Research Article

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# Characterization of Graphene Synthesized by Modified Hummers and Liquid-phase Exfoliation Method

Worawat Jansomboon, Palivut Brikshasri and Sangchai Sarawutanukul
National Center of Excellence for Petroleum, Petrochemicals and Advance Material, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand

Paweena Prapainainar*
National Center of Excellence for Petroleum, Petrochemicals and Advance Material, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand
Center for Advanced Studies in Nanotechnology and Its Applications in Chemical Food and Agricultural Industries, Kasetsart University, Bangkok, Thailand
NANOTEC-KU-Center of Excellence on Nanoscale Materials Design for Green Nanotechnology, Kasetsart University, Bangkok, Thailand

* Corresponding author. E-mail: fengpwn@ku.ac.th
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## Abstract

Graphene was synthesized through chemical cleavage followed by reduction process and through liquid-phase exfoliation methods. The characteristics of synthesized graphene were investigated by Raman spectroscopy, FTIR, SEM, XRD and UV-Visible spectrophotometry. It was found that Graphene Oxide (GO) synthesized by modified Hummer's method had carboxylic acid, hydroxyl, and ether groups confirming that graphite was successfully oxidized. The result also showed that graphene oxide consisted of 12 layers and the layer distance was in the range of 0.67–0.72 nm. In liquid-phase exfoliation method, graphene sheets were synthesized by mixing graphite with naphthalene and N-methyl-2-pyrrolidone (NMP) followed by sonication. The results indicated that the inter layer spacing of graphite was expanded from 0.3356 to 0.3364 nm. The highest graphene concentration was up to 3.26 mg/mL and the yield was 54.34%.

**Keywords**: Graphene, Graphene oxide, Graphene characterization, Modified Hummer's method, Liquid-phase mechanical exfoliation

## 1 Introduction

The interesting of nanotechnology is increasing according to high technologies which bring about many studies in material science field. After Andre Geim and Kostya Novoselov at the University of Manchester managed to extract graphene from bulk graphite in 2004 and later won the Nobel Prize in Physics, graphene has become one of the most advanced materials used in many applications. It is a one atom thick carbon sheet of $sp^2$-bonded carbon atoms packed in a honeycomb crystal lattice. It is excellent in electrical and thermal conductivities and it is a very strong material. From these reasons, graphene is very popular. However, it is quite expensive due to the high production cost which is an obstacle to be commercialized. Graphene can be synthesized by several methods such as scotch tape method, liquid-phase mechanical exfoliation,

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chemical cleavage and exfoliation, chemical vapour deposition, and epitaxial growth from silicon carbide [1]–[3]. However, properties of graphene synthesized by those methods are not the same. Each of them is suitable for different applications. In this work, two graphene synthesis methods which were chemical cleavage (modified Hummer's method) and liquid-phase exfoliation method (mixing graphite with naphthalene and N-methyl-2-pyrrolidone (NMP) followed by sonication) were studied. Appropriate factors for each method were determined and the characteristics of the synthesized graphene were also investigated.

## 2 Methodology

### 2.1 *Chemical and materials*

Graphite powder (<500 µm) was obtained from Sigma-Aldrich (USA). Sulfuric acid (98% purity) and hydrochloric acid (37% purity) were obtained from Quality Reagent Chemical (New Zealand). Phosphoric acid (85% purity), Potassium Permanganate (99.9% purity) and sodium nitrite were obtained from Ajax Finechem Pty Ltd (Australia). N-methyl-2-pyrrolidone, NMP, was obtained from RCI Labscan Limited (Thailand). Naphthalene was obtained from HiMedia (India).

### 2.2 *Synthesis of graphene oxide by modified Hummer's method*

Graphite powder and sodium nitrate were mixed with 23 mL of concentrated sulfuric acid and constantly stirred for 1 h in an ice bath. Next, 3 g of potassium permanganate was added and constantly stirred at 35°C for 12 h. Then, 500 mL of deionized water was added and stirred at 98°C for 1 h. To stop the reaction, 5 mL of hydrogen peroxide was added. After centrifugation, the residue was washed by 1 M hydrochloric acid followed by deionized water until pH was approximately 4–5. Finally, the residue was dried at 60°C for 24 h.

### 2.3 *Synthesis of graphene by liquid-phase mechanical exfoliation method*

Firstly, 0.1 g of graphite powder was mixed with 25 g of naphthalene and 20 mL of N-methyl-2-pyrrolidone (NMP). The solution was sonicated at the frequency of 37 kHz for 90 min. After that, residue was separated by centrifugation at 3,000 rpm for 30 min. Finally, the residue was dried at 60°C for 24 h.

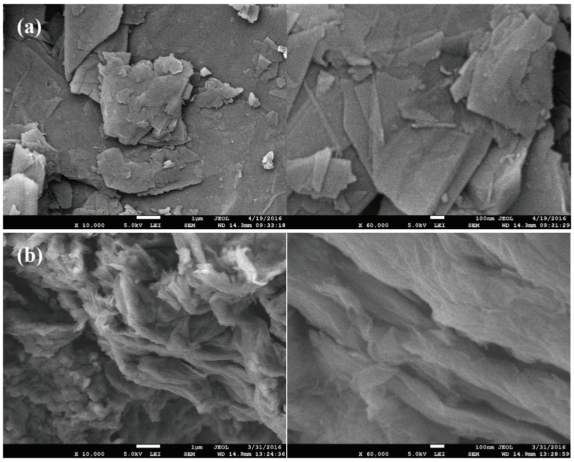

**Figure 1**: SEM images of graphite and graphene oxide synthesized by modified Hummer's method at magnification of 10,000x (left) and 60,000x (right); (a) Graphite, (b) Graphene oxide.

### 2.4 *Characterization of graphene*

Graphene was characterized by Fourier transform infrared spectroscopy, FTIR (Bruker TENSOR 27), X-ray Diffractrometer, XRD (Bruker Advance A25), Scanning electron microscope, SEM (FEI QUANTA 450), Energy Dispersive X-ray Spectrometer, EDXS (FEI QUANTA 450), UV-Visible spectrophotometry (GENESYS 10S UV-Vis), and Raman spectroscopy (Perkin Elmer System 2000).

## 3 Results and Discussion

### 3.1 *Characterization of graphene oxide synthesized by modified Hummer's method*

In this study, modified Hummer's method was applied for graphene oxide synthesis. Although there were additional steps for reducing graphene oxide to graphene, it was not included here. Therefore, characterization of graphene oxide was represented in this study.

The morphology of graphene oxide was characterized by SEM and FTIR. The SEM images of graphene oxide synthesized by modified Hummer's method are shown in Figure 1. It pointed out that the separation occurred

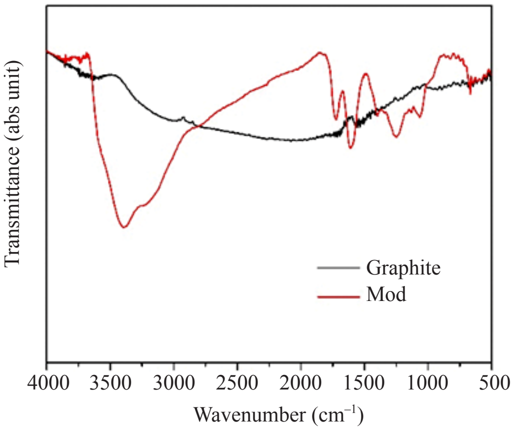

**Figure 2**: The FTIR spectrum of graphite and graphene oxide synthesized by modified Hummer's method.

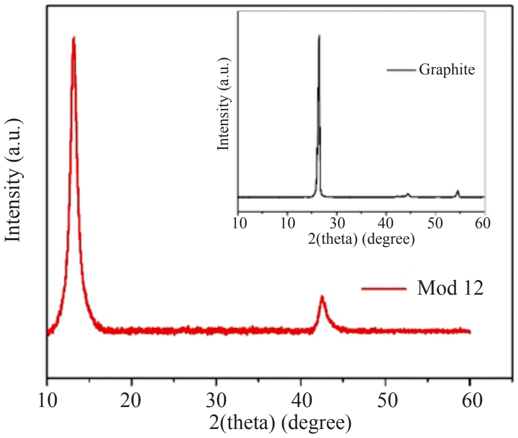

**Figure 3**: XRD spectrum of graphite and graphene oxide (GO).

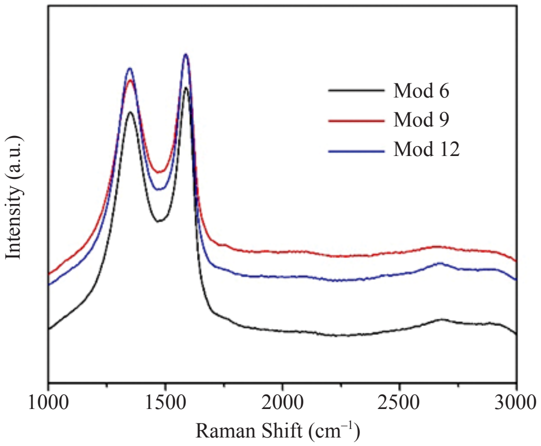

**Figure 4**: Raman spectrum for graphene oxide with various reaction times; 6 h (Mod 6), 9 h (Mod 9), 12 h (Mod 12).

at the edge and fold of graphene oxide was higher than that of graphite. Therefore, it was an evident that graphene oxide sheets were exfoliated and successfully synthesized in this study by modified Hummer's method.

The FTIR spectrum of graphene oxide synthesized by modified Hummer's method is shown in Figure 2. A broad peak at 3,000–3,700 cm$^{-1}$ and a peak at 1,624 cm$^{-1}$ indicated the O-H bond of water molecule remaining between graphene oxide layers. A peak at 1,726 cm$^{-1}$ represented the C=O bond which is the functional group of carboxylic acid including ketone and quinone. O-H functional group of carboxylic acid, C-O-C of ether, and C-OH of alcohol were represented at 1,398, 1,250 and 1,068 cm$^{-1}$, respectively. It was concluded that many functional groups occurred between layers of graphene oxide from the oxidation reaction of the synthesis [4], [5].

The crystallite structure of graphene oxide was characterized by XRD as shown in Figure 3. The results showed that the spectrum of graphene oxide appeared with the peaks occurred at diffraction angle (2ϴ) of 13.19°,which was shifted from the diffraction angle (2ϴ) of graphite at 26.5°. Moreover, the calculation based on Bragg equation indicated that graphene oxide consisted of 12 layers and the layer distance was in the range of 0.67–0.72 nm. The result pointed out that after the oxidation reaction the structure of graphite was changed to graphene oxide, which consisted of many functional groups on each layer that affected an increasing distance between layers [4].

The level of oxidation reaction was determined by EDXS and Raman spectroscopy. The result of EDXS shown in Table 1 indicated that the ratio of carbon and oxygen in graphene oxide synthesized by modified Hummer's method for 6 h (Mod 6) was the highest, while those synthesized for 9 h (Mod 9) and 12 h (Mod 12) were resemble. The results of Raman spectroscopy represented in Table 2 and Figure 4 showed that the peak at D and G positions were 1,350 and 1,580 cm$^{-1}$, respectively. The ratio of peak intensity between D and G ($I_D/I_G$) disclosed the structural arrangement and level of oxidation reaction on graphene oxide. It was found that the $I_D/I_G$ of Mod 6 was the lowest, and the ID/IG of Mod 9 and Mod 12 were quite

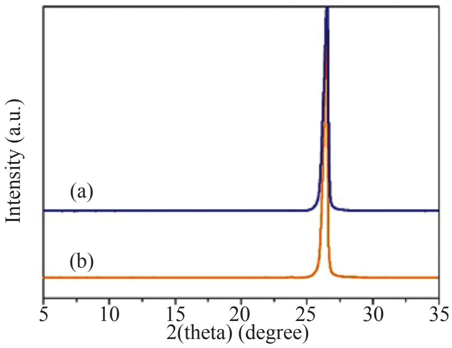

**Figure 5**: XRD spectrum of (a) graphite before adding naphthalene and (b) graphene after adding naphthalene.

similar. From that result, it could be concluded that the functional groups increasingly occurred when the duration of oxidation reaction was long. However, the reaction was steady after 9 h, representing in a constant ratio between oxygen and carbon.

**Table 1**: EDXS results for graphene oxide with various reaction times

| Sample | Mod 6 (6 h) | Mod 12 (9 h) | Mod 12 (12 h) |
|---|---|---|---|
| % Carbon | 70.46 | 67.04 | 66.67 |
| % Oxygen | 29.54 | 32.96 | 33.33 |
| Ration of Carbon and Oxygen | 2.40 | 2.03 | 2.01 |

**Table 2**: $I_D/I_G$ of graphene oxide with various reaction times

| Sample | Mod 6 (6 h) | Mod 12 (9 h) | Mod 12 (12 h) |
|---|---|---|---|
| $I_D$ | 12220.70 | 11201.20 | 12629.11 |
| $I_G$ | 13312.97 | 11725.77 | 13061.55 |
| $I_D/I_G$ | 0.92 | 0.96 | 0.97 |

### 3.2 *Characterization of graphene synthesized by liquid-phase mechanical exfoliation method*

To study the effect of adding naphthalene into graphite, the characterization was determined by XRD as shown in Figure 5. The peak of 2ϴ before adding naphthalene was 26.531°, which was shifted to 26.474° after adding naphthalene. From Bragg's equation, the distance between layers was 0.3356 nm before adding naphthalene and 0.3364 nm after adding naphthalene [6]. It pointed out that the distance between layers was changed because of naphthalene insertion between the layers leading to the decreasing of lattice energy between carbon layers.

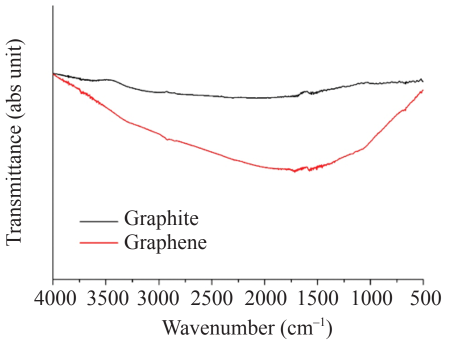

**Figure 6**: FTIR spectrum of graphite and graphene synthesized by liquid-phase mechanical exfoliation method.

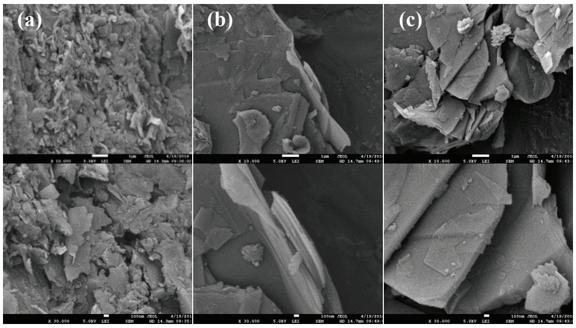

**Figure 7**: SEM images of graphite and graphene synthesized by liquid-phase mechanical exfoliation method with various sonication times at magnification of 10,000x (upper) and 30,000x (lower); (a) Graphite, (b) graphene with 5 min sonication, (c) graphene with 120 min sonication.

The FTIR spectrum of graphite and graphene synthesized by liquid-phase mechanical exfoliation method is shown in Figure 6. Both had broad peaks at 1,556 and 1,630 cm$^{-1}$, which indicated the benzene structure (C=C aromatic). A peak at 2,900 cm$^{-1}$ represented $CH_2$ both symmetric and asymmetric bonds which were due to the vibration of graphene structure. From this reason, it pointed out that the structure and functional group of graphene synthesized by liquid-phase mechanical exfoliation method was similar to those of graphite. It was an evidence of graphene nanosheet [7]. The SEM images of graphite and graphene synthesized by liquid-phase mechanical exfoliation method is shown in Figure 7. The SEM images showed that the graphene nanosheet increased when increasing the duration of sonication.

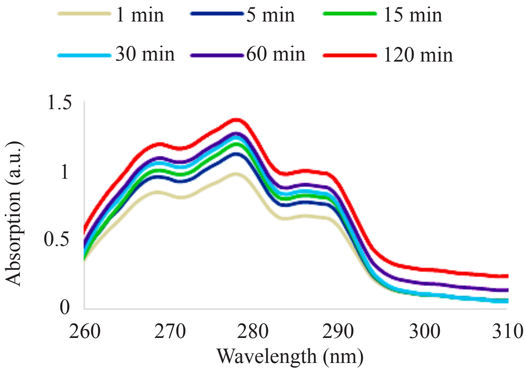

**Figure 8**: The absorption of suspended graphene in NMP solution synthesized by liquid phase exfoliation at various sonication times.

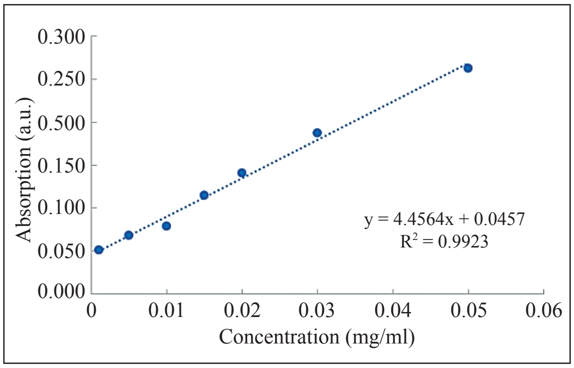

**Figure 9**: Calibration curve of graphene concentration and light absorption.

The absorption of suspended graphene in NMP solution synthesized by liquid phase exfoliation at various sonication times (1, 5, 15, 30, 60 and 120 min) is shown in Figure 8. The results from UV- Visible spectroscopy indicated that the highest absorption value of graphene was at the wavelength of 278 nm. The absorption value increased when the sonication time increased, corresponding with Beer-Lambert law [7].

To determine the concentration of graphene dispersing in NMP solution, the calibration curve was establish by measuring the light absorption value at the wavelength of 280 nm of 7 graphene concentrations in the range of 0.001–0.05 mg/mL [7] as represented in Figure 9. The slope of the calibration curve was 446.96 mL/mg.m$^{-1}$ based on Beer-Lambert law.

Table 3 shows the yield of graphene exfoliated into NMP solution at several sonication times. The results showed that at sonication time of 1 min, 18.33 out of 48 mg of graphene was exfoliated into the solution, representing 38.18% yield. The exfoliation of graphene with sonication time of 120 min was the highest, which was 26.08 mm or 54.34% yield. Therefore, higher sonication time led to higher exfoliation of graphene.

All results above indicated that there were some differences when compared liquid-phase exfoliation method with modified Hummer's method. The graphene solution was obtained by liquid-phase exfoliation method, while graphene oxide was obtained by modified Hummer's method which required some steps for transforming graphene oxide to reduced graphene oxide (very close structure to graphene). Depending on the purpose of using graphene, it had to be carefully considered that which method was appropriate for graphene synthesis.

**Table 3**: The yield of graphene exfoliated into NMP solution at several sonication times

| Sonication Time (min) | Initial Graphene (mg) | Exfoliated Graphene (mg) | Yield (%) |
|---|---|---|---|
| 1 | 48 | 18.326 | 38.179 |
| 5 | 48 | 21.201 | 44.168 |
| 15 | 48 | 22.579 | 47.039 |
| 30 | 48 | 23.524 | 49.008 |
| 60 | 48 | 24.114 | 50.238 |
| 120 | 48 | 26.083 | 54.340 |

## 4 Conclusions

Graphene oxide can be successfully synthesized by modified Hummer's method. Functional groups on graphene oxide such as carboxylic acid and hydroxyl were detected by FTIR due to the oxidation reaction of graphite oxide synthesis. XRD results showed that at 2θ of 12.21–13.19°, the inter layer spacing was 0.670–0.724 nm and the number of graphene oxide layers of 12 was found. The result from EDXS showed that carbon/oxygen ratio at 6 h was the highest, while those at 9 and 12 h were lower and steady. This indicated that the steady state residence time was approximately at 9 h. In liquid-phase exfoliation method, the effects of naphthalene and sonication time were examined. The results showed that the inter layer spacing of graphite was expanded from 0.3356 to 0.3364 nm. When the sonication time of the solution increased, the absorption value increased. The highest yield of exfoliation of 54.34% was found at 120 min of sonication time. Therefore, the sonication time was directly proportional to graphene concentration in NMP.

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