

STUDY AND SYNTHESIS OF GRAPHENE OXIDE BY CHEMICAL METHOD

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Abstract

Graphene oxide (GO) could be synthesized by the oxidation of graphite via one of three principal methods developed by Brodie, Hummers, and Staudenmaier. In this work, GO was synthesized by modified Hummers method through the intermediate product (graphite oxide- GtO). The results from SEM, DLS, FTIR measurement described the oxidation of graphite layers, the layers separation, as well as the appearance of functional groups.

These were initial results for our research project on this material at Nhatrang Institute of Technology Research & Application (NITRA). We obtained the manufactured process from graphite \rightarrow graphite oxide \rightarrow graphene oxide. The GO products were oriented in mass production to fabricate the reduced graphene oxide (rGO) materials for the supercapacitor research and application as oil absorbing materials.

Keywords: Graphene oxide, graphite, Hummers method, super capacitors.

1. INTRODUCTION

Graphene is defined as a planar hexagonal ring containing a sp^2 hybridized carbon atom with a two-dimensional (2D) honeycomb lattice [1]. Graphene has been known since 2004, until 2010 when Geim and Novoselov won the Nobel Prize for their research about this material, graphene became the popular subject of scientists. This material is used in many fields such as: solar cells, biosensor devices, touch screens, flexible LCDs, waste filtration systems, drug delivery, or even in the field of space technology because of the excellent electrical properties (electron mobility $\sim 300000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), thermal conductivity ($5000 \text{ Wm}^{-1} \cdot \text{K}^{-1}$, 10 times more

Cu), high mechanical strength with high Young's modulus and high fracture strength $\sim 125 \text{ GPa}$, Optical properties (Ability to absorb $\sim 2.3\%$ of white light) [2].

Graphene is separated from graphite with the stable C-C bond (fig 1). The distance between two carbon atoms is 0.142 nm , single layers are bonded by Vander Walls forces and form a 3D structure with layer spacing about 0.334 nm . Characteristics of the structure are loosely bonded between graphite layers so they easily slide over each other. However, the carbon atoms in the same single layer are strongly bonded, thus graphite has high mechanical strength but often easy to separate.

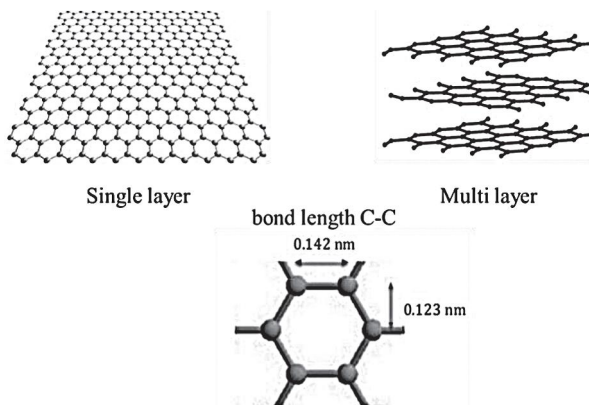


Figure 1. Graphite layers with stable C-C bond

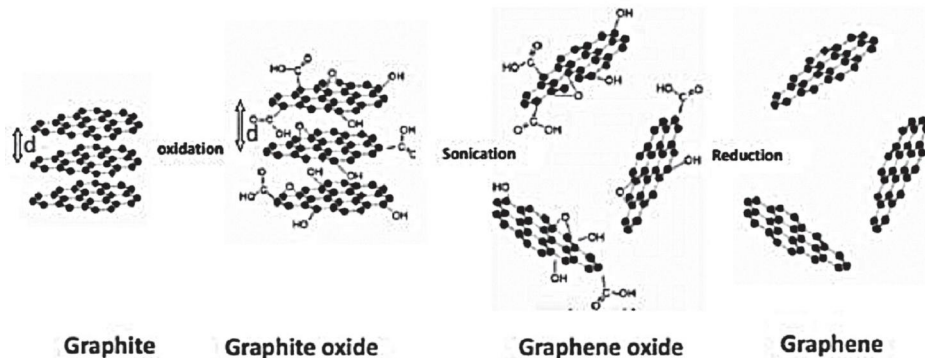


Figure 2. Graphene formation process by chemical methods [3]

GO is produced by the oxidation of graphite via one of three principal methods developed by Brodie, Hummers [4], and Staudenmaier [5]. It still retains a layered structure, but the color is lighter than graphite due to the loss of electronic conjugation by the oxidation [6]. And, in this work, the GO manufacture process is studied by modified Hummers method.

The structure and properties of GO depend on the synthesis method as well as factors affecting the synthesis, like as: concentration of graphite; the concentration of graphite higher, lesser the penetration of oxidation. The concentration of acid (H_2SO_4): the concentration of acid higher lead to the exfoliation of graphite to GO stronger, but also dangerous and difficult to filter when obtaining products. An oxidizer ($KMnO_4$), it increases the temperature of the reaction and may lead to incomplete oxidation at the end. Water and reaction temperatures lead to dangerous reactions and affect GO quality.

In the exfoliation of graphene from graphite, the graphene oxide (GO) is interested because of low cost, easy access, and widespread ability to convert to reduced graphene oxide (rGO) or graphene. Although GO contains some functional groups on the surface leading to the decline their conductivity, (fig 2) but they also have the advantage of functionalized surface materials to apply in fields where electrical conductivity is not required.

2. EXPERIMENTAL METHOD

Graphene oxide was prepared from graphite powder, the oxidants are: $KMnO_4$, HNO_3 , H_2SO_4 , the process was following steps:

1. Graphite (2g), $KMnO_4$ (2g) and HNO_3 (4ml) were mixed well in 5 minutes for the oxidation reaction to open the graphite layers, HNO_3 inserted between layers to spread the layers spacing. Then, the mixture was heat-shocked at $100^\circ C$ for 2 minutes; heat shock process causes NO_3^- rapid evaporation created a large amount of gas to push and reduce layers bonding.

2. The oxidation of the separated layers graphite (Gts) to graphite oxide (GtO); Gts, $NaNO_3$ (2g) and H_2SO_4 (90 ml) were mixed in the ice bath ($0-5^\circ C$) and continuous stirring, then added $KMnO_4$ (12g) slowly into mixture, this process was in 90 minutes ($0-5^\circ C$: was a suitable condition for the substances slowly and dispersed deep into the graphite layers structure, as well as the oxidation reactions occur in a safe manner) [7].

3. The ice bath was removed and the mixture was stirred at 50°C for 1h. After that, the system was decreased to room temperature, added 80ml H₂O for the strong reaction, continuous stirring in 1h.

4. H₂O (200 ml) was added to dilute the solution and continuous stirring. H₂O₂ (40 ml) was added into the solution for finishing the reaction and the resulting suspension has a bright yellow color (graphite oxide solution).

5. The filter extraction process to obtain pure graphite oxide; the solution was stable and settled for 24 h at 10°C, washed by centrifugation with 10% HCl and then with deionized (DI) water several times until it forms a gel-like substance (pH~7).

6. Graphite oxide after being separated, diluted with solvent ethanol-acetone (1: 1), the graphite oxide was exfoliated into graphene oxide (GO) sheets by ultrasonication for 30 minutes. The as-obtained yellow-brown aqueous suspension of GO was stored at room temperature.

3. RESULTS AND DISCUSSION

3.1. SEM analysis

Graphite and GO samples are analyzed by SEM image (at Institute of Materials science-IMS, VAST), fig 3 shows that graphite powder form is closely packed bulk before oxidation.

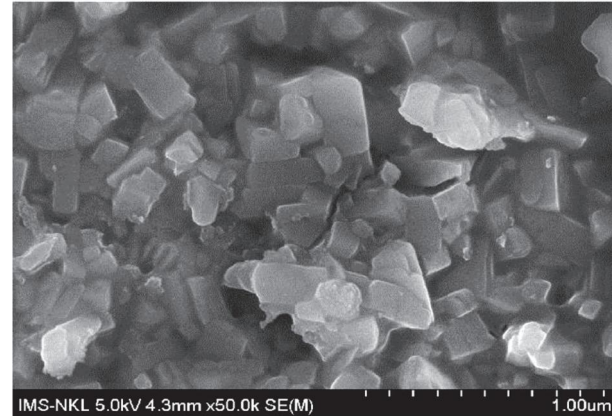


Figure 3. SEM image of graphite powder

After oxidation, layers of graphite are separated (fig 4) with a thickness of 50 nm, and their bonds are weaker [8].

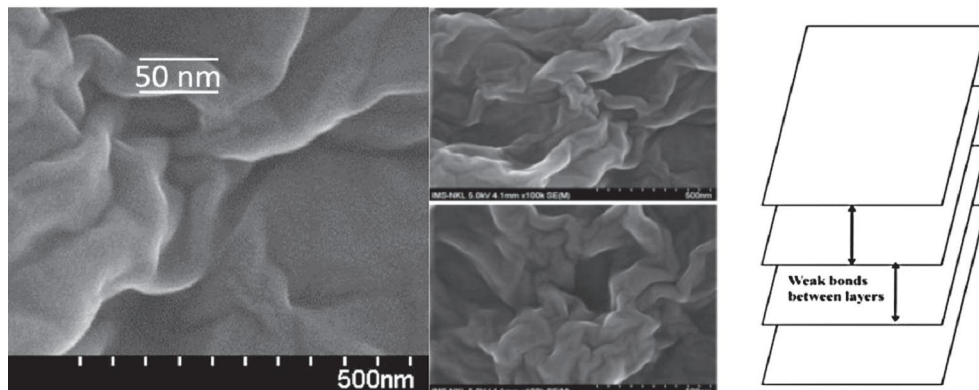


Figure 4. The graphite was exfoliated

The solution of GtO after centrifugation (pH ~ 7) was dispersed in a polar solvent and ultrasonic vibrations to achieve GO plates (Fig 5).

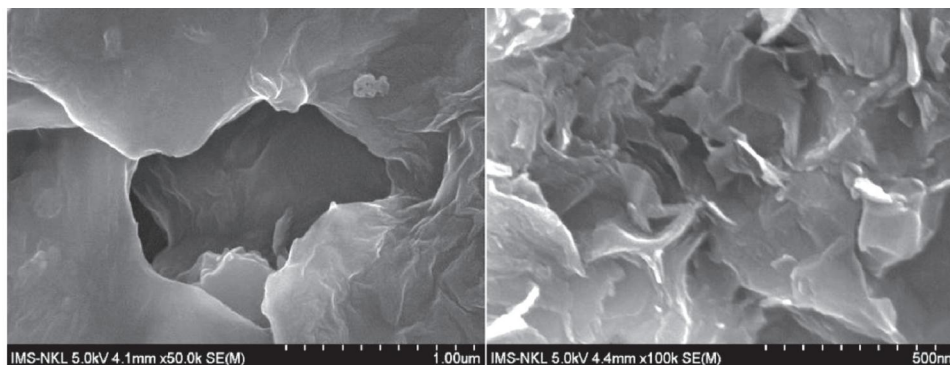


Figure 5. The GO sheets with multi-layers in solvent

Results show that GO plates, and plates are multi-layers separated but still overlap.

3.2. Dynamic light scattering (DLS) analysis

Dynamic light scattering (DLS) is a

technique in physics that can be used to determine the size distribution profile of small particles in suspension or polymers in solution [9].

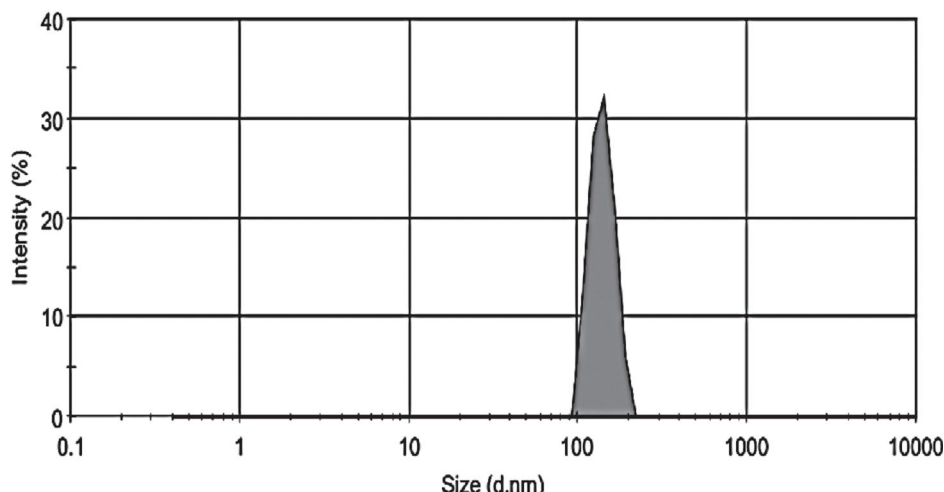


Figure 6. Size distribution of GO

The result of the GO size distribution shows that the sample has the uniform distribution with an average size of 140 nm.

3.3. FTIR spectral analysis

The FTIR results are used to investigate the bonding interactions of the oxidation from graphite to GO. The intensity of the peaks corresponding to amount of functional groups (Fig 7).

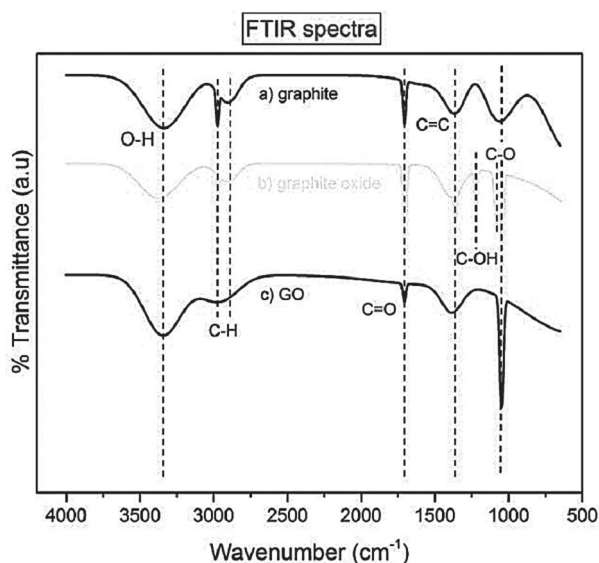


Figure 7. FTIR spectrum of Gt (a), GtO (b) and GO (c).

Figure 7 shows the FTIR spectra of graphite, graphite oxide, graphene oxide.

On spectra, the oxidation is confirmed by the appearance of several peaks attached to functional groups from Oxy. The different types of functionalities in graphite oxide (GtO) are determined at $3278 - 3384 \text{ cm}^{-1}$ (O-H stretching vibrations), at 2974 and 2890 cm^{-1} of C-H vibrations, stretching vibrations at 1730 cm^{-1} of C=O at the edge of graphite layers [10], at 1400 cm^{-1} of C=C bonds, at 1220 cm^{-1} shows the C-OH stretching vibrations while no peak are found in graphite. The result shows that the oxidation occurs on graphite layers, and this functional group is also lost or decreased on GO spectrum, this may be due to the effect of ultrasound during the separation of single-layers. Besides that, the oxidation of graphite oxide to GO also increases the peak intensity at 1050 cm^{-1} , it prove that a large amount of C-O bonds appear on GO.

4. Conclusion

Via modified Hummer's method, this work showed that Graphene oxide can be obtained by the simple and convenient method. Besides that, the analysis results confirmed the existence of oxygen functional groups, the

exfoliation of graphite sheets were confirmed by SEM images, as well as the nanoscale of GO powder by DLS measurement.

Thus, GO can continue to synthesis by this manufacturing, this GO product will be

studied to control functional groups, applied in the specific areas. In addition, GO will be used as an intermediate product for the synthesis of GO, approach to graphene with many interesting properties

REFERENCES

1. A. K. Geim and K. S. Novoselov, The rise of graphene. *Nat. Mater*, 6 (2007), 183–191
2. Wonbong Choi, Jo-won Lee. Graphene- synthesis and application. International Standard Book Number-13, (2012). 978-1-4398-6188-2 (eBook - PDF)
3. Brodie BC. Sur le poidsatomique du graphite. *Ann ChimPhys* 1860;59:466–72
4. Hummers W, Offeman R. Preparation of graphitic oxide. *J Am ChemSoc* 1958;80:1339
5. Staudenmaier L. Verfahrenzurdarstellung der graphitsaure. *BerDtschChemGes* 1898;31:1481–99
6. Sasha Stankovich, Dmitriy A. Dikin, Richard D. Piner, Kevin A. Kohlhaas, Alfred Kleinhammes , YuanyuanJia, Yue Wu, SonBinh T. Nguyen, Rodney S. Ruoff. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45 (2007) 1558–1565.
7. William S. HummersJr., Richard E. Offeman. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.*, 1958, 80 (6), pp 1339-1339
8. Ayrat M. Dimiev and James M. Tour. Mechanism of Graphene Oxide Formation. *ACS Nano*, 2014, 8 (3), pp 3060–3068
9. Berne, B.J.; Pecora, R. *Dynamic Light Scattering*. Courier Dover Publications (2000) ISBN 0-486-41155-9
10. Blanco, M.; Alvarez, P.; Blanco, C.; Jimenez, C.V.; Perez-Torrente, P.; Oro, L.A.; Menendez, R. Graphene-NHC-iridium hybrid catalysts built through –OH covalent linkage. *Carbon*, 83, 21-31, (2015).
11. Eun-Young Choi, Tae Hee Han, Jihyun Hong, JiEun Kim, Sun Hwa Lee, HyunWook Kim andSang Ouk Kim. Noncovalent Functionalization of Graphenewith End-Functional Polymers. *J. Mater. Chem*, 2010,20, 1907-1912