

Evaluating the Effect of Graphite Source and Operating Conditions on the Synthesis of Graphene Oxide

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Abstract

In this research graphene oxide was synthesized by two methods. These methods were achieved by changing the improved Hummers' and modified Hummers' methods. Structure of graphene oxide was characterized by scanning electron microscopy (SEM) images, X-ray diffraction (XRD) patterns, Raman spectroscopy and Fourier transform infrared (FTIR) spectra. According to SEM image, the thickness of graphene oxide sheets prepared by improved Hummers' method is about 66 nm. In improved Hummers' method excluding NaNO_3 from reacting gel and performing reaction in a 9:1 volume ratio of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ mixture improved the oxidation process by elimination of toxic gases, finally the prepared GO contains well-oxidized carbon materials. XRD results implied more oxidation for synthesized GO by improved Hummers' based method. Importance of graphite source was shown in synthesis of pure GO. Two sources of graphite supplied by Daejung and Fluka Companies were used to synthesis GO in improved Hummers' method. According to SEM images and XRD patterns, the graphite source prepared by Fluka Co. was more efficient towards production of pure GO than other graphite source. The results also indicated that temperature and mixing condition are two important factors for synthesis of GO.

Keywords

Graphite source;
Graphene oxide;
Operating condition;
Synthesis.

1. Introduction

Graphite is a crystalline form of carbon. In each layer of graphite, the carbon atoms are arranged in a honeycomb lattice with the interval of 0.142 nm, and the distance between

planes is 0.335 nm [1]. Bonding between layers is via weak van der Waals bonds, which allows layers of graphite to be easily separated, or to slide over each other. After graphite layer separation, each layer is named graphene, a two-dimensional structure, with single layer of sp^2 -hybridized carbon atoms in a honeycomb crystal lattice. Graphene is one of the most exciting materials that is being investigated today.

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In 2004, for the first time, graphene was introduced to scientific community [2, 3]. Due to its unique structure and geometry, graphene possesses remarkable physicochemical properties, including a high Young's modulus, high fracture strength, and excellent electrical and thermal conductivity, fast mobility of charge carriers, large specific surface area and biocompatibility [4]. These properties enable graphene to be used in many fields such as quantum physics, nano-electronics, energy research, catalysts and engineering of nanocomposites and biomaterials [5, 6].

Graphene is highly hydrophobic and this property limits its applications in many fields such as biological science and nanomedicine. Despite, GO shows excellent hydrophilicity because of large amount of oxygen containing functional groups (i.e., carboxyl, hydroxyl, epoxy, carbonyl), and is relatively, easily dispersed in water [7-9]. Graphene oxide aggregates in physiological buffers in the presence of salts. Therefore, to achieve desired GO, it is needed to perform surface modification [10]. The most common method is the use of strong oxidizing agents to have graphene oxide (GO) as the hydrophilic carbon material. Interlayer spacing for graphite increases from 0.335 nm to more than 0.625 nm after oxidation of graphene disrupting the lattice [11, 12]. Using an oxidizing agent, sheets of graphite are separated easily because of weak van der Waals bonds and carbon atoms bind with O and H, to form graphene oxide (GO).

Although the exact structure of GO is unclear, but the basal planes of the graphene oxide sheets contain mostly epoxide and hydroxyl groups, also carbonyl and carboxyl groups are in the structure, mostly decorated at the edges [13]. The first one who demonstrated the synthesis of GO was Brodie [14]. The synthesis was achieved by adding a portion of potassium chlorate to graphite in fuming nitric acid [14]. Staudenmaier [15] improved this protocol, using concentrated sulfuric acid and fuming nitric acid and adding the chlorate to multiple aliquots. This change in the procedure resulted production of highly oxidized GO in a vessel of single reaction significantly more practical.

Hummers and Offeman [16] reported a procedure that most commonly used today. They oxidized graphite in sulfuric acid by adding KMnO_4 and NaNO_3 as oxidizing agents. These procedures commonly produce toxic gases like NO_2 or N_2O_4 because of using the fuming nitric acid or sodium nitrate. Marcano and co-workers, reported an improved synthesis of GO. They used the mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ in a 9:1 volume ratio, and elimi-

nated using of NaNO_3 and increased the amount of KMnO_4 [12]. By removing sodium nitrate and fuming nitric acid during these procedures, production of toxic gases like NO_2 and N_2O_4 was inhibited, also in this procedure the yield of GO was increased. Based on the 3 g of graphite, Hummers method yields the production of 4.2 g graphene oxide while the yield by improved method was 5.8 g graphene oxide. This oxidation procedure (KMnO_4 and a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$), called the "improved method" which could be used to prepare improved GO (IGO), containing fewer defects in the basal plane comparing with GO prepared by the Hummers' method [12]. By electrical reduction of graphene oxide, the formed reduced graphene oxide (rGO) is similar to graphene but contains some oxygen and other heterogeneous atoms [17]. GO and rGO have great applications in nano composite materials [18, 19], polymer composite materials [18], energy storage [19], biomedical applications [20-22], catalysis [23], and as a surfactant [24].

Cote and co-workers exposed that GO sheets are amphiphilic with hydrophobic and hydrophilic domains that distributed in the edge to center of GO sheets [25]. Therefore GO can attach to interfaces, playing role of surfactant. Understanding this new property of GO can help to identify the solution properties of GO which can originate new material assembly and processing method such as for manufacturing thin film with controllable micro-structures and segregation GO sheets of different sizes. Further, GO can be used as a surfactant sheet to emulsify organic solvent with water and disperse insoluble materials such as graphite and carbon nanotubes in water, that opens up chances for developing functional hybrid materials of graphene and other π -conjugated systems [25].

This study focuses on comparison between two synthesis procedures of graphene oxide, considering oxidation degree, purity of the synthesized product and evaluation of the two graphite sources (Daejung and Fluka CO.). As well, the effects of temperature and mixing in oxidation process have been investigated.

2. Structural Features

Aside from the oxidative mechanisms, the chemical structure of GO has been the subject of considerable debate over the years, even to this day no clear model has been suggested. Considerable efforts have been done successfully to understand the structural features of GO. Hofmann and Holst,

Ruess, Scholz and Boehm, Nakajima and Matsuo studied on the structure of GO [11]. The lattice-based model was rejected by most of the recent models, and a non-stoichiometric, amorphous alternative have been investigated more. The most well-known model is the one prepared by He and co-workers. (Fig. 1) used solid state nuclear magnetic resonance (NMR) spectroscopy to characterize the material and structural features [[11, 26]. In addition to other ketone groups, carboxylic acid groups were present in very low quantities at the periphery of the graphitic sheets [11].

3. Experimental Details

3.1. Materials and reagents

Two graphite sources as powders (Fluka, purity 99.99% and Daejung), sulfuric acid (Merck, 98 wt. %), orthophosphoric acid (Merck, 85 wt. %), potassium permanganate (Merck 99.99%), Hydrogen peroxide (Mojallali, 37 wt. %), and sodium nitrate (Merck 99.99%) were prepared and used without any further treatment.

3.2. Synthesis procedure

3.2.1. First method

This synthesis method was achieved by changing the improved Hummers' method. A mixture of 9:1 concentrated acids, H_2SO_4/H_3PO_4 (40.5:4.5 ml) was added to graphite powder (1.0 g). $KMnO_4$ (6.5 g) was gradually added during one hour, at the controlled temperature below $20^\circ C$. The reaction mixture was then heated up to $37 \pm 2^\circ C$ and mixed using a mechanical agitator (home made agitator) for two days. Then the mixture was sonicated (Digital ultrasonic cleaner, CD 4820, 170 W) for 30 min, in order to exfoliate graphite oxide to graphene oxide. Thereafter, the reaction mixture was cooled down to room temperature. Diluted H_2O_2 , a 4:1 (v/v) mixture of de-ionized water/ H_2O_2 , was added drop wise to the graphene oxide in an ice bath in order to remove heat generated from reaction. Addition of H_2O_2 was applied to convert remained

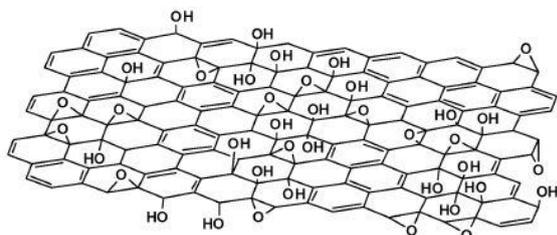


Figure 1. The proposed structural model of GO [11].

MnO_2 to Mn^{+2} . The best way for treating GO is to add diluted H_2O_2 drop wise while controlling the temperature below $20^\circ C$, otherwise there will be greenish yellow solution that is due to reduction of produced GO and existence of both rGO (reduced GO) and GO in final product. Then the mixture was centrifuged (7000 rpm) and washed repeatedly with de-ionized water and ethanol (96% v) until the supernatant becomes neutralized to prevent any inorganic ion sedimentation. The obtained solid was vacuum-dried for one day at $50^\circ C$ to obtain GO-A.

3.2.2. Second method

Second method was achieved by changing the modified Hummers' method. For this method, concentrated H_2SO_4 (45 mL) was added to a mixture of graphite powder (1.0 g) and $NaNO_3$ (0.5 g). Same as previous procedure, $KMnO_4$ (6.0 g) was added slowly in portions controlling temperature below $20^\circ C$. Afterward, the mixture was heated up to $37 \pm 2^\circ C$, and mixed using mechanical agitator for two days. Then the mixture was cooled down to room temperature and sonicated (170 W). Similar to previous method, diluted H_2O_2 , a 4:1 (v/v) mixture of deionized water/ H_2O_2 , was added drop wise to the graphene oxide in an ice bath. At this time, the color of the mixture changed to bright yellow. Then the mixture was centrifuged and washed repeatedly with de ionized water and ethanol similar to the previous procedure. The obtained product was vacuum-dried for one day at $50^\circ C$ to obtain GO-B.

3.3. Characterization

X-ray powder diffraction (XRD) patterns were obtained by D8 ADVANCE X-Ray (Bruker AXS) diffractometer (Cu $K\alpha$ radiation). Fourier transform infrared (FTIR) spectra were carried out using Perkin-Elmer spectrometer in frequency range of $800-4000\text{ cm}^{-1}$. Scanning electron microscope (SEM) images were recorded with Hitachi-S4160 microscope operating at 30 kV. Sample morphologies were investigated by transmission electron microscopy (TEM) images with Philips-cm30 apparatus and acceleration voltage of 150 kV. Raman spectroscopy was performed on a Renishaw Raman microscope, with an excitation wavelength at 785 nm.

4. Results and Discussions

4.1. Stages of synthesis

In this research, the proposed structure for graphene oxide considering very well oxidation is $COH_{0.5}$, by regarding absence of carboxylic acid

groups in He's model, assuming O:H ratio as two, and C:O ratio as one. The stoichiometry for reaction, considering full oxidation, can be considered as below:



Considering the obtained stoichiometry, 6.5 gram potassium permanganate is necessary to fully oxidize 1 gram of graphite powder. H_2SO_4 diffuses between layers of graphite to generate graphite intercalate compound (GIC). In this step, the layers of graphite are relatively separated and $KMnO_4$ as oxidizing agent easily diffuses between layers and oxidizes graphite [27]. Structure of IGO is a more regular structure; it may be due to using phosphoric acid and formation of five-membered cyclic phosphate groups that is formed between phosphoric acid and two vicinal diols on the graphite basal plane [12, 28]. After completion of reaction, GO is synthesized and MnO_2 is produced during synthesis. Treating with H_2O_2 is an important step to remove MnO_2 and formation of soluble Mn^{2+} , preventing any inorganic ion sedimentation:



Mn^{2+} can be removed by washing with water or alcohol in the final step.

4.2. Evaluation of graphite source influence

First method was applied for synthesis of GO with the same operating conditions but two graphite sources supplied from two companies (Daejung G-D and Fluka G-F). XRD patterns and SEM images show that the source of graphite is an important factor to produce pure GO.

SEM images of G-D and synthesized GO from this source, GO-D, are shown in Fig. 2a and b, respectively. Comparison of Fig. 2a and 2b reveals that small changes have occurred on the initial graphite source and it means that the graphite is not completely oxidized and the layers are not well separated.

During the synthesis with this source and after treating with H_2O_2 , some of the suspended graphite material was observed in the final solution. However, the black particles were removed by 1000 rpm centrifugation.

SEM images of Fluka graphite source, G-F and synthesized graphene oxide from this source (GO-F) are shown in Fig. 3a and b.

Fig. 3b illustrates that the GO layers are laid on each other. According to this image, thickness of sheets is about 66 nm. During GO synthesis, after

treating with H_2O_2 there were no black particles left in the final solution. Enhanced oxidation of G-F and production of GO-F nano-sheets are obviously concluded from Fig. 3b against Fig. 2b.

The XRD analysis were applied on sources and products and they are observed in Fig 4a and b. XRD patterns of G-D and GO-D are presented in Fig. 4a. In this pattern, a typical peak around $2\theta=26^\circ$, is observed due to the graphite phase structure. The specific peak of GO can be observed at $2\theta=10.32^\circ$ and d-spacing about 8.56 Å. As seen in Fig. 4a, presence of graphite impurity is observed in the product of GO-D, as well some other impurities can be observed around $2\theta=20^\circ$ and $2\theta=36^\circ$. The original G-D graphite has also some impurities and it is appeared in the pattern of GO-D.

Fig. 4b presents XRD patterns of G-F and GO-F. XRD pattern of GO-F shows a peak on $2\theta=10.5^\circ$ with d-spacing about 8.6 Å, and the peak of graphite is completely eliminated. Therefore it can be concluded that a qualified product of GO can be synthesized from an appropriate source of graphite.

4.3. Comparison of two GO synthesis methods

Graphite powder was oxidized to graphene oxides

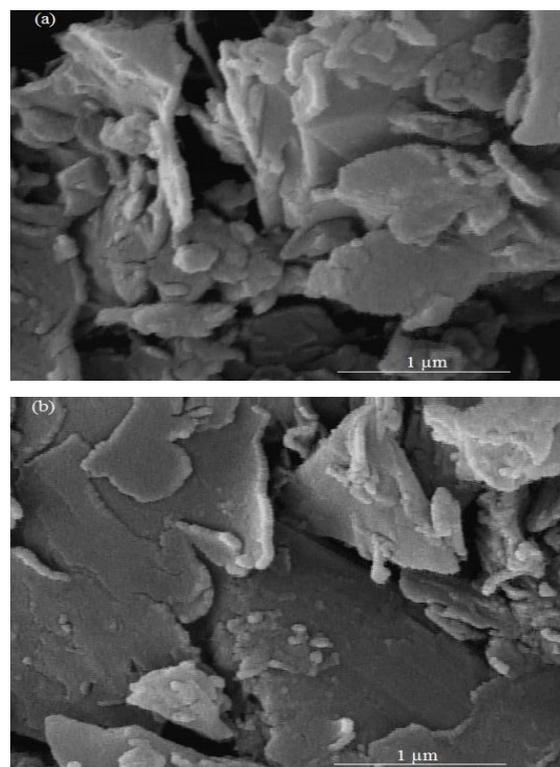


Figure 2. SEM images, a) Graphite source from Daejung (G-D), b) Synthesized GO from graphite source of Daejung (GO-D).

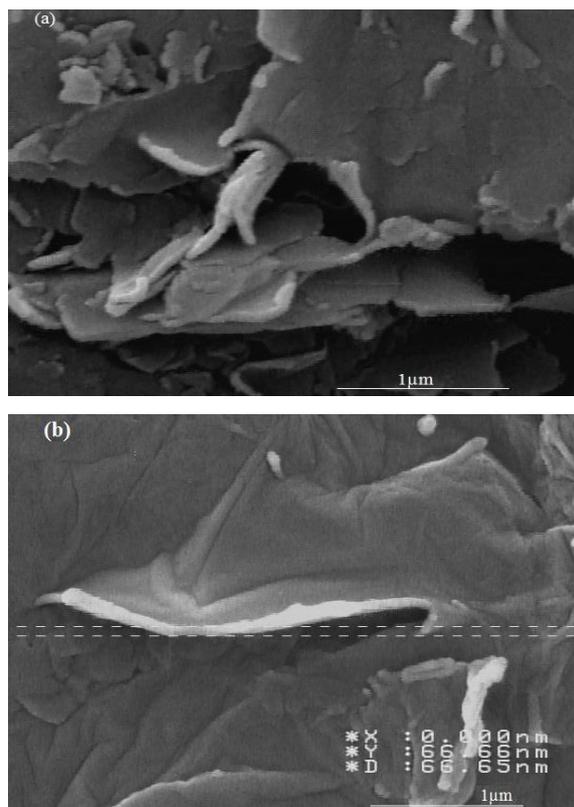


Figure 3. SEM images, a) Graphite source of Fluka (G-F), b) Synthesized GO from graphite source of Fluka (GO-F).

using the two mentioned methods. XRD analysis was performed to figure out the resulting materials. The XRD spectra of GO-A and GO-B are shown in Fig. 5. For GO, the interlayer spacing (d) of the product is proportional to the degree of oxidation [12, 16]. As shown in Fig. 5, there are two diffraction peaks for GO-B at $2\theta=11.7^\circ$ ($d=7.5 \text{ \AA}$) and $2\theta=25.5^\circ$ ($d=3.4 \text{ \AA}$). The weaker peak with $d=3.4 \text{ \AA}$ corresponds to the normal graphite spacing. This peak reveals that graphite was remained in final product.

The stronger peak with $d=7.5 \text{ \AA}$ corresponds to the typical diffraction peak of GO. On the other hand, there are just a diffraction peak for GO-A at $2\theta=10.5^\circ$ ($d=8.6 \text{ \AA}$) that corresponds to the typical diffraction peak of GO (Fig. 5).

Compared with GO-B, the interlayer spacing of GO-A is larger, implying more extensive oxidation [29]. As well, diffraction peak of GO-A is shifted to left in comparison to GO-B, because of more oxidation that it is obvious in Fig 5.

4.4. Structural characterization of GO-A

XRD analysis and SEM images clarified effective

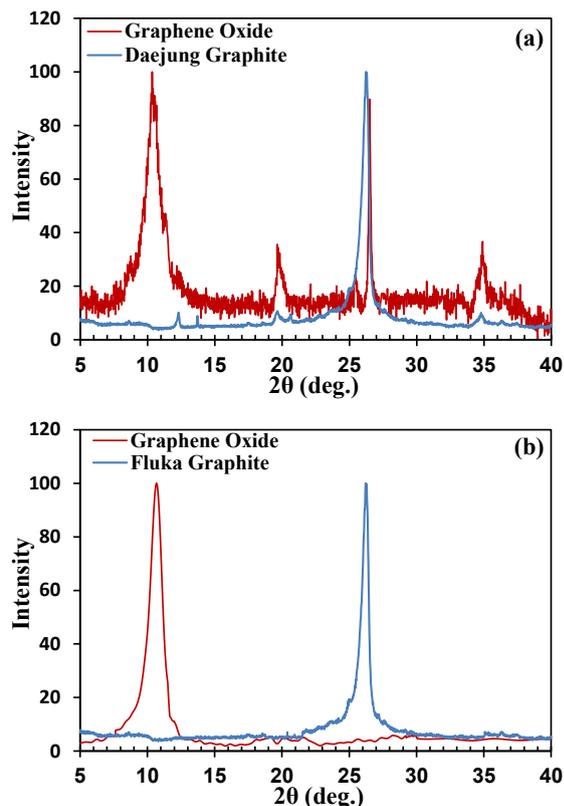


Figure 4. X-ray diffractogram, a) G-D and GO-D, b) G-F and GO-F.

graphite source, synthesis protocol and operating conditions. Synthesized GO-A using Fluka graphite source and operating conditions was characterized with complementary analysis such as Raman spectroscopy, FTIR, and TEM. Raman spectroscopy is widely used to characterize the structural and electronic properties of carbon-based materials. The Raman spectrum of GO-A is shown in Fig. 6. The main features in the Raman spectra of graphitic carbon-based materials are the G and D peaks and their overtones [30]. The G peak at 1581 cm^{-1} , and the D peak at 1335 cm^{-1} are recorded (Fig. 6). The G peak corresponds to the bond stretching of sp^2 carbon pairs in both rings and chains. The D peak represents the breathing mode of aromatic rings arising due to the defect in the sample. The D peak intensity is therefore often used as a measure tool for the degree of disorder [31, 32]. Higher disorder in graphite leads to a broad D-band of higher relative intensity compound to that of the G-band [33]. The I_D/I_G is a measure of disorder. As a result, $I_D/I_G > 1$ shows a great disorder in aromatic structure because of attachment of functional groups on the carbon [29].

FTIR spectrum has been recorded in the wave number range of 800-4000 cm^{-1} , to further investigation of graphene oxide chemical structure (Fig. 7). The broad peak at 3425 cm^{-1} and the sharp peak at 1629 cm^{-1} are attributed to the stretching and bending vibration of OH groups of water mol-

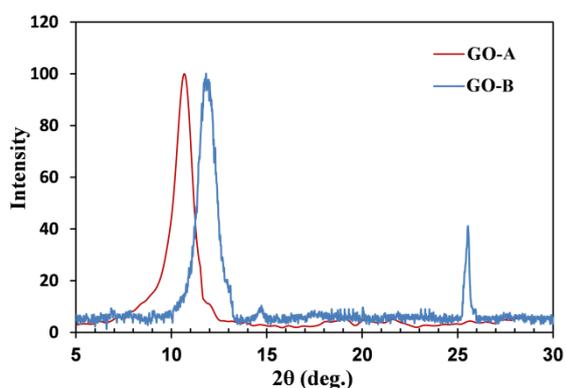


Figure 5. X-ray diffractogram of GO-A and GO-B.

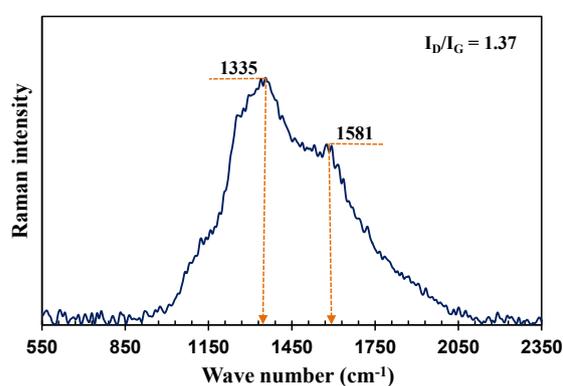


Figure 6. Raman spectra of GO-A.

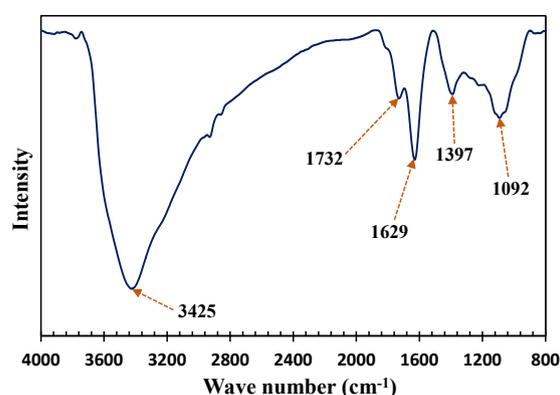


Figure 7. FTIR spectra of GO-A.

ecules adsorbed on graphene oxide. The absorption peak at 1092 cm^{-1} can be attributed to epoxy groups of GO (Fig. 7).

The absorption peaks at 1732 cm^{-1} and 1397 cm^{-1} are attributed to stretching vibration of C=O and C-OH deformation of carboxylic acid and carbonyl groups presented at the edges of graphene oxide (Fig. 7). Therefore, oxygen functional groups of graphene oxide investigated by FTIR spectrum, showed that graphene oxide has strong hydrophilic property [30, 34]. TEM image of the GO-A is shown in Fig. 8. Sheets of graphene oxide are clearly shown in this image.

4.5. Effect of temperature

To study the effect of temperature, GO was prepared using first method at room temperature. At the instant of adding KMnO_4 in solution, the color was converted to green, because of one step reduction of permanganate (MnO_4^-) to manganite (MnO_2) on the surface of graphite. The process of reduction in presence of oxidant was carried out. After four days, the color of the mixture was changed to brown because of formation of MnO_2 . Hence, increasing the reaction temperature is useful for rising rate of reaction. The effect of high temperature is also significant towards GO synthesis, heating up the mixture causes reduction of graphene oxide. Therefore, temperature of the media should be adjusted at a specific level. In this work, the temperature was set at $37 \pm 2^\circ\text{C}$.

Addition of H_2O_2 was required to reduce MnO_2 to colorless Mn^{+2} , whereas during addition of H_2O_2 the temperature of solution was increased and the color was changed to greenish yellow, which means that the reverse reaction (reduction of graphene oxide) is taking place and some of MnO_2 is converted to MnO_4^{2-} . Thus, temperature must be controlled below 20°C .

4.6. Effect of mixing

To study the effect of mixing, GO-A was prepared using magnetic stirrer (Heidolph, D-91126 schwabach). By adding potassium permanganate after a while, viscosity of the reaction mixture began to increase. So that, magnet stirrer was not able to mix the whole mixture uniformly. After three days, color of the mixture was changed to brown. After graphite oxidation process, H_2O_2 solution was added to the mixture. At this time, the color of the mixture was changed to greenish yellow. This indicates that un-oxidized graphite and oxidant was remained in reaction media because of inappropriate and non-uniform mixing. It can be concluded that uniform mixing with appropriate round per

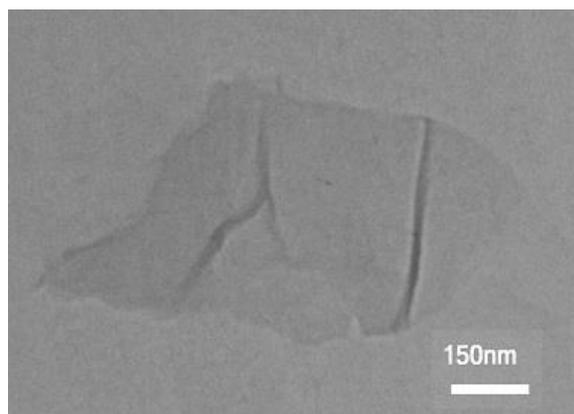


Figure 8. TEM image of GO-A.

minute is one of the prominent points in synthesis of graphene oxide.

5. Conclusions

In this study, the graphene oxide was prepared by oxidizing graphite powder using two methods based on modified Hummers and Improved methods. The XRD spectra shows that interlayer spacing of GO-A ($d=8.6 \text{ \AA}$) is higher than GO-B ($d=7.5 \text{ \AA}$). Therefore oxidation level of GO-A is more than GO-B. As well, diffraction peak of graphite ($2\theta=25.5^\circ$) was revealed for GO-B, but this peak was disappeared for GO-A. It can be concluded that GO-A is more pure than GO-B. Hence, first method can be considered as promising method for synthesis of graphene oxide. The Raman spectrum of GO-A shows that ID is higher than IG. Therefore, a great defect has been created in aromatic structure of GO-A.

The FTIR spectrum shows that functional groups (hydroxyl, carboxyl, epoxy, and carbonyl) have been created in GO-A. Additionally, source of graphite is an important factor for synthesis of pure GO. Some of graphite sources that have impurities and ashes would not allow the exfoliation and complete oxidation of graphite layers.

According to the preformed analysis, XRD patterns and SEM images, although un-reacted graphite was separated by centrifugation, some of the un-reacted materials were remained in the product. As well treating with H_2O_2 is an important step. The best way for treating is adding diluted H_2O_2 drop wise and controlling temperature below 20°C . In this way color of GO would be bright yellow that shows existence of GO. While in any other treating procedures the color of solution is green-

ish yellow that shows reduction of GO and existence of both GO and reduced GO. In addition, the results show that temperature and mixing are two important factors for synthesis of graphene oxide.

Nomenclature

| | |
|----------|--|
| SEM | Scanning electron microscopic |
| FTIR | Fourier transform infrared |
| IGO | Improved graphene oxide |
| NMR | Nuclear magnetic resonance |
| G-D | Graphite source supplied from Daejung Company |
| GO-D | Synthesized graphene oxide from G-D |
| d | The distance between similar atomic planes in a mineral (\AA) |
| XRD | X-ray diffraction |
| GO | Graphene oxide |
| rGO | Reduced graphene oxide |
| GIC | Graphite intercalate compound |
| G-F | Graphite source supplied from Fluka Company |
| GO-F | Synthesized graphene oxide from G-F |
| θ | Angle of diffraction (degree) |

References

- Moktadir, Z. (2014). "Graphene nanoelectromechanics (NEMS), in *Graphene: properties, preparation, characterisation and devices*, First edition. London, GB, Woodhead, pp. 341-358.
- Geim, A.K. and Novoselov, K.S. (2007). "The rise of graphene." *Nature Materials*, Vol. 6, No. 3, pp. 183-191.
- Stankovich, S., Dikin, D.A., Dommett, G. H., Kohlhaas, K.M., Zimney, E.J. (2006). "Graphene-based composite materials." *Nature*, Vol. 442, No. 7100, pp. 282-286.
- Geim, A.K. (2009). "Graphene: status and prospects." *Science*, Vol. 324, No. 5934, pp. 1530-1534.
- Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V. and Firsov, A.A. (2004). "Electric field effect in atomically thin carbon films." *Science*, Vol. 306, No. 5696, pp. 666-669.

6. Kim, K.S., Zhao, Y., Jang, H., Lee, S.Y., Kim, J.M. (2009). "Large-scale pattern growth of graphene films for stretchable transparent electrodes." *Nature*, Vol. 457, No. 7230, pp. 706-710.
7. Kovtyukhova, N.I., Ollivier, P.J., Martin, B.R., Mallouk, T.E., Chizhik, S.A. (1999). "Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations." *Chemistry of Materials*, Vol. 11, No. 3, pp. 771-778.
8. Wang, Y., Xie, L., Sha, J., Ma, Y., Han, J. (2011). "Preparation and chemical reduction of laurylamine-intercalated graphite oxide." *Materials Science*, Vol. 46, No. 10, pp. 3611-3621.
9. Yoon, S., and In, I. (2011). "Role of poly (N-vinyl-2-pyrrolidone) as stabilizer for dispersion of graphene via hydrophobic interaction." *Materials Science*, Vol. 46, No. 5, pp. 1316-1321.
10. Liu, J., Cui, L., and Losic, D. (2013). "Graphene and graphene oxide as new nanocarriers for drug delivery applications." *Acta Biomaterialia*, Vol. 9, No. 12, pp. 9243-9257.
11. Dreyer, D.R., Park, S., Bielawski, C.W. and Ruoff, R.S. (2010). "The chemistry of graphene oxide." *Chemical Society Reviews*, Vol. 39, No. 1, pp. 228-240.
12. Marcano, D.C., Kosynkin, D.V., Berlin, J.M., Sinitskii, A., Sun, Z. (2010). "Improved synthesis of graphene oxide." *ACS Nano*, Vol. 4, No. 8, pp. 4806-4814.
13. Stankovich, S., Piner, R.D., Chen, X., Wu, N., Nguyen, S.T., and Ruoff, R.S. (2006). "Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly (sodium 4-styrenesulfonate)." *Journal of Materials Chemistry*, Vol. 16, No. 2, pp. 155-158.
14. Brodie, B.C. (1859). "On the Atomic Weight of Graphite." *Philosophical Transactions of the Royal Society of London*, Vol. 149, pp. 249-259.
15. Staudenmaier, L. (1898). "Verfahren zur Darstellung der Graphitsaure." *Berichte der Deutschen Chemischen Gesellschaft*, Vol. 31, No. 2, pp. 1481-1487.
16. Hummers, W.S. and Offeman, R.E. (1958). "Preparation of Graphitic Oxide." *American Chemical Society*, Vol. 80, No. 6, pp. 1339-1339.
17. Chua, C.K. and Pumera, M. (2014). "Chemical reduction of graphene oxide: a synthetic chemistry viewpoint." *Chemical Society Reviews*, Vol. 43, No. 1, pp. 291-312.
18. Huang, X., Qi, X., Boey, F. and Zhang, H. (2012). "Graphene-based composites." *Chemical Society Reviews*, Vol. 41, No. 2, pp. 666-686.
19. Lightcap, I.V. and Kamat, P.V. (2012). "Graphitic design: prospects of graphene-based nanocomposites for solar energy conversion, storage, and sensing." *Accounts of Chemical Research*, Vol. 46, No. 10, pp. 2235-2243.
20. Sun, X., Liu, Z., Welsher, K., Robinson, J.T., Goodwin, A., Zaric, S. and Dai, H. (2008). "Nanographene oxide for cellular imaging and drug delivery." *Nano Research*, Vol. 1, No. 3, pp. 203-212.
21. Chung, C., Kim, Y.K., Shin, D., Ryoo, S.R., Hong, B.H., Min, D.H. (2013). "Biomedical applications of graphene and graphene oxide." *Accounts of Chemical Research*, Vol. 46, No. 10, pp. 2211-2224.
22. Wang, Y., Li, Z., Wang, J., Li, J. and Lin, Y. (2011). "Graphene and graphene oxide: biofunctionalization and applications in biotechnology." *Trends in Biotechnology*, Vol. 29, No. 5, pp. 205-212.
23. Pyun, J. (2011). "Graphene oxide as catalyst: application of carbon materials beyond nanotechnology." *Angewandte Chemie International Edition*, Vol. 50, No. 1, pp. 46-48.
24. Kim, J., Cote, L. J., Kim, F., Yuan, W., Shull, K. R., and Huang, J. (2010). "Graphene oxide sheets at interfaces." *American Chemical Society*, Vol. 132, No. 23, pp. 8180-8186.
25. Cote, L.J., Kim, J., Tung, V.C., Luo, J., Kim, F., Huang, J. (2010). "Graphene oxide as surfactant sheets." *Pure and Applied Chemistry*, Vol. 83, No. 1, pp. 95-110.
26. He, H., Riedl, T., Lerf, A. and Klinowski, J. (1996). "Solid-state NMR studies of the structure of graphite oxide." *Physical Chemistry*, Vol. 100, No. 51, pp. 19954-19958.

27. Dimiev, A.M. and Tour, J.M. (2014). "Mechanism of graphene oxide formation." *ACS Nano*, Vol. 8, No. 3, pp. 3060-3068.
28. Higginbotham, A., Kosynkin, D., Sinitskii, A., Sun, Z., Tour, J.M. (2010). "Lower- defect graphene oxide nanoribbons from multiwalled carbon nanotubes." *ACS Nano*, Vol. 4, No. 4, pp. 2059-2069.
29. Shi, C., Chen, L., Xu, Z., Jiao, Y., Li, Y. (2012). "Monitoring influence of chemical preparation procedure on the structure of graphene nanosheets." *Physica E: Low-dimensional Systems and Nanostructures*, Vol. 44, No. 7-8, pp. 1420-1424.
30. Shahriary, L. and Athawale, A.A. (2014). "Graphene oxide synthesized by using modified hummers approach." *Renew. Energy and Env. Engg*, Vol. 2, No. 1, pp. 58-63.
31. Tuinstra, F. and Koenig, J.L. (1970). "Raman spectrum of graphite." *Chemical Physics*, Vol. 53, No. 3, pp. 1126-1130.
32. Ferrari, A.C. and Robertson, J. (2000). "Interpretation of Raman spectra of disordered and amorphous carbon." *Physical Review B*, Vol. 61, No. 20, pp. 14095-14107.
33. Kudin, K.N., Ozbas, B., Schniepp, H.C., Prud'Homme, R.K., Aksay, I.A. and Car, R. (2008). "Raman spectra of graphite oxide and functionalized graphene sheets." *Nano Letters*, Vol. 8, No. 1, pp. 36-41.
34. Guo, H., Wang, X., Qian, Q., Wang, F., Xia, X. (2009). "A green approach to the synthesis of graphene nanosheets." *ACS Nano*, Vol. 3, No. 9, pp. 2653-2659.