ammonium persulfate (APS) solution (20 g/ 1 L) for 5 hours. The PMMA/Gr layer was then transferred onto SiO₂ substrate, followed by baking at 80 °C for 24 hours to improve the adhesion. Finally, the PMMA layer was removed by acetone.

Characterization. Optical microscopy (OM) images were captured by NIKON ECLIPSE LV 100 ND OM installed with NIS Elements D 4.20.00 software. RENISHAW Raman spectrometer was used to characterize the quality and uniformity of the prepared graphene films. The Raman spectra were obtained using an Ar laser (514 nm) with a

spot size of 1 μ m.

DCFH-DA Fluorescence Measurements. The generation of secondary reactive oxygen species (ROS) was measured with the fluorescence of 2', 7'-dichlorofluorescin diacetate (DCFH-DA) probe (Sigma Aldrch, Ex/Em: 495 nm/529 nm, 2 μ M).¹⁶ The measurements for all test groups were performed after designated amounts of incubation periods with 5 mL of total volume.

Ion-exchange HPLC Analysis. For the analysis of oxidative destruction of phenols, hydrogen column (Aminex 87H column, 300x10mm, Bio-Rad, USA) ion-exchange high performance liquid chromatography (HPLC, Dionex Ultimate3000) was utilized. Total injection volume was set to 10 μL in all test samples with 0.01 N H₂SO₄ eluent and the flow rate of 0.5 mL/min. Time-resolved HPLC analyses were performed over 90 minutes of injection time, and the intermediate structures were identified with the RI detector (ERC, RefractoMAX520, Japan). The identification of produced organic acid was carried out by the organic acid analysis coupled to the HPLC, based on the reference peaks and the retention times.

2.5. Supplementary information



Figure. 2-S1. Supplementary HPLC data for the degraded products. (a) HPLC analysis of hydrogen peroxide (100 mM) and phenols (1 mM). Hydrogen peroxide show strong, broad signals peaking at 7.43 and 8.65 minutes. (b) Time-dependent HPLC analysis and (c) quantified intensities with 9 cm² graphene film after 0, 3, 6, 12 and 24 hours of incubation with 1 mM phenols and 100 mM hydrogen peroxide.



Figure. 2-S2. XPS analysis on graphene pre- and post-phenol degradation. C_{1s} (left) and O_{1s} (right) XPS analysis pre- and post-phenol degradation respectively from the top. The characteristic C_{1s} signals exhibited distinctive atomic ratio changes from 0.12 \rightarrow 0.10, 0.2 \rightarrow 0.22, 0.06 \rightarrow 0.04 and 0.62 \rightarrow 0.64 respectively at 289 eV (C-O=O), 286.8 eV (C=O), 286.1 eV (C-O) and 285 eV(C_{sp2}). Likewise, the characteristic O_{1s} signals displayed atomic ratio changes from 0.04 \rightarrow 0.04 and 0.96 \rightarrow 0.96 at 535 eV (C-O) and 533 eV (H-O-C).

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Chapter 3

Photocatalytic degradation of phenol using CVD graphene

column

3.1. Introduction

As modern industrialization exacerbates environmental problems, studies related to ecological health gain traction across disciplines and geographies. Water pollution is especially detrimental to local and global health as it disrupts the key to ecosystem mediation and balance; clean water. Much like the human body, clean water is essential to nurture native environments, and though pollutants can be naturally occurring, any number in excess can prove hugely detrimental to the well-being of the system. The pollutants of focus in this study are phenol and phenolic compounds. They are hazardous substances in industrial wastewater generated by plastics and petroleum refinement plants. Phenol is water-soluble which means it travels in groundwater and is toxic to both the marine and terrestrial ecosystems with even just a few tens of ppm^[1]. In humans, persisting dermal and pulmonary exposure to aqueous phenol toxins may lead to skin irritation, muscle weakness, and severe inflammation^[2,3].

The advanced oxidation process (AOP) is used to treat toxic organic materials by oxidizing organic compounds with hydroxyl radicals (·OH). Ferrous ion-based Fenton's reagent is commonly used to complete the process; however, the reaction only activates in acidic conditions (pH 2.5-3.5) and requires additional steps to collect the purified water. In addition, the residual ferrous ions can cause DNA damage in humans through intracellular infusion and increase oxidative stress^[4,5].

Until recently, graphene's application in wastewater treatment included only graphene oxides (GOs), or in combination with a complex with other materials. These forms of graphene catalyze the degradation of toxic organic pollutants^[6,7], or in microbial fuel cells^[8,9]. However, GOs exhibit limitations in commercialization because they require an additional metal catalyst.

Graphene as a nanomaterial is renowned for its superb physicochemical properties as well as its ability to fabricate into diverse sizes and forms. It is this flexibility that allows for its application in an assortment of research areas. Our group validated that a large-scale graphene film synthesized by the chemical vapor deposition (CVD) method could be used as a catalyst for organic acid degradation^[10,11] used in wastewater treatment.

In the study, a monolayer graphene film generated hydroxyl radicals by accelerating the AOP of phenol and breaking down physisorbed hydrogen peroxide (H₂O₂) on its surface. This study reports an upgraded graphene catalyst which, when combined with UV irradiation, further expedites AOP. We enhanced the catalytic effects by constructing a graphene-coated column which allows for continuous phenol degradation. The column shows graphene's practicality when combined synergistically with UV light^[12]. From the synthesis of graphene to the phenol degradation, all the processes carried out are environmentally friendly and cost-effective when compared to the previous wastewater catalysts and methods.

3.2. Results and Discussion

Previous studies prove graphene reduces hydrogen peroxide into hydroxyl radicals by temporarily forming a bond^[13-16], which facilitates its functioning as an AOP catalyst^[17,18]. Since UV light is also known to break hydrogen peroxide into hydroxyl radicals, we examined the combination of graphene and UV light as a method of catalytic enhancement. To ensure the integrity of its surface during the catalytic process, we examined the potential that either AOP or UV light could destroy the graphene structure (Figure 3-1a). Raman spectroscopy provides the characteristic peaks for graphene where the G peak (~1590 cm⁻¹) shows sp² bonded graphitic domain, and the D peak (~1390 cm⁻¹) shows structural defects. Thus, the I_D/I_G value is a key indicator to represent graphene's structural integrity. The D peak observed in pristine graphene was barely visible, where the average value of I_D/I_G was 0.22±0.03. The I_D/I_G value of the same graphene samples used for the AOP experiment with and without UV irradiation displayed 0.21±0.07 and 0.35±0.04, respectively, indicating little or no damages on the surface (Figure 3-1b). Also, to note was that the I_{2D}/I_G value stayed around 2, showing predominant monolayer coverage, and displaying the preserved integrity of graphene's surface and thus suggesting its recyclability (Figure 3-1c).



Figure 3-1. Characterization of graphene before and after usage. (**a**) Representative optical microscopic images of pristine graphene and graphene used for AOP with and without UV treatment. (Magnification x1k, scale bar 10 μ m) (**b**) Raman mapping of each graphene samples' I_D/I_G (Magnification ×500, scale bar 1 μ m), and (**c**) representative Raman spectra.

The proposed mechanism of the enhanced catalytic effect of graphene by UV irradiation is illustrated in Figure 3-2a. Graphene assists the reduction of hydrogen peroxide, as well as the UV light, which both contribute to the adequate supply of hydroxyl radicals for phenol degradation. Due to UV light's ability to photolyze phenol directly^[19], we validated the extent of its degradation as a factor of distance from the light source (Supplementary Figure 3-S1). Even without hydrogen peroxide, UV light degraded 23.8% of phenol at a shorter distance (2 cm). This induced 10.4 times more degradation than the UV irradiated from further away (4 cm), while a negligible

change in the concentration occurred in the absence of UV light. Therefore, to maximize the UV light's effect, we fixed the distance as 2 cm for the rest of the experiments.

We prepared a mixture of phenol and hydrogen peroxide solution. Then we removed a PMMA coating from a graphene film $(2 \times 2 \text{ cm}^2)$ and transferred on an SiO₂ wafer. From the control (CTL) sample, there was negligible phenol degradation after three hours of incubation in the absence of graphene and UV light (Figure 3-2b). However, when introducing graphene and UV irradiation, the result was respectively 9.7% phenol degradation with graphene and 76.8 % degradation with



UV irradiation. Only when combined, did graphene and UV treatment degrade phenol completely. The catalytic effect of graphene with UV exposure is analogous to that of the 0.05 mM Fenton's reagent, one of the most used AOP catalysts (Supplementary Figure 3-S2). Although the degradation rate is slower, the graphene film is reusable without an additional process to remove the catalyst from the degraded mixture.

Figure 3-2. UV exposure enhances the catalytic effect of graphene on phenol degradation. (**a**) Schematic illustration of phenol degradation under UV exposure with graphene as the AOP catalyst. (**b**) Degradation of phenol by CTL (without graphene and UV), UV (UV irradiation), Gr/SiO₂ (graphene), and Gr/SiO₂ w/ UV (graphene with UV irradiation) within three hours.

Graphene is bendable when transferred onto a flexible surface. This flexibility allows for the construction of a graphene-coated column with UV-resistant polyimide (PI) film as the substrate (Figure 3-3a)^[20]. Before assembling the column, we verified

whether phenol could adhere to either surface, as phenol can interact with graphene and PI through π - π interactions^[21] (Supplementary Figure 3-S3). When floating the PI film on phenol solution for three hours, there was almost no change in concentration. However, following the introduction of 2×2 cm² graphene, transferred on the PI film (Gr/PI), we detected a slight reduction, of which the change was continuously negligible.

Whether the substrate change could affect graphene's catalytic ability was validated by transferring graphene 2×2 cm² on the PI film. Despite the substrate change, phenol was 17.7% degraded by Gr/PI (Supplementary Figure 3-S4). However, as PI can interfere with UV penetration, when we floated the sample so that the graphene faces down, the synergistic introduction of UV light degraded phenol of only 51.2%, displaying decreased catalytic activity comparison with Gr/SiO₂. Since the UV irradiation nonetheless improved the degradation efficiency, we increased the dimension of graphene film on PI and rolled it into a glass column so that graphene covers the inside of column entirely. We used a syringe pump connected to one end of the column and injected the phenol solution at a constant flow rate while the degraded product was collected from the other end.

Of various possibilities, the evaluated factors include the flow rate, hydrogen peroxide concentration, and UV penetration through PI on phenol degradation^[22]. First, we fixed the hydrogen peroxide concentration to 50 mM, and controlled the flow rate (Figure 3-3b). At the fastest flow rate, 1.2 ml/min was the minimum catalytic activity, as it only allows the short exposure time to graphene and UV light. While the flow rate of 0.6 ml/min achieved the maximum performance, there was a lurking factor of syringe replacement during the experiment. By employing the flow rate of 0.3 ml/min, the final phenol concentration was similar to 0.6 ml/min without additional changes. On average, the flow rate resulted in 21.8% of constant phenol degradation, despite the constant incoming of new phenol, suggesting an optimal flow rate of 0.3 ml/min for ensuing experiments.

As hydrogen peroxide can naturally reduce to water and oxygen, increasing its concentration does not pose serious concern. At the flow rate of 0.3 ml/min, 100 mM of hydrogen peroxide yielded the most favorable outcome (Figure 3-3c). Since we obtained the experiment's maximum efficiency at the flow rate of 0.3 ml/min and 100 mM of hydrogen peroxide, we set these variables as the optimized condition.

Regarding the UV light blockage by PI film, we validated the degradation efficiency with only the lower half of the column covered with graphene (Figure 3-3d). The degradation rate was slower when using smaller graphene; however, the final concentration of phenol was saturated to around 6.7 mM. The efficiency is nearly equivalent to that obtained with full graphene coverage, suggesting that graphene size is a more critical factor than the amount of UV penetration.

In accordance with Gr/SiO₂, the graphene column's degradation efficiency was highest in the combination of graphene and UV light. Respectively, phenol degraded around 8.3% with graphene and 23.6% under UV irradiation (Figure 3-3e). When the PI film was rolled into the column and introduced UV light, 13.4% was degraded. Therefore, considering the blockage of UV light penetration by PI substrate, a considerable synergistic effect between graphene and UV led to improved catalytic efficiency.

Persistent UV irradiation increased the column's temperature to around 60~70 °C, whereas the outflowing solution remained around room temperature (Supplementary Figure 3-S5a). To verify the sole effect of increased temperature on degradation, we incubated phenol at 60 °C in the presence of Gr/SiO₂ (Supplementary Figure 3-S5b)^[23]. While the increased temperature degraded 20.8% of phenol, which is better than Gr/SiO₂ at room temperature, the efficiency was significantly lower than the combined treatment of Gr/SiO₂ and UV.

In order to improve efficiency, we connected two graphene columns in series and introduced UV light (Supplementary Figure 3-S6a). Although we observed a slower catalytic efficiency at the earlier time point, overall, 36.9% phenol was degraded at the three-hour mark (Supplementary Figure 3-S6b). Compared to the one column system, even better efficiency was observed beyond two hours, expecting the doubled volume of safely treated phenol.



Figure 3-3. Optimizations of continuous phenol degradation by the graphene column. (a) Schematic drawing of the graphene column. The optimal condition of graphene column was found by comparing the effect of (b) flow rate of solution (10 mM phenol and 50 mM H_2O_2), (c) concentration of H_2O_2 at a fixed flow rate of 0.3 ml/min, and (d) the extent of graphene's column coverage. (e) The synergistic effect of graphene and UV light treatment is considerable compared to either graphene or UV light treatment.

From the two-column system, we detected and analyzed various AOP intermediates in chronological order. We compared the retention time and UV spectrum of each organic acids and illustrated the phenol's degradation pathway (Figure 3-4a). From the beginning to 30 minutes of UV exposure, we identified hydroquinone (HQ) and dihydroxy benzene (DB), the very first intermediates formed

by the attack of hydroxyl radical on phenol (Figure 3-4b). The concentration of DB increased until an hour later, where we started to observe muconic acid (MU). An hour and a half later, we consistently detected *p*-benzoquinone (*p*-BQ), the oxidized product of HQ, and maleic acid (MA), the final product of phenol degradation, until the three-hour mark.

Interestingly, the combination of Gr/SiO₂ and UV irradiation showed greater catalytic efficiency than the graphene column. From this combination, we only examined DB and MU, and within two hours, even these intermediates became undetectable (Supplementary Figure 3-S7a). Coherent with the intermediate analysis by the graphene column, HQ was not examined from the Gr/SiO₂ sample due to its rapid oxidation. However, the same intermediates were constantly identified until the three-hour mark with Fenton's reagent (Supplementary Figure 3-S7b). Therefore, graphene with UV treatment can be deemed a promising catalyst for safer phenol degradation treatment.

While we analyzed other phenol-degraded intermediates by the purchased products, MU was confirmed by the reaction of DB and Fenton's reagent (Supplementary Figure 3-S2b). The oxidation of DB produces subsequent intermediates, including cis-muconic acid^[24,25]. By comparing the UV spectrum and retention time, we concluded that the intermediate at timepoint 38~39 minutes of



the high-performance liquid chromatography (HPLC) spectrum matches MU.

Figure 3-4. Analysis of oxidized derivatives from phenol. (a) Summarized diagram of the phenol degradation process with the UV spectra of intermediates detected at each retention time and experimental time point. (b) The change in the area under the HPLC curve of phenol and each intermediate.

3.3. Conclusion

In this study, we enhanced graphene's catalytic effect in phenol degradation through AOP by introducing a synergistic UV treatment. We achieved the continuous degradation of phenol using a customized graphene column along with optimized conditions such as the flow rate and adjusted the concentration of hydrogen peroxide.

The intermediates from the degraded phenol were analyzed by HPLC and UV spectra, showing the phenol's conventional degradation process. Compared to Fenton's reagent, graphene film can be activated under relatively mild conditions. In addition, the use of graphene film does not require additional steps for salt removal or water collection, making it a cost-effective and environmentally friendly AOP catalyst.

This work's objective was to develop a hydroxyl radical generation method as once the radicals are made, they react non-selectively with phenol and the intermediates at near diffusion-controlled rates^[26,27]. Graphene with UV irradiation synergistically functioned as the catalyst for hydrogen peroxide splitting, resulting in the enhancement of phenol's AOP. TiO₂ is a standard photocatalyst, in which Evonik P25 has been reported to completely degrade phenol 25 ppm in 400 min^[28], and TiO₂-coated guartz tube could degrade phenol of 100 mg/L within 4 hours under UV irradiation^[29]. Compared to both cases, the initial phenol concentration we used in this study (941.1 mg/L, 941 ppm) is much higher, showing a better catalytic efficiency. Although the graphene column only degraded 33% of phenol, the initial phenol concentration was much higher than that of normal polluted water^[3,30]. Therefore, we expect a better catalytic effect of graphene and UV treatment at more average phenol concentrations. Doping graphene with nitrogen can improve the catalytic activity as electronegative nitrogen favorably changes the electron density of the graphitic domain, thus producing more active sites for more hydroxyl radical generation^[15,31]. Increasing graphene's surface area or repeating the degradation process can also lead to enhanced phenol degradation.

Beyond the possibility of AOP catalyzation, graphene's superb physicochemical properties make it an ideal candidate for other wastewater treatment processes. As suggested previously, GOs or reduced GOs can effectively adsorb pesticides through π – π interactions and due to their large surface area^[32,33]. In addition, nanoporous graphene can selectively transport specific ions for further treatments^[34]. Graphene can also be applied for water desalination, thanks to its high salt rejection rate and anti-fouling capability^[35]. Therefore, with appropriate modifications depending on intended use, the continuous graphene column system promises wholesome innovations across many processes of commercial water treatment.

3.4. Experimental

Synthesis and characterization of graphene

Graphene was synthesized using a chemical vapor deposition method based on the previous research^[36]. Cu foil (99.95%, Alfa Aesar, USA) was rolled in a quartz tube and annealed for 90 minutes while increasing temperature up to 1000 °C at the maximum rate while flowing 10 sccm H₂. The graphene synthesis was done by flowing 70 sccm CH₄ at 1000 °C for 30 minutes, followed by rapid cooling. On one side of the Cu foil, the prepared PMMA solution (poly(methyl methacrylate) (182265-500G, Sigma Aldrich, USA) dissolved in chlorobenzene (319996-2.5 L, Sigma Aldrich, USA)) was spin-coated on one side for protection, and the synthesized graphene on other side was removed through reactive ion etching. Then, in order to dissolve Cu, we floated the Cu foil on the 100 mM ammonium persulfate aqueous solution (248614-2.5KG, Sigma Aldrich, USA), after which we rinsed with deionized (DI) water. Th graphene was then transferred onto either SiO₂/Si wafer or PI film (PI-Film 0.05t, Alphaflon, South Korea). Right before using the graphene, PMMA was removed by acetone to prevent oxidation.

Degradation of phenol using graphene transferred on a wafer

Graphene was cut by the size of $2 \times 2 \text{ cm}^2$ and transferred on to the SiO₂/Si wafer or the PI film. PMMA was removed right before its usage to prevent oxidation. The mixture of phenol 10 mM (328111, Sigma Aldrich, USA) and H₂O₂ 100 mM (34.5%, 092817, Samchun, South Korea) aqueous solution was prepared and kept immersed in darkness. In a glass petri dish, the graphene and 5 ml of the solution were added, and 200 µl of the solution was aliquoted every hour for three hours. UV ozone cleaner (UVC-300, Omniscience, South Korea) was used as the UV light source, of which the wavelength is 184.9 and 253.7 nm.

Comparison with Fenton's reagent

Fenton's reagent was prepared by making an aqueous solution of Iron (II) sulfate heptahydrate (215422-5G, Sigma Aldrich, USA) at the final concentration of 0.05 mM to compare its catalytic activity with graphene. The final concentration of phenol and H_2O_2 was the same as mentioned in '**Degradation of phenol using graphene transferred on a wafer'**. In a glass petri dish, 5 ml of the solution was added, and without the exposure to UV light, aliquoted 200 µl of solution every hour for three hours.

Temperature measurement

The solution flowing out from the column was collected in a 20 ml vial, which was replaced every 30 minutes. The temperature of the column inside the UV ozone cleaner and the solution gathered in the vial was measured by an infrared thermometer.

Graphene column

Graphene of size 6×11.5 cm² was transferred on a PI film, and after removal of PMMA, it was rolled inside a quartz column. The phenol solution was prepared, as described in in '**Degradation of phenol using graphene transferred on a wafer'** Around 50 ml of the solution was filled inside the column, connected to the 50 ml syringe filled with the same solution. After placing the column inside the UV equipment, the flow rate was set by a syringe pump (KDS101 Legacy syringe pump, 78-1101, kdScientific, USA). The solution flowing out of the column was aliquoted every thirty minutes for three hours.

Raman Spectroscopy

The surface integrity of graphene before and after using it as a catalyst was detected by Raman spectroscopy (Renishaw, UK) with a 514 nm laser. Graphene transferred on a SiO₂/Si wafer was used for the measurement.

High-Performance Liquid Chromatography

Degradation of phenol was detected through HPLC (Ultimate3000, Thermo Dionex, USA). Hydroquinone (H9003-100G, Sigma Aldrich, USA), 1,2-dihydroxybenzene (135011-5G, Sigma Aldrich, USA), *p*-Benzoquinone (B10358-5G, Sigma Aldrich, USA),

and maleic acid (M0375-100G, Sigma Aldrich, USA) were dissolved in DI water for



HPLC analysis. The monochromatic light wavelength was set as 280 nm and used Chromeleon software (Version 6.80, Dionex Corporation, Sunnyvale, CA, USA) for data analysis.

Dihydroxybenzene reaction with Fenton's reagent

An aqueous solution of dihydroxybenzene 10 mM was mixed with Fenton's reagent 0.05 mM and H_2O_2 100 mM. The reaction proceeded immediately, and HPLC analysis was followed.

3.5. Supplementary information

Figure 3-S1. The intensity of UV light's illumination affects the extent of phenol degradation. The phenol solution of 10 mM was prepared, and the intensity of light was controlled by changing the distance between the light source and the sample. The lamp's power is 170 W, and the intensity of illumination



is 28 mW/cm² at 10 mm.

Figure 3-S2. Comparison of the graphene's catalytic effect on Fenton's reagent. Fenton's reagent 0.05 mM exhibited a similar catalytic ability to the graphene transferred on a SiO_2/Si wafer with UV treatment. The mixture of phenol 10 mM and H_2O_2 100 mM was prepared and left in darkness for control (CTL). Due to the immediate response of the Fenton's reagent, the initial concentration of phenol turned out to be close to 0.

Figure 3-S3. Adhesion of phenol on graphene or PI surface does not significantly reduce the phenol concentration. The PI film and graphene of size $2 \times 2 \text{ cm}^2$ transferred on PI film were kept in the phenol 10 mM solution for 3 hours. The change in concentration due to the phenol's adhesion on graphene is negligible. The HPLC spectrum of the Gr/PI sample at 3 hours is in the inset, where only phenol is detectable.



Figure 3-S4. Graphene transferred on PI film still exhibits the catalytic effect. Phenol degradation by 2×2 cm² graphene transferred on PI film with and without UV treatment.

Figure 3-S5. The effect of temperature on phenol degradation. (a) The temperature of the column inside



the UV ozone cleaner and the solution flowing out of the tube was measured for 3 hours. (**b**) The mixture of phenol 10 mM and H_2O_2 100 mM was prepared, and the degradation of phenol by Gr/SiO₂ at 60 °C was measured.



Figure 3-S6. The two-column system for the improvement in degradation efficiency. (**a**) Schematic drawing of the two graphene columns connected in series. (**b**) Degradation of phenol by two graphene columns in 3 hours.



Figure 3-S7. The AOP intermediates detected when using graphene and Fenton's reagent. The HPLC spectra of samples obtained at each time points when using (**a**) Gr/SiO_2 with UV treatment and (**b**) Fenton's reagent 0.05 mM as the catalyst. (**c**) Left: The HPLC spectrum of the DB reacted with Fenton's reagent. Right: The corresponding UV spectra of each peak.

3.6. References

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Chapter 4

Stacking-specific reversible oxidation of bilayer graphene

4.1. Introduction

Since its first discovery, numerous studies on graphene have been made to utilize its unique physical and chemical properties. As a part of the endeavor to exploit the outstanding features of graphene, modification of electronic properties of graphene through chemical, physical and contact-mediated doping method was proposed^{1,2}. Accompanied by such advancements, bilayer graphene (BLG) was spotlighted for its facile tunability of bandgap that can be controlled by stacking angles, external electric field, or chemical doping^{3,4}. It was also reported that BLG can change from a superconductor to an insulator by simply changing its stacking angle^{5,6}. However, with exfoliated BLG, exploring such stacking-specific properties of BLG is difficult due to its complicated fabrication processes^{7,8}, and thus is hard to be fully implemented in practical devices. On the other hand, the graphene layers synthesized by chemical vapor deposition (CVD) methods are reported to form BLGs *in situ*, which is relevant for practical applications, including chemical sensors⁹, barrier films^{10,11}, fuel cells¹²,

batteries¹³, *etc.* The exfoliated BLGs dominantly show the AB-stacked structures with carbons on the upper layer positioned in the middle of the hexagonal lattice on the lower layer, while the CVD-grown BLGs show various stacking orders, which provide a better system to study various stacking-dependent phenomena. While some studies have been carried out to characterize the structures of oxidized monolayer graphene (MLG)^{14,15}, there has been no study on the stacking-specific chemical reactivities of BLGs.

4.2. Results and discussion

In this study, we, for the first time, show that O₂ and H₂ flow at elevated temperature can induce fully reversible redox reactions of CVD-grown BLG, which is different from the redox reactions of epitaxially grown¹⁶ or exfoliated¹⁷ samples. More importantly, we observe that the oxidized Bernal (AB) and non-Bernal (AA`) stacked BLG show drastically different Raman spectral features (peak-shifts and line-shapes), strongly suggesting that the two structures produce two different oxide products. The stacking order of CVD-grown BLG was separated by scattering-Scanning Nearfield Optical Microscopy (sSNOM) measurement contributed by Dr. Gyouil Jeong.

The sample (Fig.4-1; see methods for sample preparation procedure) is comprised of a SiO₂/Si substrate uniformly covered with mono-layer graphene (MLG) and an additional graphene layer island (diameters of ~10 μ m) formed on top of the MLG. The islands provide BLG with a various stacking domain. The sample was placed in a vacuum furnace and heated to 873 K with the O₂ (g) flow of 100 ml / min or H₂ (g) flow of 150 ml / min to induce oxidation and reduction of BLG (see Fig. 4-1).



Figure 4-1. Schematic illustration of oxidation / reduction processes of BLG. The BLG on SiO₂ / Si wafer

is placed in a quartz tube at the temperature of 873 K, and O_2 (g) and H_2 (g) are flowed through the vacuum furnace at the flow rates of 100 ml / min and 150 ml / min respectively.



Figure 4-2. Raman spectral changes of AB and AA`-BLG following the O₂ and H₂ exposure. **a-f**, G, 2D, and combination-mode peaks of Raman spectra of AB-BLG (a, c, e) and AA`-BLG (b, d, f) before (blue) and after (red) the exposure to O₂ (30 min). After the exposure to O₂, G-peak is split into two components (G⁺ and G⁻), which are fitted to two Lorentzian functions (dashed curves). The peak at 2331 cm⁻¹ (marked in * in e) appearing in e and f is the Raman peak of the ambient N₂ gas present. **g-i**, Evolutions of G-peak center position (g), 2D peak position (h), and ratio of D and G peak intensities ((i), I_D / I_G) of AB-BLG (green) and AA`-BLG (violet) under the two sequential H₂ and O₂ exposure (30 min each). Shaded regions in (g) and (h) refer to the ranges of center frequency changes of G and 2D peaks of AB-BLG (green) and AA`-BLG (purple).

The Raman scattering spectra of AB-BLG and AA'-BLG reversibly change upon O₂ and H₂ exposure (Fig. 4-2; Raman spectra of BLG, covering wider range of spectral window are shown in Supplementary Information Fig. 4-S1), which may arise from the mechanical strain¹⁸ and / or the chemical-doping¹⁶ caused by the oxides on BLG. For the particular data shown, the stacking angle of AA`-BLG is estimated to be¹⁹ $\theta \sim$ 26°. The most pronounced changes are the peak-center shifts of G and 2D peaks (Fig. 4-2a-d, g, h), indicating the doping level changes induced by the redox reaction. The line-shapes of G peaks of pristine and reduced AB-BLG (blue trace in Fig. 4-2a) and AA`-BLG (blue trace in Figure 4-2b) are nearly identical to each other, and they appear as a single peak (with a FWHM of 20 cm⁻¹), corresponding to the doubly degenerate E_{2g} phonon vibration of BLG^{8,20,21}. Upon oxidation (red traces in Fig. 4-2a and b), the single G-peak is split into two components (denoted as G⁺ and G⁻). The G-peak

splitting can arise from uniaxial mechanical strain²² induced by oxides, lifting the degeneracy of E_{2g} -mode frequency, or from the asymmetric doping induced by oxides, leading to the mixing of E_{2g} (Raman-active) and E_{1u} (Raman-inactive) phonon modes²³. The D versus G peak intensity ratio (I_D / I_G), which is a widely accepted measure of the defect-density on graphene, remains nearly unchanged (see Fig. 4-2i) during these reversible processes.

We also note that above-mentioned spectral changes are different for AB and AA`-BLG, strongly suggesting that the AB and AA`-BLG may have different redox reactivities and/or generate different kinds of oxide products. Specifically, when exposed (30 min) to the same dosage of H_2 and O_2 , the magnitudes of peak-center shift in G and 2D peaks are similar to AB and AA'-BLG. (Figure 3g and h; see the shaded regions). However, the magnitude of G-peak splitting ($\Delta v_{G} = v_{G+} - v_{G-}$), and the intensity ratios of the v_{G+} and v_{G-} components (I_{G+} / I_{G-}) are different for AB and AA'-BLG. Additionally, we find that reduced AB and AA`-BLG both show combinationmode peaks at 1860 cm⁻¹, 1983 cm⁻¹, and 2220 cm^{-1 24,25}. Upon oxidation, these peaks of AB-BLG completely disappear, whereas those of AA`-BLG remain nearly unchanged (Figs. 4-2e and f). As previously shown²⁴, the peak positions and intensities of the combination peaks of graphite and few-layer graphene critically depend on the number of layers, doping, and stacking²⁶. Overall, the observed differences suggest different reactivities and / or different oxide structures of AB and AA'-BLG. As shown in Figure 4-2i, we find that the D versus G peak intensity ratio (I_D / I_G) show a clear correlation to the O₂ / H₂ exposure cycle (i.e., the ratio increases and decreases with oxidation and reduction, respectively).

Raman spectra show that exposure to O_2 and H_2 under elevated temperature leads to reversible oxidation and reduction processes without apparent increased defect densities (Figs. 4-2g-i). More importantly, the result suggests that the oxide structure and/or reactivities are different for differently stacked BLG. We find that such reversible change occurs only for the mild reaction condition described above: Prolonged exposure to O_2 (> 3 hrs) at an elevated temperature generates irreversible formation of etch pits¹⁷ in AB and AA`-BLG, which are accompanied by the drastic increase in D peak in the Raman spectra. To better characterize the oxidized sample, we have attempted to carry out the high-resolution electron microscopy measurement (CS-corrected STEM), but without success: the grids for the TEM could not withstand harsh oxidation condition employed, and the PMMA (poly(methyl methacrylate)) and ammonium persulfate residues further impeded the measurement.

4.3. Conclusion

Formation of stacking domains and their crystallographic characterization have been extensively studied thus far^{20,25}. However, the stacking-dependent chemical reactivity of BLGs has not yet been explored. We have shown, based on the Raman spectroscopy measurements, that CVD-grown BLG allows reversible redox reaction with O₂. The Raman spectral shapes of the oxidized BLG also indicate that different oxide structures are formed on the AB-BLG and the AA`-BLG. The *Ab Initio* Molecular Dynamics (AIMD) simulation result from Dr. Eunhak Lim who is one of co-authors suggests that the singlet and triplet O₂ molecules behave differently on AA`- and AB-stacked BLGs, resulting in epoxides and endoperoxides, respectively. The CVD-grown bilayer graphene is useful for many applications. In this regard, we believe that the current study provides a new strategy to design high-performance graphene-based catalysts useful for various electrochemical, biological, and environmental applications.

4.4. Experimental

Sample preparation (CVD bilayer graphene). Graphene films were synthesized on 25 μ m thick copper foil through the CVD method using methane (50 s.c.c.m.) and hydrogen (5 s.c.c.m.) gas with vacuum pumping (~1.5 mtorr) at 1000 °C for ~2 hours. Methane was used only during the growth stages of graphene and was not used during the cooling process. Poly (methyl methacrylate) (PMMA) was spin-coated on top of graphene, and the copper foil was etched in an ammonium persulfate solution (20 mM with distilled water). The achieved monolayer graphene films were transferred onto SiO₂ (thickness of 285 nm)/Si substrates. The monolayer covers nearly all areas of the SiO₂/Si substrate, and bilayer domains appear as islands with an average radius of ~10 μ m.

Oxidation and reduction of CVD bilayer graphene. Graphene films were oxidized under atmospheric pressure, with 100 ml/min of oxygen and 300 ml/min of argon gas flow, in a 1-inch quartz tube furnace. When the temperature of the furnace reached 873 K, the furnace was slid to cover the sample to heat the sample for 30 min. After the reaction, the sample was rapidly cooled by sliding the furnace away. Reduction reaction was conducted in the same procedure, but 150 ml/min of hydrogen gas flow was used in place of oxygen gas. Graphene films were alternately oxidized and reduced.





Figure 4-S1. Wide-range Raman spectrum of AB- and AA`-BLG before and after oxidation. a, Wide range Raman spectra of Bernal- stacked BLG before and after oxidation. b, Changes in the G band shape through reduction and oxidation. c, Changes in In-plane phonon mode. d, Changes in the 2D band shape through reduction and oxidation. e, Wide range Raman spectra of non-Bernal-stacked BLG before

and after oxidation. f, Changes in G band shape through reduction and oxidation. g, Changes in the Inplane phonon mode. h, Changes in the 2D band shape through reduction and oxidation.



Figure 4-S2. Raman spectral changes of MLG following the O_2 and H_2 exposure. a-c, G, 2D, and combination-mode peaks of Raman spectra of MLG before (blue) and after (red) the exposure to O_2 . d-f, Comparison of the Evolutions of G-peak center position (d), 2D peak position (e), and ratio of D and G peak intensities ((f), I_D/I_G) of AB-BLG (green), AA`-BLG (violet) and MLG(black) under the H_2 and O_2 exposure.

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Appendix

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4. J. Kim[†], **<u>B. Park[†]</u>**, D. H. Shin[†], J. M. Yoo, H. Lee^{*}, B. H. Hong^{*} "Photocatalytic degradation of phenols using CVD graphene column" *Catalysts*, **10**, 1251. (2020)

3. M. J. Park, H.-H Choi, **<u>B. Park</u>**, J. Y. Lee, C.-H Lee, Y. S. Choi, Y. Kim, J. M. Yoo, H. Lee, B. H. Hong^{*}. "Enhanced Chemical Reactivity of Graphene by Fermi Level Modulation" *Chemistry of Materials*, **30**, 5602-5609. (2018)

2. J. M. Yoo[†], **<u>B. Park[†]</u>**, S.-J. Kim, Y.S. Choi, S. Park, E.H. Jeong, H. Lee^{*} and B.H. Hong^{*}. "Catalytic degradation of phenols by recyclable CVD graphene films" *Nanoscale*, **10**, 5840-5844. (2018)

1. G. Jeong, B. Choi, D.-S. Kim, S. Ahn, **<u>B. Park</u>**, J. H. Kang, H. Min, B. H. Hong, Z. H. Kim^{*}. "Mapping of Bernal and non-Bernal Stacking Domains in Bilayer Graphene Using Infrared Nanoscopy." *Nanoscale*, **9**, 4191-4195. (2017).

Selected presentations

The 2018 MRS Spring Meeting & Exhibit (Poster). *Catalytic degradation of phenols by recyclable CVD graphene film.* Phoenix, AZ, USA (April 2018)

The 4th Korean Symposium on Graphene and 2D Materials (Poster). *Catalytic degradation of phenols by recyclable CVD graphene film.* Buyeo, Republic of Korea (April 2017)

The 3rd Korean Symposium on Graphene and 2D Materials (Poster). *Catalytic degradation of phenols by recyclable CVD graphene film.* Buyeo, Republic of Korea (April 2016)

The 2nd International Conference on Two-Dimensional Layered Materials (2DLM) (Poster). Enhanced Catalytic Activity of Doped Graphene for Wastewater Treatment. Hong Kong (January 2016)

Graphene Flagship – Graphene Week 2015 (Poster). Enhanced Catalytic Activity of Doped Graphene for Wastewater Treatment. Manchester, UK (June 2015)

Abstract in Korean



화학적기상증착을 이용한 그래핀의 합성에 대한 연구와

불균일촉매로의 응용

서울대학교 대학원

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박 배 권

그래핀이 발견되고 나서 특이한 물리 화학적 성질로 인해 많은 주목을 받아왔고, 많은 연구 개발을 통해 이론과 실제의 간극을 좁혀오고 있다. 그러나 아직까지 그 간극은 존재하며, 이 차이를 이해하는 것은 그래핀의 응용에 있어서 필수적이다. 특 히, 그래핀의 표면 성질을 이해하는 것은 그 응용에 있어서 매우 중요한 부분이라 고 할 수 있다. 왜냐하면 모든 화학반응이 물질의 표면에서부터 일어나기 때문에 표면의 성질의 이해에 따라 화학반응의 이해 정도를 결정한다고 말할 수 있기 때문 이다. 그래핀 표면의 성질을 결정하는 요인에는 기판, 온도, 압력, 전자기장 등이 있 고 이를 조절하여 다양한 연구가 진행되고 있다. 특히, 그래핀이 원자 한 층으로 이 루어져 있기 때문에 기판의 영향을 많이 받는다. 게다가 이론적으로 그래핀은 Dirac cone 모양의 밴드 갭을 가지고 있으나, 실제로는 기판 및 주위환경 (온도, 전자기장 등)의 영향으로 반도체 또는 도체의 성질을 띌 수 있다. 그리고 그래핀 표면에서는 전자 전이가 일어날 수 있어서 촉매로서 효과도 기대할 수 있다.

본문에서는 학위과정 동안 그래핀의 표면에서 일어나는 현상에 대해 연구한 것들을 총 망라하였다. 특히, 그래핀의 표면에서 일어나는 전자 전이에 대해 흥미를 가졌고, 그래핀의 주위환경을 바꿔가며 활성산소종 (Reactive Oxygen Species; ROS) 를 활성화하여 라디컬을 생산하고 이를 조절하여 수처리로 응용해보았다. 이 실험 을 통해 그래핀 표면에서 전자 전이가 일어날 때 어떻게 활성산소종과 반응하는지 메커니즘도 고려하였다. 이와 더불어 그래핀 표면과 분자와의 상호작용을 분석 및 응용하는 연구들을 진행하였다. 그래핀을 가열하여 반응성을 높인 후 기체를 바꿔 가며 그래핀 표면에서 일어나는 화학적인 반응들(산화, 환원, 흡착)을 분석해보았고, 이 과정에서 그래핀 표면이 산화될 때 나타나는 분광학적 특징을 분석하였다.

1장에서는 그래핀의 역사와 합성법을 간략하게 설명하고, 한층 그래핀 그리 고 그 이상 층을 이루는 그래핀의 성질을 정리하였다. 그리고 그래핀의 표면 개질 및 응용분야에 대해 간략히 소개하였다. 2장에서는 그래핀에 활성산소종을 혼합하여 전자 전이를 통한 라디컬 생성으로 수처리에 응용하였다. 수처리 과정에서도 가장 최종단계인 고도산화공정 (Advanced Oxidation Process; AOP) 과정에 활용하여 분자 단위의 오염물질을 분해하는 실험결과를 보여주었다. 그래핀을 이용한 수처리는 중 성조건에서 반응시킬 수 있으며 환원과정없이 재사용가능하기 때문에 기존 고도산 화공정 과정들이 가지는 단점들, 산성조건에서 반응을 보내고 촉매환원과정을 거쳐 야하는 점 등을 보완할 수 있다.

3장에서는 그래핀의 면적에 의존하여 활성산소종의 생산량이 증가하기 때 문에 이를 응용하여 대면적으로 합성한 그래핀을 칼럼 형태로 제작한 뒤에 고도산 화공정 실험을 진행하였다. 이때 반응성을 높이기 위해 UV를 사용해서 광촉매효과 를 적용하였다. 이 효과로 인해 짧은 시간 동안에 많은 양의 페놀을 분해할 수 있 음을 확인하였다. 이를 통해 연구를 위한 연구가 아닌 실제로 적용 가능한 연구를 통해 상업적으로 사용할 수 있는 결과를 얻었다.

4장으로는 이층 그래핀을 가열하여 반응성을 높인 후 실생활에 자주 접하 는 산소를 주입하여 그래핀의 표면과 분자와의 상호작용을 분석하였다. 이층 그래 핀은 반도체 물질로 주목받기 때문에 이층 그래핀의 산화를 이해하는 것은 응용에 있어서 필수적이다. 특정 조건하에서 산소를 주입했을 경우에는 표면이 산화되는 듯이 했으나 수소를 주입하여 환원 과정을 거치니 완전히 돌아오는 것을 확인하였 다. 그리고 이 과정이 반복적으로 일어나는 것을 확인하고, 산화된 그래핀 표면을 분석하여 어떤 구조의 형태로 산화되어 있는지 유추하였다.

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