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공학석사 학위논문

**Direct exfoliation of graphite using
non-ionic polymer surfactant for
fabrication of transparent and
conductive graphene film**

비이온성 고분자 분산제를 이용한 그래파이트의
박리와 이를 통한 그래핀 투명전극의 제조

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Direct exfoliation of graphite using non-ionic polymer surfactant for fabrication of transparent and conductive graphene film

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Abstract

Direct exfoliation of graphite using non-ionic polymer surfactant for fabrication of transparent and conductive graphene film

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A high-yielding dispersion of graphene at high concentration in solvent is critical for practical applications. Herein, we demonstrate the formation of stable dispersion of pristine graphene in ethanol by exfoliating graphite flakes into individual graphene layers using a non-ionic polymer surfactant under bath-type sonication. Oligothiophene-terminated poly(ethylene glycol) was synthesized and used as a non-ionic and amphiphilic surfactant for exfoliating graphite into graphene. High-quality graphene film was fabricated from the exfoliated graphene solution by the vacuum filtration method. TEM and SEM reveal that the size of exfoliated graphene flake is larger than 1 μm . When the graphene film was treated with nitric acid and thionyl chloride after washing with solvent, the film showed high performance with a sheet resistance of 0.3 $\text{k}\Omega \text{sq}^{-1}$ and a transparency of 74% at 550 nm.

Keywords: graphene, exfoliation, surfactant, dispersion, vacuum filtration

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Chapter 1. Introduction

Transparent and electrically conductive electrodes have been an essential part for organic electronics such as organic light-emitting diodes and organic photovoltaics. Recently, due to its unique physical properties such as room temperature quantum effect, ambipolar electric field effect and high charge carrier mobility, graphene has attracted great attraction from both academia and industry as a transparent and electrically conductive electrode material.^{1,2} For these advantages of graphene to be realized in practical applications, it is essential to develop high-yield and high throughput fabrication method of graphene. The approaches to fabricate graphene are categorized into two methods: (1) top-down exfoliation of graphite into graphene by breaking π -bonding between graphite sheets³⁻⁷ and (2) bottom-up formation of sp^2 -bonding between carbon atoms in a monolayer.⁸⁻¹³ The first method includes mechanical and chemical exfoliation of graphite and the second one does the chemical vapor deposition (CVD) and the epitaxial growth on silicon carbide. Though recent works based on the CVD method using catalytic metal substrates have shown the possibility to grow large-area graphene layer and therefrom to fabricate highly transparent and flexible conducting electrode,¹⁴ the production cost is very high due to expensive substrate and high-temperature process.

Chemical exfoliation methods based on the Hummers' method,¹⁵ oxidation of graphite to produce graphene oxide (GO) followed by chemical or thermal reduction (Figure 1.1), have an advantage of potentially low-cost and solution-processed fabrication.¹⁶⁻¹⁸ However, the reduction process may not completely recover graphene from GO containing a substantial amount of structural defects such as carboxylic acid, carbonyl, hydroxyl and epoxide groups, which degrade the electrical properties of graphene: the reported sheet resistance obtained from reduced GO film ranges from 1 to 70 k Ω sq⁻¹ (<80% transmittance) or from 31 k Ω sq⁻¹ to 19 M Ω sq⁻¹ (at 95% transmittance), which is much higher than that of ITO.¹⁹⁻²¹ Although several other top-down methods for preparation of stable suspension of graphene have been reported, including the direct dispersion of graphite in organic solvents such as *N*-methyl-2-pyrrolidone,²² dimethylformamide²³ and *o*-dichlorobenzene,²⁴ the graphene yield by those methods is very low. The dispersion of graphene by ionic polymer surfactants has recently been reported.^{25,26} However, the resulting graphene films do not exhibit impressive conductivity because the interaction between graphene sheet and the ionic surfactant is not so strong as to fully exfoliate graphite flakes. Also, it is well known that residual surfactant on the graphene film is the main reason for low conductivity of graphene film because it disturbs charge carrier to pass through graphene film (Figure 1.2). It is important to remove surfactant effectively to fabricate highly conductive graphene film.

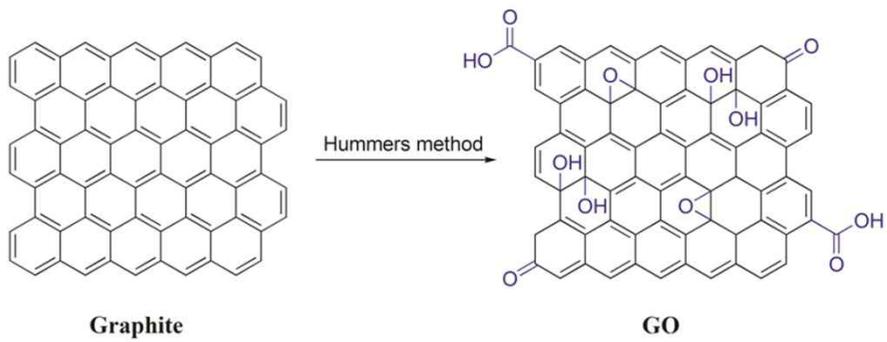


Figure 1.1 Oxidation of graphite to produce graphene oxide

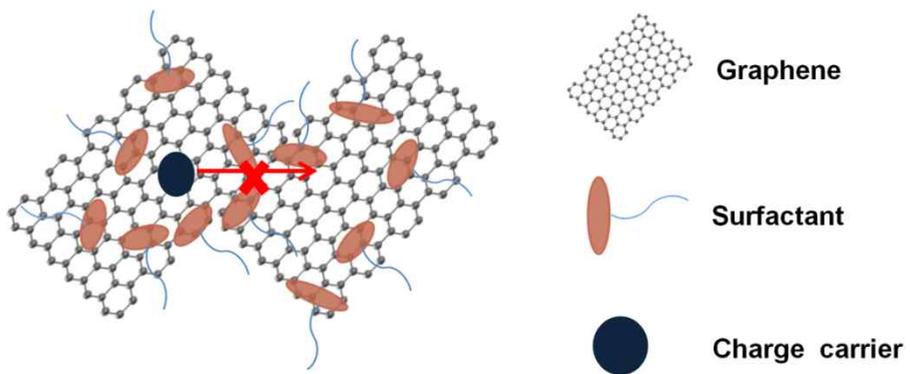


Figure 1.2 Schematic diagram of surfactant affecting electrical conductivity of graphene

In previous work,²⁷ we synthesized a non-ionic surfactant composed of oligothiophene and polyethylene glycol (PEG), and used a surfactant to disperse single-walled carbon nanotubes (SWCNTs) in aqueous media for fabrication of highly conductive and transparent thin films. Since oligothiophene part in the surfactant is absorbed on the SWCNT surface due to π - π interaction between thiophene and CNT, and PEG is soluble in ethanol, the surfactant easily disperses SWCNTs in ethanol. Hence, it is expected that this concept can also be applied to exfoliation and dispersion of graphene layers from graphite in organic media. Other groups have recently used various types of surfactant for exfoliation of graphite,²⁸⁻³⁰ but the conductivities of graphene films are not satisfactory. In this paper, we report the fabrication of highly conductive and transparent graphene film from graphite by using quinquethiophene-terminated PEG (5TN-PEG) as a surfactant. This method has an important advantage over other top-down exfoliation methods, because this method does not require an extra process for exfoliation of graphite while other methods such as the oxidation/reduction method need extra chemical processes. When the film fabricated by our method was treated with nitric acid and thionyl chloride after the 5TN-PEG surfactant was removed by washing with THF during vacuum filtration, the film exhibited a very low sheet resistance of $0.3 \text{ k}\Omega \text{ sq}^{-1}$ with 73% transmittance at 550 nm. This value is the lowest sheet resistance among graphene films prepared by the top-down fabrication of graphene at the best of our knowledge.

Chapter 2. Experimental

2.1 Materials

Graphite flakes and 3-thiopheneacetic acid were purchased from Sigma Aldrich and used without further purification. Poly(ethylene glycol) methyl ether (PEG-COOCH₃, Aldrich, M.W. = 2000 g mol⁻¹) was dissolved in a small amount of methylene chloride and then precipitated in cold diethyl ether for purification.

2.2 Synthesis

2.2.1 Synthesis of (2, 5-dibromo-thiophene-3-yl)-acetic acid (2Br-1TN)

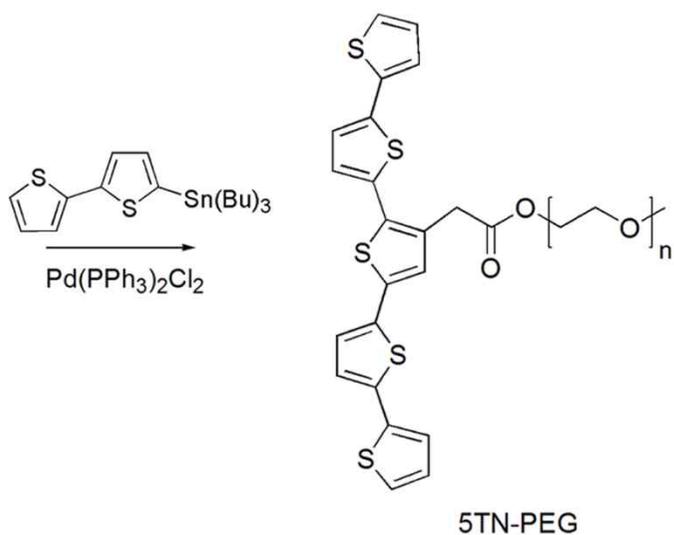
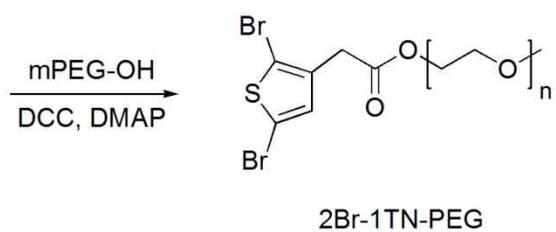
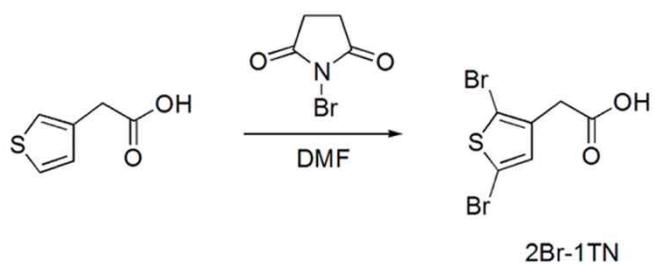
3-Thiopheneacetic acid (5 g, 35 mmol) was dissolved in 40 ml of N,N-dimethylformamide (DMF) and then 14.24 g (80 mmol) of N-bromosuccinimide (NBS) was subsequently added to produce 2Br-1TN. After stirring overnight at room temperature, the reaction mixture was diluted in ethyl acetate and extracted with water for two times to remove DMF. The ethyl acetate layer was dried with 2 g of MgSO₄ for 2 hours and then filtered and evaporated under vacuum pressure. The product 2Br-1TN was recrystallized from ethanol (yield 60%).

2.2.2. Synthesis of 2Br-1TN-PEG

15 g of PEG and 3.178 g of 2Br-1TN (10.5 mmol) were placed into a three-neck round-bottom flask, and then the flask was dried at 80 °C for 2 h to remove water. CH₂Cl₂ (120 ml) and 0.129 g of 4-dimethylaminopyridine (1 mmol) were placed to the flask after purging with N₂ gas, to which 10.6 ml of 1M 1,3-dicyclohexylcarbodiimide (DCC)/CH₂Cl₂ solution was added using a syringe. The mixture was allowed to react for 24 h at room temperature under stirring to yield 2Br-1TN-PEG. The resulting solution was filtered and precipitated in cold diethyl ether to remove unreacted reagents. Then the product 2Br-1TN-PEG was dried in vacuum for 24h.

2.2.3. Synthesis of quinquethiophene-PEG (5TN-PEG)

2Br-1TN-PEG (10.8 g, 4 mmol) and 10.5 ml of 2-(tributylstannyl)-bithiophene (20 mmol) were dissolved in 50 ml of DMF. The solution was deaerated under vacuum and repeated 10 times to addition of Pd(PPh₃)₂Cl₂ catalyst (2–5 mol%). The solution was allowed to react at 100 °C for 24 h to yield the product 3TN-PEG. The resulting solution was precipitated in cold diethyl ether to remove the catalyst and unreacted reagents. The precipitate (5TN-PEG) was filtered and dried in vacuum at room temperature. Overall synthesis route is represented in Scheme 2.1.



Scheme 2.1 Synthesis of 5TN-PEG

2.3 Preparation of graphene solution

To exfoliate graphite into graphene in ethanol, graphite flakes (5.2 mg) and 5TN-PEG (52 mg) were added in a vial which was filled with 10 mL of ethanol, and the solution was stirred for 5 h. The amount of graphite flake is 10 times less than that of 5TN-PEG for fully exfoliate graphite flake. The graphene solution was then sonicated in a bath-type sonicator (Hwashin Instrument, Power Sonic 410) for 5 h. To sonicate solution effectively, we put a solution vial into sonication bath water to be sunken in a half of vial. After sonication for 5h, the solution was centrifuged at 2000 rpm for 90 min to sink unexfoliated graphite flakes to the bottom of the solution. The supernatant was carefully decanted. The supernatant was again centrifuged at 4000 rpm for 30 min and the supernatant was removed by syringe and the residual solution was carefully decanted to get large size graphene flakes. The residual solution was diluted with 1 L ethanol for vacuum filtration.

2.4 Fabrication of graphene film

The graphene solutions of 0.01, 0.05 and 0.09 mL were diluted with ethanol to control the thickness of graphene films. During vacuum filtration, film was rinsed sequentially with ethanol, methanol, THF, DMSO and DMF. After the graphene films deposited on alumina oxide (AAO) film were annealed at 60 °C for 5 h, the films were floated on 3

M NaOH aqueous solution while AAO is dissolved. Glass substrate should be in NaOH solution before floating the films. After 30 mins when the AAO is etched completely, only graphene film floated on the solution. Solution was imbibed completely and Water was added with syringe until the pH of solution reached 7, and then water was imbibed completely to transfer graphene film to the glass substrate. The film was dried in air for 2 h and then annealed at 120 °C for 5 min. Finally, films were chemically treated with HNO₃ (60%) and SOCl₂ (>99%) for hole doping and/or removal of residual surfactant by dipping the films in HNO₃ (60%) for 3h covered with a lid and drying in air for 30 min followed by dipping in SOCl₂ for 3 h covered with a lid and drying in air for 30min.

2.5 Measurements

The transmittance of graphene film was measured by an UV–visible spectrophotometer (HP 8452A). The morphology of graphene film was observed by a transmission electron microscope (JEOL, JEM-1010). TEM image was prepared by depositing droplets of the dispersed solution onto the carbon-coated copper grid. Electrical property of graphene film was characterized by a four-point probe measurement system (Napson, CRESBOX). The chemical structure of graphene film was analyzed by a FT-IR spectrometer (Thermo Scientific, Nicolet 6700). Fluorescence spectra were obtained on a fluorescence

spectrometer (RF 5301, Shimadzu). X-ray photoelectron spectra were obtained on AXIS-His (Kratos). Film thickness was measured by AFM (Surface imaging system, NS4A).

Chapter 3. Results and Discussion

3.1 Exfoliation and dispersion of graphene

One of the goals of this work is to prepare homogeneous dispersion of graphene in solution directly from graphite using a polymeric surfactant (5TN-PEG) whose chemical structure is shown in Figure 3.1. It has been known that the oligothiophene part (5TN) in 5TN-PEG is strongly physisorbed onto the graphene surface *via* strong π - π interaction³¹ while PEG is soluble in ethanol, THF and other various solvents. Among organic solvents tested, ethanol was the best solvent to disperse SWCNTs in the presence of 5TN-PEG in previous study.³²

When the graphite is exfoliated and dispersed in various organic solvents using 5TN-PEG as a surfactant, as shown in Figure 3.2, it is realized that graphite is well exfoliated and dispersed in ethanol while graphite is not dispersed in THF. It should be noted here that the color of graphite/5TN-PEG solution in THF is reddish purple, indicating that THF dissolves selectively the surfactant, 5TN-PEG.

When UV-vis absorption spectra of graphite/5TN-PEG in ethanol is compared with that of THF solution, as shown in Figure 3.3, the graphite/5TN-PEG in ethanol shows a wide range absorption of graphene (500–700 nm) with an absorption peak at 410 nm corresponding to the absorption of 5TN,³³ whereas the graphite/5TN-

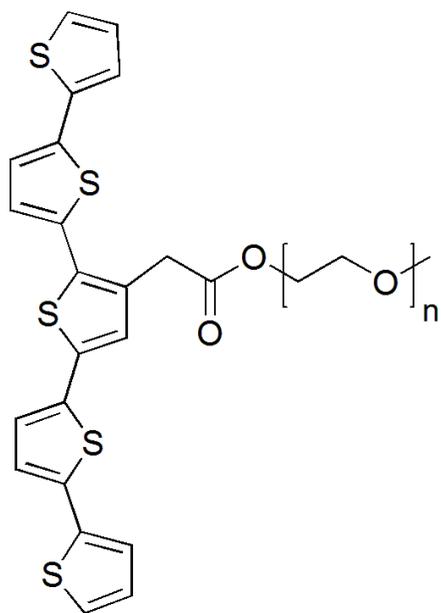


Figure 3.1 Chemical structure of 5TN-PEG.

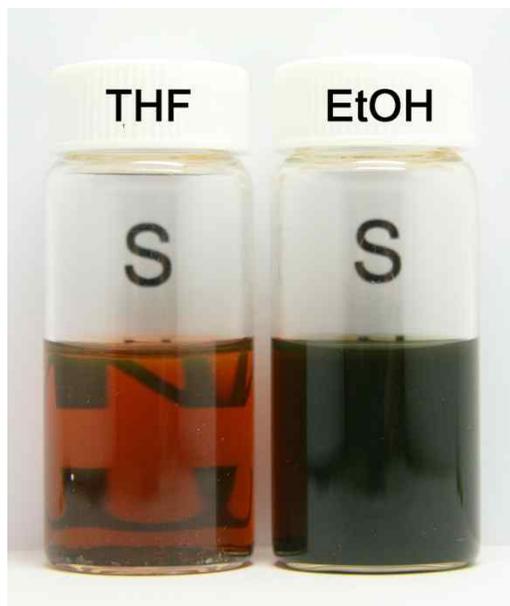


Figure 3.2 Comparison of graphite/5TN-PEG in THF and ethanol.

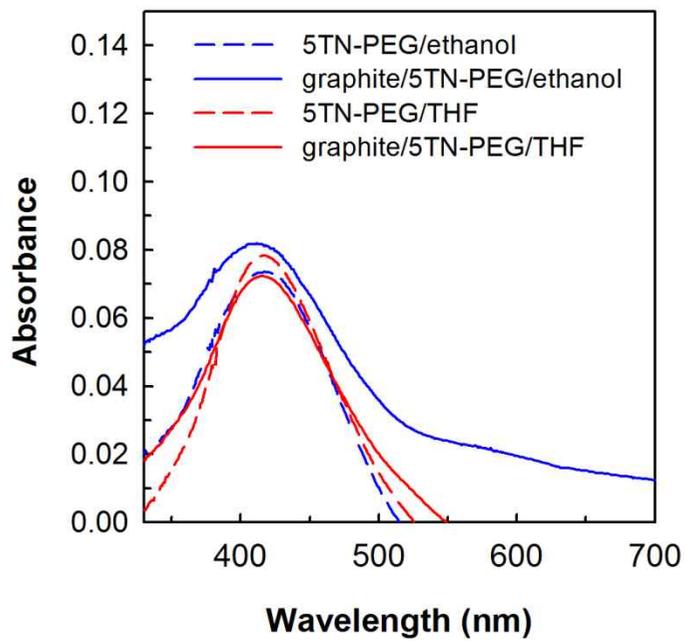


Figure 3.3 UV-vis absorption spectra of 5TN-PEG/ethanol (dashed blue) and graphite/5TN-PEG/ethanol (solid blue), 5TN-PEG/THF (dashed red), and graphite/5TN-PEG/THF (solid red).

PEG in THF does not show the wide absorption of graphene, indicating that graphite is not exfoliated in THF. The poor exfoliation and dispersibility of graphene in THF is presumably because both 5TN and PEG are very soluble in THF, while ethanol cannot dissolve 5TN which allows the 5TN to interact with the graphene surface by π - π interaction. The interaction between 5TN and graphene is further evidenced by fluorescence emission spectroscopy. The emission intensity of 5TN-PEG is decreased in ethanol solution of graphene/5TN-PEG due to interaction between 5TN and graphene, while the emission intensity of graphene/5TN-PEG in THF shows almost the same as the intensity of pure 5TN-PEG solution (see Figure 3.4a and 3.4b). Therefore, THF is not a proper solvent for exfoliation and dispersion of graphite, but would be rather a good solvent for washing out excess 5TN-PEG physisorbed on the graphene surface after fabrication of graphene film. The transmission electron microscope (TEM) image of graphene sheets dispersed in ethanol shows that graphene sheets with the size larger than 1 μm are homogeneously dispersed in ethanol by 5TN-PEG (Figure 3.5).

3.2 Fabrication of graphene film

Various methods for solution-based graphene deposition including vacuum filtration (VF),³⁴ spraying,²³ dip coating³⁵ and spin coating³⁶

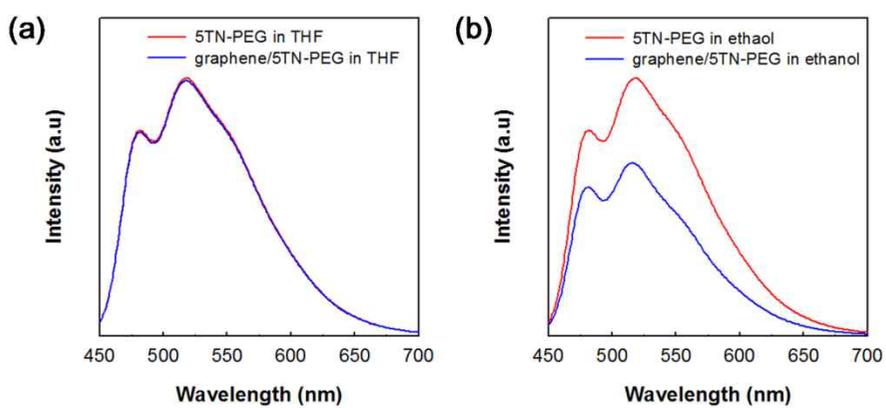


Figure 3.4 Photoluminescence spectra of (a) 5TN-PEG and graphene/5TN-PEG in THF; (b) 5TN-PEG and graphene/5TN-PEG in ethanol.

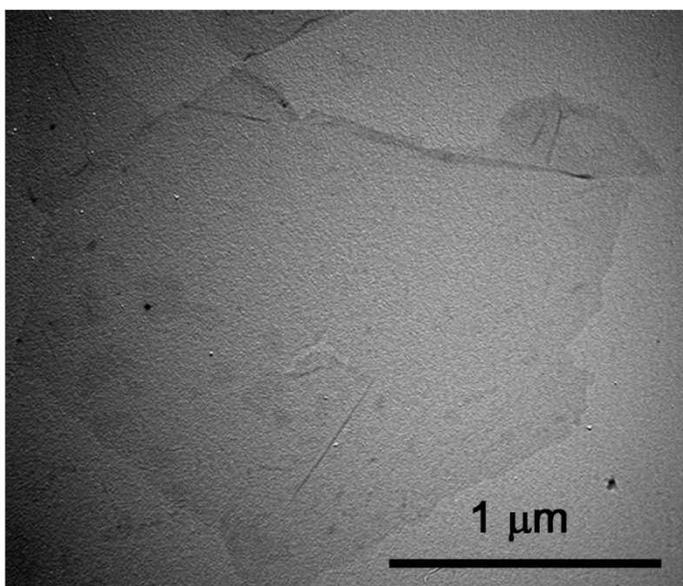


Figure 3.5 TEM image of exfoliated graphene.

have been reported. To prepare highly transparent graphene film, we used the vacuum filtration method because of the ease of transfer, thickness control, solvent treatment, and uniformity of the film.

Surfactant removal is an important step for fabrication of highly conductive graphene film, because the surfactant adsorbed on the graphene surface prevents charge carrier transport through graphene layers.³⁷ UV-vis spectra of graphene films washed with various solvents were measured and compared to identify the removal of surfactant.

The film washed with ethanol still has a strong absorption in the range of 400–550 nm due to the absorption of 5TN, while the absorptions of the films washed with other solvents are relatively weak, as shown in Figure 3.6. The transmittances of films at 470 nm corresponding to the maximum absorption of 5TN are listed with the corresponding sheet resistances in Table 3.1. The film washed with THF has a transmittance of 90.3% at 470 nm while the film washed with ethanol exhibits a transmittance of 68.1%. Furthermore, the film washed with THF has lower sheet resistance ($19 \text{ k}\Omega \text{ sq}^{-1}$) than other films. These results suggest that THF is the most suitable solvent for washing 5TN-PEG from graphene film to prepare highly conductive and transparent graphene film. When the infrared spectrum of as-prepared graphene/5TN-PEG film was compared with that of the graphene film washed with THF (see Figure 3.7), the spectrum of THF-washed film shows a characteristic peak of graphene at 1600 cm^{-1} ,³⁸

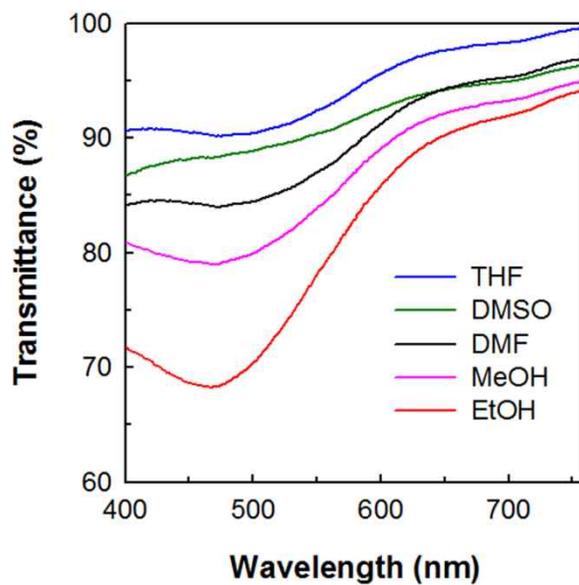


Figure 3.6 Transmittance spectra of graphene films washed with various solvents.

Table 3.1 Transmittance at 470 nm and sheet resistance of films washed with various solvents.

Solvent	Transmittance at 470 nm (%)	Sheet resistance ($k\Omega \text{ sq}^{-1}$)
Ethanol	68.1	76
Methanol	79.2	30
DMSO	88.3	21
DMF	83.9	26
THF	90.3	19

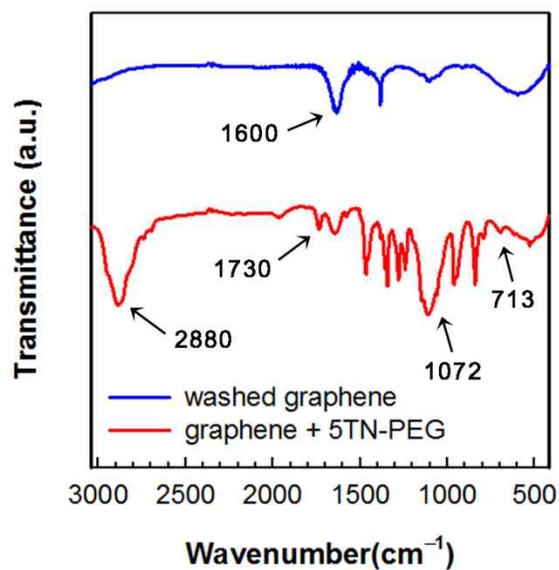


Fig. 3.7 Comparison of FT-IR spectra of washed graphene with that of graphene + 5TN-PEG.

but does not show characteristic peaks of 5TN-PEG (2880 and 1280–1210 cm^{-1} , C–H stretching; 1730 cm^{-1} , ester C=O stretching; 1072 cm^{-1} , C–S stretching; 713 cm^{-1} , =C–H bending of thiophene),^{39,40} indicating that most of 5TN-PEG were removed after washing with THF.

3.3 Chemical treatment of graphene film

For the purpose to enhance electrical and optical properties of graphene films, the washed graphene films are further treated with HNO_3 and SOCl_2 . The color of graphene film is changed from reddish to gray as both HNO_3 and SOCl_2 are treated (inset of Figure 3.8). When the UV–vis spectra of graphene films are compared before and after acid treatment (Figure 3.8), the transmittance at 470 nm corresponding to the absorption peak of 5TN-PEG is increased from 90.1% to 95.4% after $\text{HNO}_3/\text{SOCl}_2$ treatment, indicating that the residual 5TN-PEG surfactant was removed by $\text{HNO}_3/\text{SOCl}_2$ treatment. It should be noted here that the thiophene ring can easily be decomposed into sulfur and trioxide by nitric acid.⁴¹

When the sheet resistance of graphene film is plotted against the transmittance, as shown in Figure 3.9, it is found that the $\text{HNO}_3/\text{SOCl}_2$ treatment not only increases the transmittance but also significantly reduces the sheet resistance of graphene film. The graphene film with 73% transmittance at 550 nm has a low sheet resistance of 0.3 $\text{k}\Omega \text{sq}^{-1}$

after HNO₃/SOCl₂ treatment, which is lower by one order of magnitude as compared with the graphene film washed only with THF. It has been reported that the HNO₃/SOCl₂ treatment of graphene enhances the electrical conductivity by the doping effect of HNO₃ and SOCl₂.⁴²⁻⁴⁴

Figure 3.10 shows comparison of the Raman spectrum of washed graphene film with that of HNO₃/SOCl₂ treated film. The Raman spectrum of acid treated film shows only characteristic peaks of graphene, G peak at ~1580 cm⁻¹, D peak at ~1350 cm⁻¹ and 2D peak at ~ 2700 cm⁻¹, while the spectrum of washed film exhibits additional peaks at 1450–1530 cm⁻¹ and 2900 cm⁻¹ corresponding to thiophene ring stretching and C–H stretching, respectively, indicating that residual 5TN-PEG was successfully removed by the HNO₃/SOCl₂ treatment.

Analysis of 2D peak in Raman spectrum is an accepted method to estimate the number of graphene layers.⁴⁵ It has recently been proposed that the number of graphene layers increases as the intensity ratio of G peak to 2D peak (I_G/I_{2D}) increases: the values of I_G/I_{2D} for bilayer graphene and trilayer graphene are about 2.2–3.5 and 3.5–4.5, respectively.⁴⁶ The intensity ratio of our graphene film is smaller than 2.5 (Figure 3.10), indicating that our film has 2–3 graphene layers. The number of graphene layers can be directly counted from high-resolution TEM image. The TEM image of randomly imaged graphene edge shows 2 layers (see Figure 3.11), which is very consistent with the above result. Atomic force microscope (AFM) image also shows a

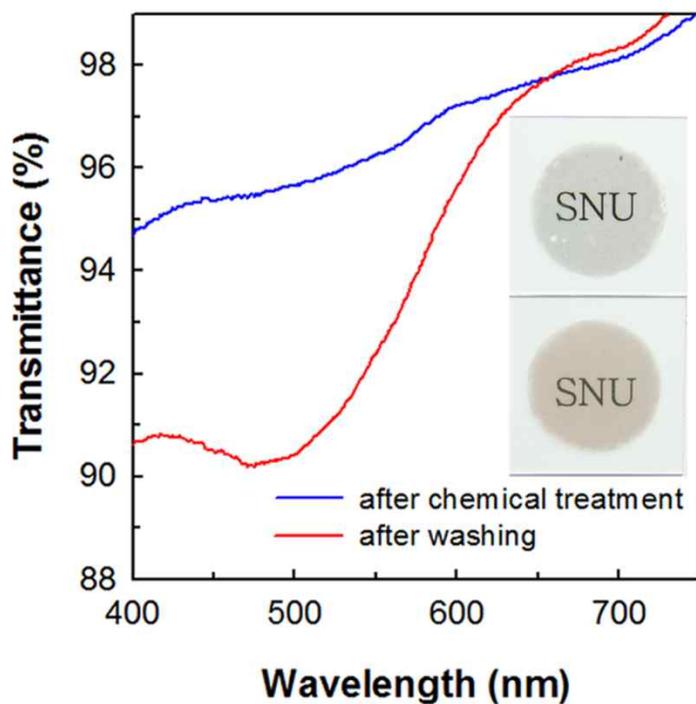


Figure 3.8 Transmittance of graphene films before and after chemical treatment, where the inset shows the visual transparency of graphene films with transmittance of 80% at 650 nm deposited on 25 mm x 25 mm bare glass after washing (lower one) and after chemical treatment (upper one).

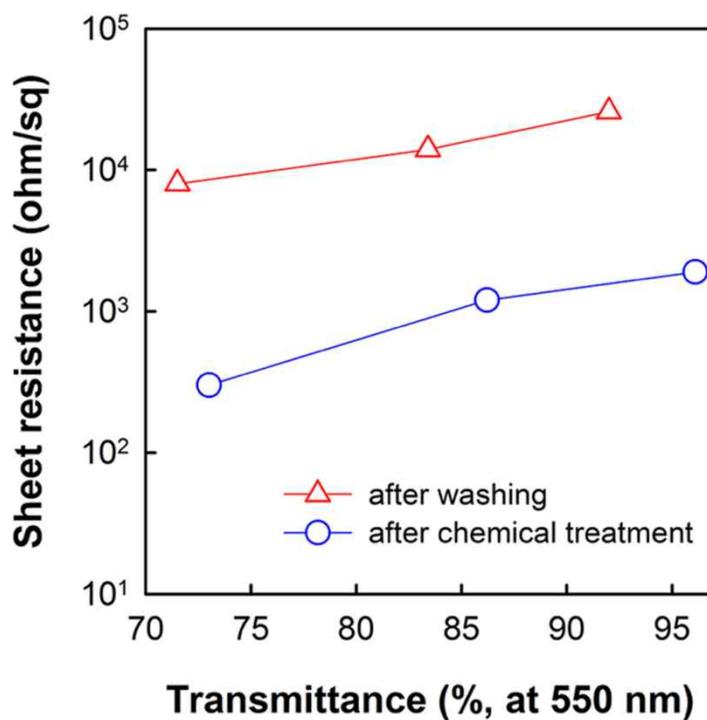


Figure 3.9 Plot of the sheet resistance of graphene film as a function of the transmittance at 550 nm.

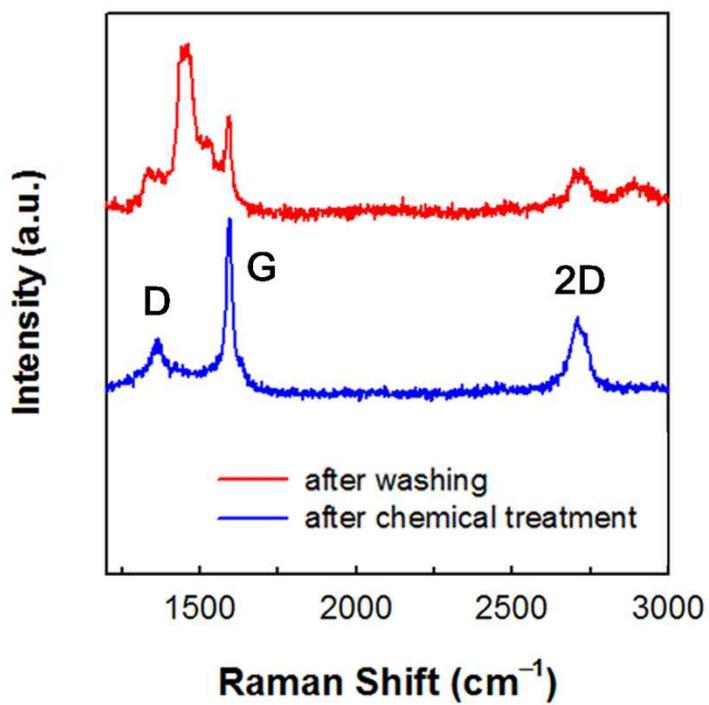


Figure 3.10 Comparison of Raman spectrum of graphene film after washing with the spectrum after chemical treatment.

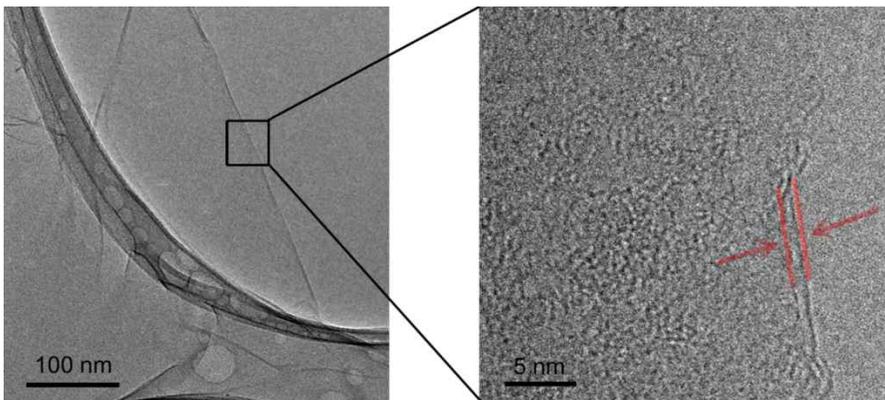


Figure 3.11 HRTEM image of graphene film edge.

thickness of 1.14 nm, corresponding to the thickness of bilayer or trilayer graphene (Figure 3.12).

It has been known that another intensity ratio of D to G peak (I_D/I_G) is related to the crystalline quality of graphene layers: the smaller the value, the better the crystalline quality. The I_D/I_G value of our graphene film is below 0.35, which is much smaller than those of reduced graphene oxide (> 0.8)⁴⁷ and other graphene films fabricated *via* intercalation method,³⁴ indicating that the graphene layers directly exfoliated from graphite flakes using 5TN-PEG as a surfactant have much less defects and thus exhibit better electrical properties as compared to those prepared by other methods.

The effect of chemical treatment on the electrical property of graphene film was also examined by X-ray photoelectron spectroscopy (XPS) (Figure 3.13). The C 1s peak at 283.1 eV for graphene film was downshifted to 282.8 eV after the HNO₃/SOCl₂ treatment, providing an evidence for *p*-type doping by the chemical treatment.^{14,48} The *p*-doping is expected to enhance the electron mobility, which results in lowering the sheet resistance. Because the energy band of graphene is smooth-sided cone, *p*-doping increases the carrier concentration and thus further reduces the resistance of the film.

3.4 Comparison of electro-optical property of our graphene film with other works reported in the literature

Figure 3.14, Figure 3.15 and Table 3.2 compare our result with other data reported for electro-optical properties of graphene films. Our graphene film prepared by direct exfoliation of graphite flakes shows better electro-optical performance than most of other films. Although Li and his coworkers⁴⁹ have reported an excellent performance of 657 $\Omega \text{ sq}^{-1}$ sheet resistance with 96% transmittance at 550 nm, they fabricated graphene films through a complicated procedure of electro-chemical exfoliation of graphite in sulfuric acid, while our method to exfoliate graphite and to disperse graphene in solvent is simpler, cheaper and more convenient.

The most important two factors to evaluate the performance of transparent electrode are the sheet resistance and transparency. However, it is not always easy to compare these two parameters at a glance because the sheet resistance of graphene film is strongly correlated to the transparency. Hence, it has recently been proposed that the ratio of direct current conductivity (σ_{dc}) to the optical conductivity (σ_{ac}) (at typically 550 nm) can be used as a figure of merit for electro-optical property of graphene film,^{50,51} where a higher value of σ_{dc}/σ_{ac} indicates better electro-optical performance of graphene film. When the σ_{dc}/σ_{ac} value of our film is compared with those of other groups, our film has much higher value than other graphene films, indicating that

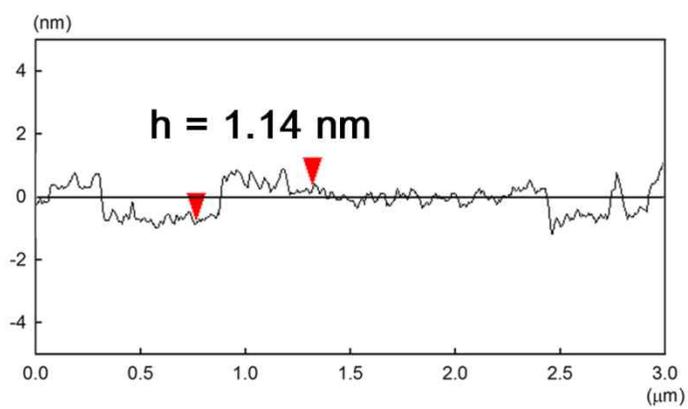
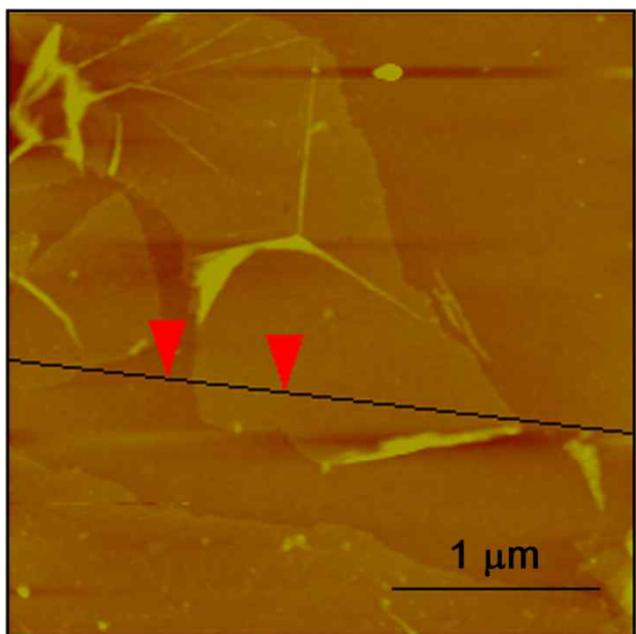


Figure 3.12 Layer analysis by AFM.

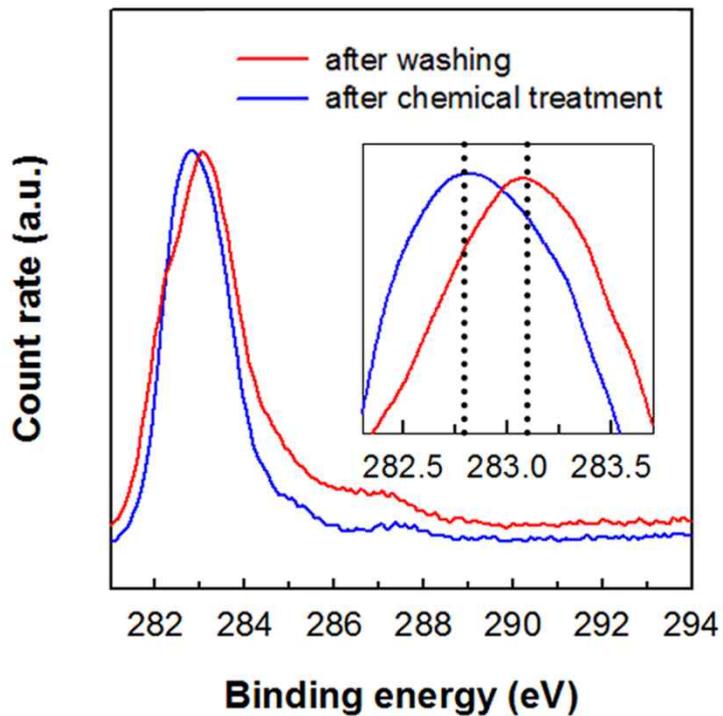


Figure 3.13 XPS spectra of C 1s of graphene after washing (red) and chemical treatment (blue).

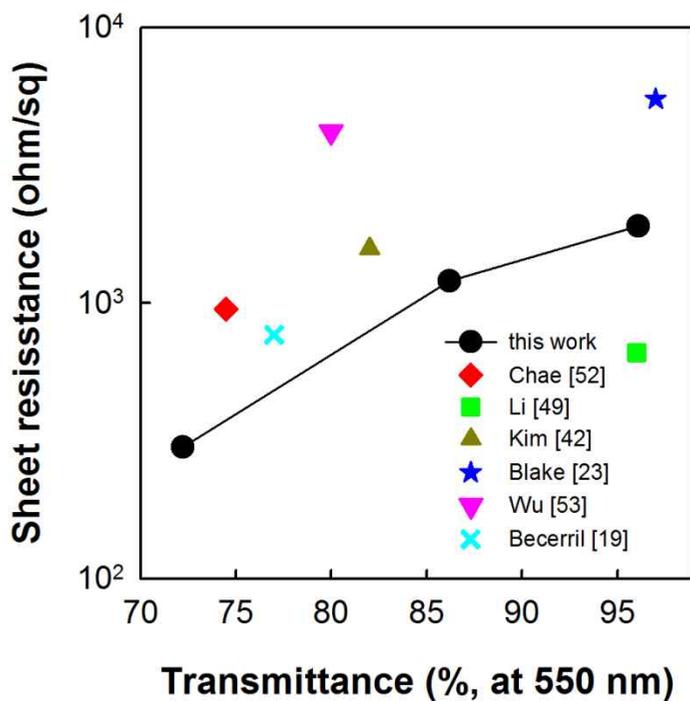


Figure 3.14 Comparison of electro-optical property of our film with those of graphene films reported by other groups.

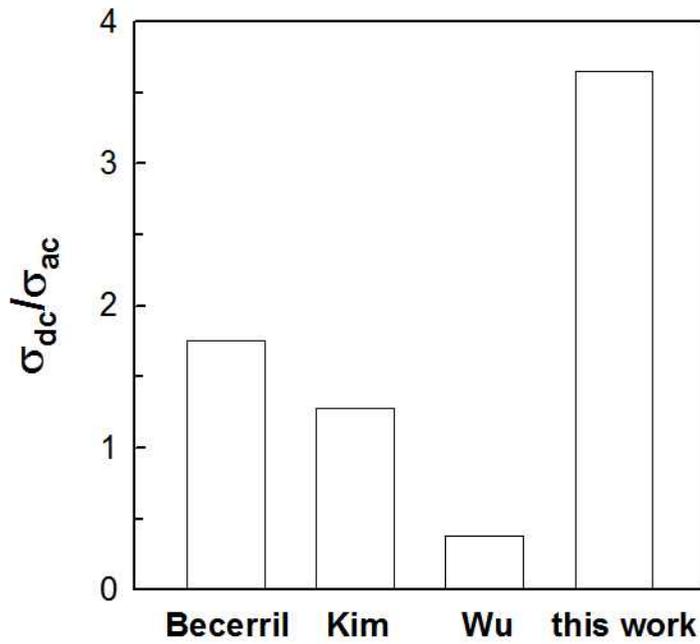


Figure 3.15 Figure of merit values of our film and graphene films reported by other groups.

Table 3.2 Comparison of electro-optical performance of our graphene film with other films reported in the literature.

Source of graphene	Surfactant	Method	Treatment	σ_{dc}/σ_{ac}
GO	None	^c SC / ^d HR	1100 °C thermal annealing	0.38 ⁵³
GO	^a SDS	^e VF	HNO ₃ / SOBr ₂	1.12 ⁴²
GO	None	^c SC / ^d HR	400 °C thermal annealing	1.75 ¹⁹
Graphite	H ₂ SO ₄	^f EC / ^g DC	HNO ₃	13.9 ⁴⁹
Graphite	None	^h SP	250 °C thermal annealing	0.67 ²³
Graphite	^b SDBS	^e VF	HNO ₃	1.22 ⁵²
Graphite	5TN-PEG	^e VF	HNO ₃ / SOCl ₂	3.65

^a Sodium dodecyl sulfate, ^b Sodium dodecyl benzene sulfonate, ^c Spin coating, ^d Hydrazine vapor reduction, ^e Vacuum filtration, ^f Electrochemical exfoliation, ^g Drop casting, ^h Spray coating.

our graphene film shows better optical and electrical performance than other graphene films.

Chapter 4. Conclusion

We have successfully exfoliated graphite directly into graphene layers by using a non-ionic surfactant, quinquethiophene-terminated poly(ethylene glycol) and dispersed homogeneously the layers in ethanol. High electro-optical graphene film was fabricated from the graphene dispersion by the vacuum filtration. After washing the surfactant with THF followed by chemical treatment with HNO₃ and SOCl₂, the graphene film exhibited high performance (a transmittance of 74% at 550 nm, a sheet resistance of 0.3 kΩ sq⁻¹ and $\sigma_{dc}/\sigma_{ac} = 3.65$). These results lead us to conclude that the direct exfoliation of graphite into graphene layers by the use of a proper surfactant has a strong potential for fabrication of highly transparent and conductive graphene film.

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초 록

2 차원 구조로 이루어진 그래핀은 탄소 원자들의 sp^2 네트워크결합으로 이루어진 물질로서, 상온에서의 양자효과, 양극성 전기장 효과 및 높은 모빌리티를 가진다. 따라서 이러한 특성을 가진 그래핀은 태양전지 및 다양한 전기적, 광학적 장치의 전극 등에 이용된다. 하지만 이러한 그래핀을 대면적 필름으로 만드는 기술은 아직까지 그 실용성이 떨어지는 것이 사실이다.

그래핀을 만드는 공정은 크게 (1) 솔루션 상에서 그래파이트를 박리하여 만드는 top-down 방식과 (2) CVD (Chemical Vapor Deposition) 방식으로 carbon atom monolayer 를 쌓아가는 bottom-up 방식이 존재한다. 그 중 solution system 에서 그래핀을 만드는 전자의 방법은 후자에 비해 생산단가가 낮고, 별다른 기계적 처리 없이 쉬운 공정으로 그래핀 필름을 만들 수 있기 때문에 편리한 방법이지만, solution 내에 그래핀이 분산되는 정도가 일반적으로 약하고, 안정한 분산이 쉽게 되지 않아 실용적인 적용면에서 그 효과가 미비한 것으로 간주되었다. 현재 그래파이트를 산화시켜 graphene oxide (GO) 형태로 박리하는 방식이 이러한 문제점들을 어느 정도 해결하고 있지만, 산화된 그래핀에 있는 oxygen group 들이 defect 로

작용하여 전도도 및 여러 특성을 감소시키는 것으로 알려져 있다.

이에 본 연구에서는, poly(ethylene glycol) (PEG)과 그 말단에 oligothiophene 을 연결하여 합성한 surfactant 를 이용하여, GO 가 아닌 순수한 그래파이트를 직접적으로 ethanol 상에서 그래핀으로 박리한 후, homogeneous 하게 분산시켜 투명하고 전도도 높은 그래핀 필름을 만들었다. 그래파이트 층의 표면에는 surfactant 의 oligothiophene 부분이 흡착을 하고 ethanol 에는 PEG 가 녹아서 결과적으로 그래핀이 안정적으로 오랜 시간 분산이 될 수 있었다.

먼저 NBS 를 통해 양쪽에 bromination 을 한 3-thiopheneacetic acid 를, esterification 반응으로 DCC/DMAP system 에서 분자량 2000 의 PEG 와 연결하고, 이어서 한 쪽에 $\text{Sn}(\text{Bu})_3$ 이 달린 bithiophene 을 촉매인 $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ 와 섞어서 말단에 PEG 가 달린 oligothiophene 형태의 surfactant 를 만든다. 그 후 surfactant 를 그래파이트와 함께 1:10 비율로 ethanol 상에 넣고 stirring 및 sonication 을 하여 그래핀을 homogeneous 하게 분산시켰다. 합성의 결과는 $^1\text{H-NMR}$ 로 확인하였고 분산된 그래핀의 크기는 TEM image 로 확인하였다. 일반적으로 그래핀 판상의 크기가 클수록 접촉저항이 줄어들어 전도도가 높는데, TEM 으로 확인한 대부분의 그래핀 판상들이 1 micro-meter 이상의 큰 사이즈로 박리가 되었음을 알 수 있었다. 이후 vacuum filtration 방식을 이용하여, aluminium oxide (AAO) 막 위에 그래핀 필름을 형성했다. Surfactant 는 그래핀을 분산시키는데

필요하지만, 필름의 저항을 낮추는 defect 역할을 하기 때문에, THF washing 을 통해 필름에 남아있는 surfactant 를 제거했다. Surfactant 의 경우, PEG 부분과 oligothiophene 부분 모두 THF 에 잘 녹기 때문에 다른 solvent 보다 제거효과가 컸고, 이를 UV spectrum 으로 확인했다. AAO 를 NaOH 로 부식시키고 필름을 glass 위에 올린 이후, 추가적인 surfactant 제거 및 그래핀의 화학적 도핑을 위해 필름을 질산 및 SOCl_2 처리하였다. 이후 그래핀 필름의 광학적, 전기적 특성을 평가하였다. 도핑의 유무는 XPS spectrum 으로 확인하였고, 생성된 그래핀 필름의 defect 정도는 Raman spectrum 을 통해 아주 적은 수치를 보임을 알 수 있었다($I_D/I_G = 0.3$). 이 연구에서 만든 그래핀 필름은 550 nm 의 파장에서 74%의 투과율을 보일 때 4-point probe 로 측정된 면 저항이 대략 300 ohm/sq 을 보였다. 이는 현재 학계에 발표된, 솔루션 시스템에서 만들어진 그래핀 필름 중 가장 낮은 면 저항 중 하나이다.

주요어: 그래핀, 박리, 분산제, 투과율, 그래파이트

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