

A new method to exfoliate Graphite oxide and application for synthesis Graphene by chemical method

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ABSTRACT

A new method to separate graphite oxide (GO) modified by polyethylene oxide (PEO) by the aid of ultrasonic radiation was developed. Modified GO (graphene oxide or single layer of graphite oxide) did not show not appear crystalline peak (d_{002}) on the X-Ray and took the form of a single layer graphene oxide on the image AFM and TEM.

Keywords: Graphene, graphite oxide, graphene oxide, polyethylene oxide (PEO).

The exfoliated graphene oxide was reduced (RGO) to graphene by the reducing agent system HI – Acetic acid (HI-AcOH). The sheet resistance of $RGO_{HI-AcOH}$ is about 120 Ω/sq in the form graphene paper. In addition, FTIR, UV-Vis and Raman spectra showed more clearly about characteristics of graphite oxide, graphene oxide and $RGO_{HI-AcOH}$.

INTRODUCTION

Graphene can be made by many different ways as the mechanical exfoliation from graphite [4, 12, 14], chemical vapor deposition (CVD) [18] and reduction of graphene oxide [2, 7, 8, 16, 17, 19, 21]. In particular, graphene made from graphite oxide has many diverse applications in many different fields. Especially, the field of polymer nanocomposite is the most important. Graphite oxide (GO) was synthesized by oxidation of graphite with strong oxidizing agents as $KMnO_4$, KNO_3 , $KClO_3$ and others in the acid conditions [1]. The most common methods using redox $KMnO_4$, KNO_3 , H_2SO_4 is Hummers [6]. Graphite oxide was attached to the surface of the polar groups such as hydroxyl, epoxy, carbonyl and carboxylic [1]. Based on

these polar groups, the distance between two layers of graphite oxide is raised from 3.3 Å to 8.0 Å [1]. This is an opportunity to insert the modified compound in between the GO layers of and to exfoliate the layers of graphene oxide. Between the GO layers can be inserted into the compound with chemical or physical interactions. In the chemical interaction, isocyanate compound was used commonly because -NCO groups can react easily with the -OH, -COOH and epoxide groups on the graphite oxide [20]. However, if GO and modifier had interacted with each other, the reduction of the GO would become more difficult [1]. So, the exfoliated methods of the GO by surface-active compounds preferred to use more. The non-ionic surfactant which the

structure interacted strongly with GO was used the modifier in this case. Polyethylene glycol (PEG) is a specific examples that our research team has used. Earlier, the PEG was grafted onto the GO with different bridge to apply in the fields of biology [10, 11, 22, 23].

In this study, polyethylene glycol was used as not only a modified agent but also preliminary reduced agent for graphite oxide because it has the OH group as a reducing agent [2]. Then, the modified graphite oxide was exfoliated easily by the aid of ultrasonic radiation. The exfoliated graphite oxide is called graphene oxide. The graphene oxide is reduced by the reducing agent to form reduced graphene oxide (RGO). The reducing agent was use such as hydrazine ($\text{NH}_2\text{-NH}_2$) [5, 17, 21], sodium borohydride (NaBH_4) [16], alcohol [2], bacteria [3], thermal reduction (reduced by heat) [8,15] and others. Conductivity of RGO depends heavily on the reduction and reducing agent. In this article, we used the same reduction as the group of In Kyu Moon but our group has reduced graphene oxide (graphite oxide modified by PEG) instead of graphite oxide as these authors.

MATERIALS AND METHODS

Materials

Graphite flake were purchased from Sigma Aldrich and did not use further purification. Sulfuric acid (95–97 wt%), hydrogen peroxide (30 wt%), potassium permanganate, sodium nitrate, hydroiodic acid (57 wt%), sodium bicarbonate, acetic acid were obtained from commercial sources and used as received. Preparation of graphite oxide. Graphite oxide was prepared from graphite flake using the modified Hummers and Offemman's method with sulfuric acid, sodium nitrate and potassium

permanganate [6]. Accordingly, 10 g graphite, 0.5 g NaNO_3 , 230 ml of H_2SO_4 (98 %) were placed in 2500 ml four-neck-flask. The mixture was stirred and cooled at 0 °C. Then, 300 g of KMnO_4 was added slowly to the system (keeping the temperature of the suspension system at 20 °C). The next, the temperature of the system was raised to 35 ± 2 °C for 30 minutes to the oxidation of graphite. Then, the reactor was diluted with 460 ml of distilled water and raised to 98 °C for 15 minutes. The end of 15 minutes, the suspension system continue to be diluted with 1400ml of distilled water and 500 ml H_2O_2 (30 wt%) was added to the mixture to remove residual KMnO_4 and other impurities. After treatment with peroxide, the reaction mixture with bright yellow was observed. Finally the product (GO) was centrifuged, washed several times with acetone and dried in vacuum at 80 °C.

Modification of graphite oxide

Graphite oxide modified polyethylene glycol (PEG) with a molecular weight of 1500 g/mol. Accordingly, 1.0 g of GO was dispersed in one liter of distilled water in the beaker by ultrasound waves (ultrasonic UP400S – Germany with a standard aluminium horn with replaceable tip diameter of 13 mm) for 30 minutes. Then, the suspension of GO was transferred to the 1.5-liter flask and added to 5.0 ml of solution NH_3 (35wt.%). In addition, 10.0 g PEG was added and stirred with a mechanical stirrer for 24 hours. The modified graphite oxide (MGO) was then split into single-layer graphene oxide under the effect of ultrasound within 1 hour. Finally, the product was deposited with solution of HCl 5 wt.%, then filtered by vacuum and washed several times with a mixture of acetone-water (50/50). Obtained MGO was a wet powder form and used to continue the process of reducing that followed

(except when necessary to analyze the property of MGO).

Reduction of MGO by HI-AcOH system

The reduction process was done similar way as In Kyu Moon [13]. Accordingly, 2.0 g of MGO was dispersed in 750 ml acetic acid (1000 ml three-neck-flask) and sonicated by a LT-60H ultrasonic bath cleaner (35kHz) for 1 hour. Then, 40 ml iodic acid (HI) was added and continued to sonicated for 30 minutes at 40°C. The mixture was stirred at 40 °C for 40 hour. The product was filtered and washed with sodium bicarbonate solution (5 wt.%) (5x50 ml), distilled water (5x50 ml) and acetone (2x50 ml). Then, It was dried under vacuum at 80 °C for 12 hours and the weight of RGO_{HI-AcOH} after purifying was 1.5 g (accounted for 75 wt.% compared with MGO).

Characterizations

RESULTS AND DISCUSSION

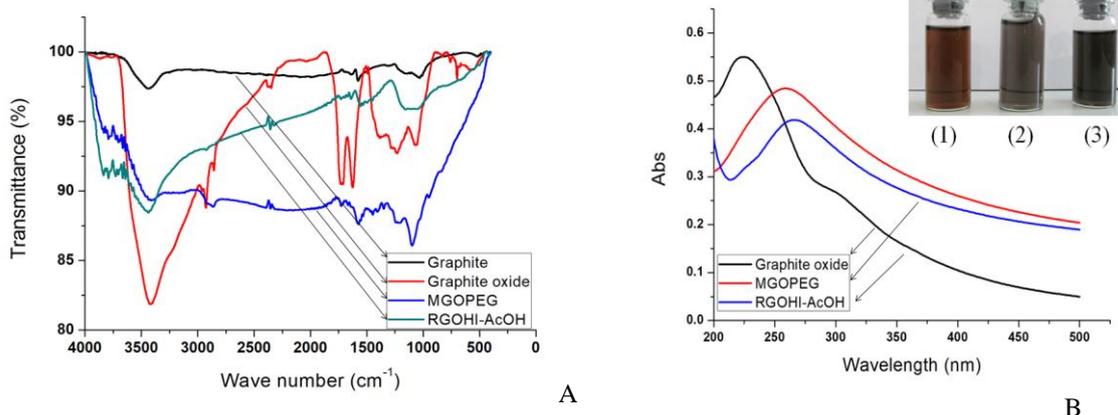


Figure 1. FTIR (A) and UV-Vis spectra (B) of graphite, graphite oxide (GO), modified graphite oxide (MGO) and RGOHI-AcOH [(1)- GO in water (1,0 mg/ 100 ml H₂O), (2)- MGO in water (1,0 mg/ 100 ml H₂O), (3)- RGOHI-AcOH in solution of SDS 0.5 wt.% (1,0 mg/ 100 ml solution SDS)].

Fourier-transform infrared spectroscopy (FT-IR) spectra of graphite, GO, MGO and RGOHI-

AcOH were observed on Figure 1A. Oxygen functional groups of powder GO showed stretching peaks at 1720 cm^{-1} (C=O), and a broad band at $2431\text{--}3722\text{ cm}^{-1}$ (OH of hydrogen bonds) compared with graphite. After modification with PEG, the oxygen peaks of MGO were slightly lower than GO and decreased dramatically in the RGOHI-AcOH. This is the result of the restoration of the electronic conjugation within the platelets and proving the ability to preliminary reduction of PEG (with the groups of OH as a reducing agent [2]). The next, the ultraviolet-visible spectra (Figure 1B) of the GO dispersion in water shows strong absorption bands at 224 nm (from the π -plasmon of carbon), a shoulder peak at 300 nm (from the $n \rightarrow \pi^*$ transitions of C=O) [13]. The peaks of MGO and RGOHI-AcOH moved to 260 nm and 266 nm respectively and corresponded to restoration of

the electronic conjugation within MGO and RGOHI-AcOH layers.

Figure 2A shows the X-ray diffraction pattern of graphite, GO, MGO and RGOHI-AcOH. The GO is a larger interlayer spacing than that of graphite (GO: major peak at $2\theta=11^\circ$ corresponding to an interlayer spacing of 7.792 \AA compared with graphite's major peak at 26.5° corresponding to 3.33 \AA) due to the oxygen functional groups and the water held in the interlayer galleries by the hydrogen bonds of GO. With MGO and RGOHI-AcOH, the major peaks ($2\theta=11^\circ$) is disappear in the XRD patterns corresponding to the breakdown of the crystal structure compared with graphite oxide. This proves that MGO and RGOHI-AcOH was exfoliated into individual platelets and then agglomerated into a powder form.

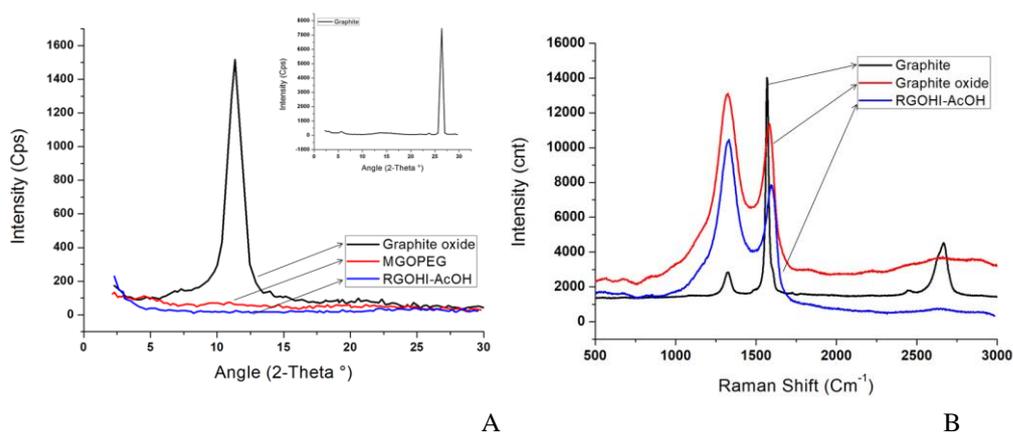


Figure 2. (A) Powder XRD patterns of graphite, GO, MGO and RGO_{HI-AcOH} and (B) Raman spectra of graphite, GO and RGO_{HI-AcOH}

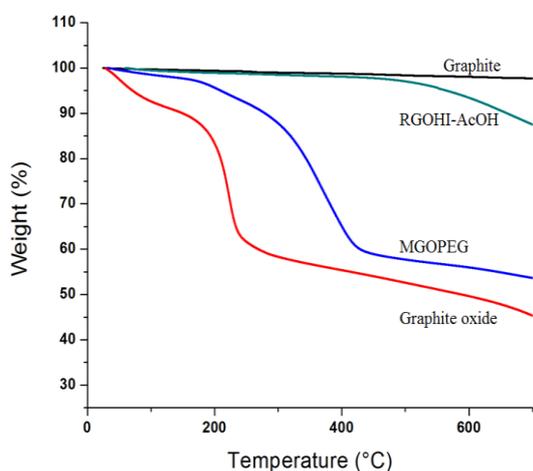
Figure 2B presents the Raman spectra of graphitic layers in the powder form. The peak for GO (1586 cm^{-1}) at the G-band was compared with that of graphite (1568 cm^{-1}). This was

attributed the presence of isolated double bonds that resonate at frequencies higher than that of the G-band of the graphite [13]. RGOHI-AcOH showed the peak of G-band at 1598 cm^{-1} , which

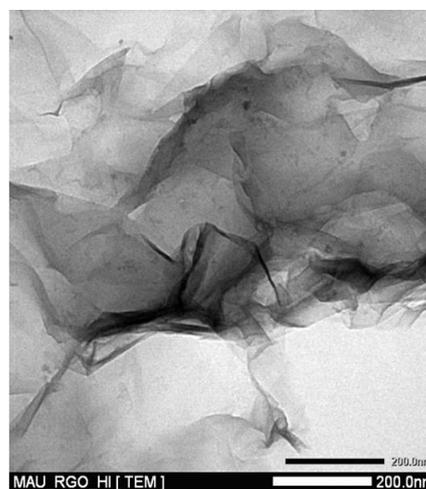
corresponds to the hard way to recover of the hexagonal network of carbon atoms with defects. The ID/IG ratio of RGOHI-AcOH (1.35) is higher than GO (1.23) and graphite (0.10). Cause of this result is the reduction process altered the structure of GO with a high quantity of structural defects [9]. The peak at 2D-band of RGOHI-AcOH and GO are not clearly compared with the original graphite. This is a weakness of chemical ways to reduce graphite oxide.

Thermo gravimetric analysis (TGA, Figure 3B) graphs show weight profiles of powder samples as variation of temperature (heating rate, 20 °C/min) under N₂ flow. Weight loss (~8.5 wt.%) of the GO up to 100 °C could be primarily

due to evaporation of water molecules held in the samples and this followed by loss of oxygen from the GO platelets themselves (such as by evolution of CO and CO₂ from the sample) at slightly higher temperatures [13]. The modified GO is higher thermal stability than GO (the temperature of peak at 268 °C compared with 222 °C of GO) because of preliminary reduction of PEG mentioned above. RGO_{HI-AcOH} showed much higher thermal stability (weight loss of 13 wt.% for RGO_{HI-AcOH} up to 700 °C) and thermal behavior similar to graphite because of the better graphitization and deoxygenation of RGO_{HI-AcOH} with enhanced Van der Waals forces between layers [13].



A



B

Figure 3. (A) Decomposition behavior of graphite GO, MGO and (B) RGOHI-AcOH and TEM images of RGOHI-AcOH

The Figure 3A show transmission electron microscopy (TEM) images of the platelets RGO_{HI-AcOH} dispersed in solution of 1 wt.% SDS

(dripping on the copper mesh substrate). The monolayers were observed next to multilayers of RGO_{HI-AcOH}.

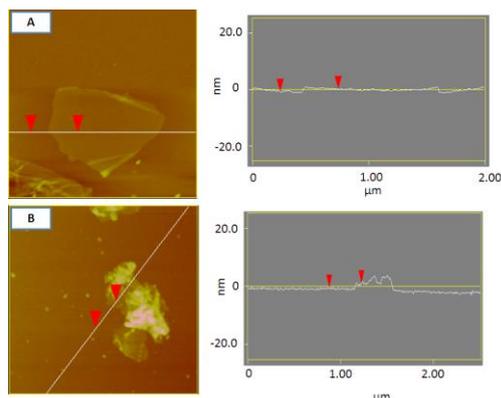


Figure 4. AFM images of MGO (A) and RGOHI-AcOH (B)

The AFM images of MGO (Figure 4A) showed the single-layer graphene oxide with thickness of 1.050 nm and diameter of about 1000 nm. Besides, Figure 4B showed the morphology of RGOHI-AcOH with thickness of 1.605 nm and diameter of about 500 nm.

This demonstrates that both MgO and RGO samples reached exfoliated structure. However, RGOHI-AcOH is easier to agglomerate than MGO and RGOHI-AcOH is also be chopped under the effect of the reduction. The more reduction is strong, the more size of RGO is smaller. The conductivity and sheet resistance of the RGOHI-AcOH paper ($\sim 5,0 \mu\text{m}$ thickness, Figure 5) was $1.66 \times 10^3 \text{ S}\cdot\text{m}^{-1}$ (electrical conductivity = $1/(\text{thickness} \times \text{sheet resistance})$) and $120 \Omega/\text{sq}$ respectively while graphite oxide and MGO were non-conductive. The high

conductivity of the RGOHI-AcOH was attributed to well restore electronic structure of layers exfoliated through the reduction.

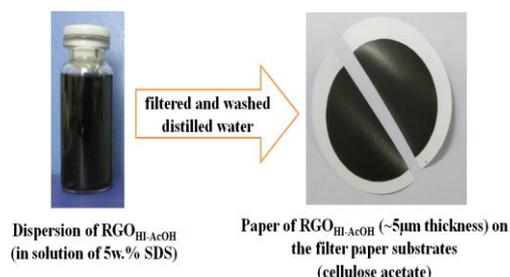


Figure 5. Fabrication process of RGOHI-AcOH paper by low pressure filtration method

CONCLUSION

We have succeeded in exfoliating GO to monolayer under the support of PEG as a modifier evidenced by XRD, TEM and AFM. RGO_{HI-AcOH} was high conductivity ($120 \Omega/\text{sq}$) and good thermal properties showed by TGA curve. RGO_{HI-AcOH} can be applied in the fields of electronics, solar cells batteries and polymer nanocomposites.

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Tách bóc Graphit oxit và ứng dụng chế tạo Graphen bằng phương pháp hóa học

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TÓM TẮT

Một hướng mới trong việc tách bóc graphit oxit dưới sự tán trợ của polyetylen oxit (PEO) và sóng siêu âm đã được tiến hành, Graphit oxit sau khi biến tính và tách bóc đơn lớp sẽ trở thành graphene oxit. Kết quả XRD cho thấy mũi kết tinh d_{002} của GO đã biến mất sau khi biến tính. Bên cạnh đó, ảnh TEM và AFM cũng xác định được đơn lớp graphene oxit với bề dày khoảng 1 nm.

Từ khóa: Graphen oxit, graphen, polyetylen oxit.

Graphene oxit được khử bằng hệ hai axit hydrocloric –axetic (HI-AcOH) tương tự như Rodney S. Ruoff và đồng nghiệp. Điện trở mặt của màng $RGO_{HI-AcOH}$ trên đế xelulozo axetat được xác định khoảng 120 Ω/sq . Thêm vào đó, phổ FTIR, UV-Vis và Raman còn cho thấy rõ hơn các tính chất của graphit oxit, graphen oxit và $RGO_{HI-AcOH}$.

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