

# Optimization of the Oxidation Temperature of Graphene Oxide

Nuruzzaman Sakib, Mohd. Mahfuzur Rahman, Md. Hasan Ali  
Department of Mechanical Engineering  
Bangladesh University of Engineering and Technology (BUET),  
Dhaka, Bangladesh

**Abstract**— Graphene Oxide (GO) is the precursor of Graphene. Hummers method is the most common methods for the preparation of GO. Researchers are heading towards the improved Hummers method because of high efficiency and environment friendly emissions than conventional Hummers method. The optimum ratio of graphite and  $KMnO_4$  and oxidation time for the preparation of GO using  $H_2SO_4$  and  $H_3PO_4$  mixture based on modified Hummers method are already determined. In this investigation, our main aim is to determine the optimum oxidation temperature using  $H_2SO_4$  and  $H_3PO_4$  mixture based on modified Hummers method. The GO obtained by varying oxidation temperatures such as 35°C, 45°C and 55°C is characterized using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and UV-vis spectroscopy. The XRD pattern for the GO shows an intense and sharp diffraction peak at 9.209°, 8.985°, 9.011° that is attributed to the (001) lattice plane, which corresponds to a d-spacing of 0.960 nm, 0.983 nm and 0.980nm, respectively. We observed maximum d-spacing (0.983 nm) for GO sample prepared for 45° oxidation temperature. Furthermore, the structural investigations using powder XRD reveals the hexagonal crystallographic phase of GO. Scanning Electron Microscope (SEM) is used to obtain information about the surface topography and composition. The structure of the synthesized GO was confirmed by Scanning Electron Microscopy (SEM). From UV-vis spectra of GO samples, absorption peaks are found at ~ 210-230 nm, which is attributed to the  $\pi \rightarrow \pi^*$  transition of the C-C bonds. This peak corresponds to the confinement of carbon rings on the basal plane. It gives the amount of energy required by the electrons for  $\pi \rightarrow \pi^*$  transitions. Therefore, suitable reaction temperature for the synthesis of GO should be 45°C according to aforementioned systematic analysis. The outcome of this investigation may be helpful for large-scale and low-cost production of graphene-based materials and their composites to meet the demands of technological applications.

**Keywords**— Graphene; Hummers' method; oxidation temperature; optimization ; nanotechnology

## I. INTRODUCTION

The thickness of graphene is one atomic. It seems sheet like shape of  $sp^2$ -hybridized carbon atoms which are arranged in a hexagonal lattice in the honeycomb form. Its stability is very high due to its tightly packed carbon atoms and a  $sp^2$  orbital hybridization(  $s$ ,  $p_x$  and  $p_y$  orbitals hybridization) that establish the  $\sigma$ -bond. The final  $p_z$  electron constitutes the  $\pi$ -bond. Hybridization occurred in  $\pi$ -bonds to form the  $\pi$ -band and  $\pi^*$ -bands. These bands are responsible for excellent electronic properties of graphene [1]. Graphene is high electricity conductive material because of its less energy gap between conduction and valence bands. Graphene has an enormous application in various field due to its excellent

electrical, mechanical, optical and thermal properties such as high conductivity, 98% transparency, 100 GPa ultimate strength, a stretching performance of 6% strain resistance [2] [3] [4]. Its specific surface area is high enough and high gravimetric energy density which is 2600 Whkg<sup>-1</sup> [5]. Its mobility is (200000 cm<sup>2</sup> v<sup>-1</sup>s<sup>-1</sup>) [6]. At the very first time, Brodie prepared graphite oxide in 1859 by using the mixture of graphite, potassium chlorate and fuming nitric acid [7]. Due to the emission of noxious gases and limitation of size, thickness, Staudenmaier kicked off a new method of GO synthesis in 1894 on which he added potassium chlorate into the mixture of graphite, concentrated Sulphuric acid ( $H_2SO_4$ ) and concentrated nitric acid ( $HNO_3$ ) [8]. Two third of fuming nitric acid was substituted by concentrated sulfuric acid ( $H_2SO_4$ ) and potassium chlorate was added in that method. By performing small modification, required oxidation time was reduced. But noxious gases such as chlorine dioxide, carbon dioxide, nitrogen were present at that time. Considering all this negative aspects Hummers introduced a new method for GO synthesis in 1958. He used graphite  $KMnO_4$ ,  $H_2SO_4$  and  $HNO_3$  [9]. Another modification was introduced in 1995 on which they varied oxidation time from 24 to 240 h and found 120 h as optimized oxidation time [9]. GO was produced by using  $H_2SO_4$ ,  $H_3PO_4$  with graphite and  $KMnO_4$  in 2010. They focused on the concentration of graphite and  $KMnO_4$ . Oxidation time and concentration of oxidizing agents have been optimized already [10]. In the present work we tried to determine an optimized oxidation temperature in which we could find high oxidation rate, large inter layer space, small particle size by using mixture of  $H_2SO_4/H_3PO_4$  based on eco-friendly improved Hummers method.

## II. METHODOLOGY

First of all oil bath was set at the definite optimization temperature for saving time. 360 ml  $H_2SO_4$  and 40 ml  $H_3PO_4$  was mixed in a round bottom flask and 3g graphite flakes was added to the mixture. Next, the flask was moved into an ice bath and 18 g  $KMnO_4$  was slowly added. The temperature was controlled by the ice bath lower than 15°C because the reaction was exothermic and there was a huge chance of explosion if the temperature remained uncontrolled. After the addition of  $KMnO_4$ , the mixture solution was transferred to oil bath and stirred for 6 hours at 35°C oxidation temperature. The mixture was cooled to room temperature and 400 ml ice was poured onto the mixture to dilute the mixture. Temperature rushed beyond 90°C after addition of ice because it helped to complete the oxidation reaction. The color of the mixture became dark brown at that time. After

that 30 vol.% 3 ml  $H_2O_2$  was added which engulfed the additional  $KMnO_4$ . The color turned into bright yellow from dark brown after adding  $H_2O_2$ .

The mixture was kept stable for 24 hours in the laboratory for ensuring accumulation of solid GO at the bottom of the flask. Next the solid GO was collected from the bottom of the flask. The filtrate was centrifuged at 5000 rpm for 10 minutes. Due to the centrifugal force the solid GO was accumulated at the wall of the tube and the supernatant was decanted away. After that it was urgent to wash the GO because of presence of some metal ions impurities like potassium ion, manganese ion etc. The solid GO was washed in succession with 200 ml  $H_2O$ , 200 ml of  $HCl$  and then 200 ml ethanol. For each wash, the mixture was centrifuged at 5000 rpm for 10 minutes.  $HCl$  removed the metal ions from the GO. For preparing other samples, oxidation time was kept constant (6 h) but oxidation temperature was varied. Following the same experimental procedure as above, other two samples were synthesized at 45°C and 55°C oxidation temperature respectively.

### III. CHARACTERIZATION

EDX gives the elemental information about the specimen. JSM-7600F Field Emission Scanning Electron Microscope was used for EDX. It is non-destructive technique having a sensitivity of 0.1% for elements heavier than C. EDS detects X-rays produced from sample placed in an electron beam. This electron beam agitates the atoms in the sample that produce X-rays for discharging the excess energy. The energy of X-rays form peaks in the spectrum. This energy is used for the characterization of the atoms from which that energy is generated. EDX spectra can be collected from a specific point on the sample which provide information for few cubic microns of material. Other method is to sweep the beam over a selected area of the sample to identify the elements on that particular area.

The field emission scanning electron microscope (FE-SEM) takes image from a sample surface by raster scanning over it using high-energy electron beam. Interaction is occurred between the electrons and the atoms from sample which helps to produce signals that contain information about surface topography, composition and other properties. The main difference between the Scanning Electron Microscope (SEM) and the Field Emission Scanning Electron Microscope (FE-SEM) is the emitter type. Thermionic Emitters use electrical current to heat up a filament: the two most common materials used for filaments are Tungsten (W) and Lanthanum hexaboride ( $LaB_6$ ). FE scanning electron microscope (FESEM) is a very important tool for high resolution imaging of surface in the fields of nano materials. Panalytical Empyrean is the instrument used for XRD test. X-ray diffraction has been mainly used for two different purposes: characterization of the fingerprint of crystalline materials and for determining of their structure. Each crystalline solid has its unique and identical X-ray powder pattern which is used as the fingerprint for its distinction. The atoms pack in crystalline state, the value of inter atomic distance and angle are determined by X-Ray crystallography. When a beam of X-rays illuminates a single

crystal, a lot of spots are created in the plane. The positions of the spots depends on the size and shape of the unit cell and the symmetry. In the diffraction pattern, the effect is that each of the spots is spread out into a ring. If the crystallites are oriented randomly, the rings are uniform, and no information is lost by measuring along a radius vector of the complete 3-dimensional diffraction pattern. The diffraction process occurs when the Braggs law (condition) is satisfied. It is expressed as:

$$n\lambda = 2d\sin\theta$$

Where,

- $\lambda$  is the wavelength of x-rays
- $d$  is the inter planar spacing
- $\theta$  is the x-ray angle
- $n$  is an integer

Shimadzu UV-2600 is used for Ultraviolet Visible Spectroscopy testing. Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. Unsaturated group is indispensable for these transitions in the molecule to provide the  $\pi$  electrons. Peaks found from  $n$  to  $\pi^*$  transitions are shifted to shorter wavelengths with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the  $n$  orbital. For  $\pi$  to  $\pi^*$  transitions reverse is occurred.

### IV. RESULTS

XRD patterns of Graphite, GO-I, GO-II and GO-III are shown in Fig. 1a, Fig. 1b, Fig. 1c, Fig. 1d respectively. The diffraction peak of Graphite is observed at  $2\theta=26.46^\circ$  corresponding to the (002) plane which is no longer can be detected in GO-I, GO-II and GO-III. The XRD pattern of GO-I exhibit a strong and sharp peak at  $2\theta=9.209^\circ$ , GO-II exhibit a strong and sharp peak at  $2\theta=8.985^\circ$  and GO-III exhibit a strong and sharp peak at  $2\theta=9.011^\circ$  corresponding to the (001) plane [11]. Inter-layer distances of GO-I is 9.60Å, GO-II is 9.83Å, GO-III is 9.80Å and Graphite is 3.36Å. Interlayer distance obtained for Graphite and GO samples matches the earlier reported interlayer distance. The larger inter-layer distances of GO samples are larger due to the formation of oxygen containing functional groups such as hydroxyl, epoxy and carboxyl in graphite layers [12].

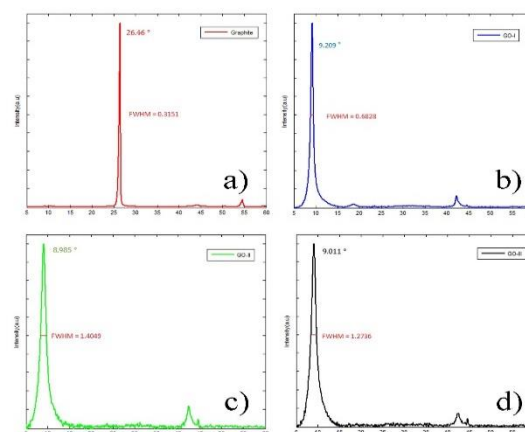


Fig. 1. X-Ray Diffraction Patterns

The XRD patterns of GOs are found at 3 oxidation temperatures which are depicted in Fig. 1. The position of diffraction peaks illustrates that the range of inter-layer space is from 0.960 nm to 0.983 nm. With the increase of oxidation temperature, the increase of interlayer space is obvious. The distinction of interlayer space of GOs reaction at 45°C is not obvious, but higher than the interlayer spaces at 35°C and 55°C which indicates the effect of increasing temperature to expand the interlayer space is weak. Therefore, suitable reaction temperature for the synthesis of GO should be 45°C according to the abovementioned analysis.

FWHM of prepared GO samples and Graphite are listed in the table below:

TABLE I. FWHM OF GO SAMPLES AND GRAPHITE

Sample	Temperature	FWHM
Graphite	-	0.3151
GO-I	35	0.6828
GO-II	45	1.4049
GO-III	55	1.2736

From the lattice sum over the entire crystal atoms, X-ray peak is obtained. In ideal crystals, delta function on coherent spectral wavelength is generated due to the sum which is over infinite number. The lattice sum is unable to converge to a diffraction line due to less atoms of nano particles but broaden out. The smaller the particle the broader the diffraction peak. From the Table I, all the peaks of GO samples are broader than Graphite. With increased temperature the peak of GO-II is broader than GO-I. But GO-III is less broader than GO-II, which means that the particle size of Go-II is the smallest of all GO samples. The UV-Visible absorption spectra of GO-I, GO-II and GO-II are shown in Fig. 2.

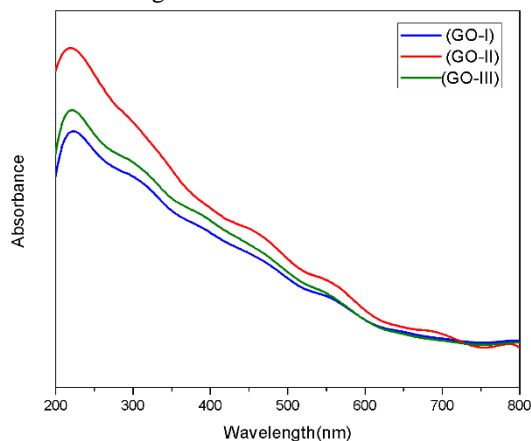


Fig. 2: UV-vis Spectroscopy of Graphene Oxide Samples

Two shoulders were observed in these spectra. The first shoulder is observed at ~ 300 nm, which is due to  $n \rightarrow \pi^*$  transition of the carbonyl groups (C=O) [13]. Another shoulder is found at approximately 210 to 225 nm, and corresponds to a  $\pi \rightarrow \pi^*$  transition for the C=C bonding. As seen from the (Fig. 2), the intensity of the peak of each sample is different. The sample formed at 35°C shows a

single less intense peak at 220 nm, while the sample GO-II which formed at 45°C shows a strong peak as a high shoulder at 214 nm. The sample GO-III obtained at 55°C showed a less intense peak than GO-II at 218 nm. The higher the intensity, the larger the degree of oxidation of GO whereas the less intensity is for less degree of oxidation [14]. So we come to a conclusion that GO-II is more oxidized than other GO samples.

EDX spectra of GO-I, GO-II and GO-III are shown in the Fig. 3a, Fig. 3b and Fig. 3c respectively.

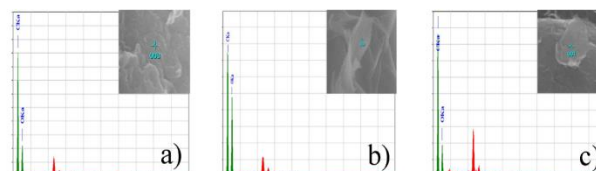


Fig. 3. EDS spectra of GO samples

From the above figures, it is obvious that oxygen content is in greater amount in the second sample (GO-II), that is because of high degree of oxidation but after certain temperature it decreases as the chemical reaction is very exothermic.

SEM images of as prepared GO samples are presented in Fig. 4a, Fig. 4b and Fig. 4 c.

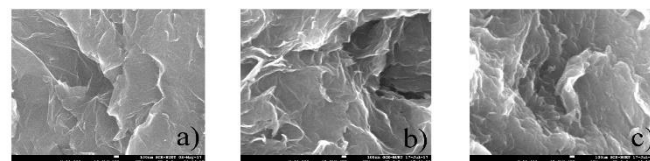


Fig. 4. a) SEM image GO-I b) SEM image GO-II c) SEM image GO-III

From the above figures GO structure is confirmed. This Scanning Electron Microscopy (SEM) in Fig. 4a, Fig. 4b and Fig. 4c, we ensure that a morphological structure is formed by several thick layers in regular patterns and characteristic stacking. The oxidation of Graphite changes in their morphology. It has a wrinkled appearance with multiple folds. This wrinkled appearance helps the oxidation process to promote the addition of functional groups. These functional groups alter the hybridization of the carbon  $sp^2$  (planar structure) to  $sp^3$  (tetrahedral structure). However, the structures formed layers are due to the degree of oxidation. High spaced functionalized layers are due to the high degree of oxidation.

## V. CONCLUSION

This improved method eliminates the generation of noxious gasses and makes the procedure of purification of GO samples easy, decreases the cost of GO synthesis. We found the sample with 45°C oxidation temperature gives the best interlayer distance (9.83Å) and also showed high oxygen functional groups than the other GO samples (prepared for 35°C and 55°C of oxidation temperature). More importantly the functional groups on GO surface offer feasible ways to further composite with other species to improve the  $H_2$  binding energy. High interlayer space helps to store  $H_2$ . The

peak of GO-II is broader than GO-I and GO-III which ensures small particle size for the GO-II. Small particle can transfer high heat for larger surface area that's why small particle can be used in magnetic refrigeration system and boiling processes. For GO-II the intensity is found higher than GO-I and GO-III which means higher degree of oxidation for sample GO-II. High oxidation indicates high band gap and limited absorption of light. Layers of GO samples are investigated from the FESEM. This layers resulted from the oxidation of GO samples.

#### ACKNOWLEDGMENT

The success and final outcome of this project required a lot of guidance and assistance from many people and we are extremely privileged to have got this all along the completion of our project.

We heartily thank Dr. Md. Ashiqur Rahman, Associate Professor, Department of Mechanical Engineering, BUET, Dhaka for his continuous support and guidance as a supervisor.

We would like to acknowledge the support provided by the Nanotech Research Group especially by Dr. MA Basith, Professor, Department of Physics, BUET, Dhaka.

#### REFERENCES

- [1] Daniel R. Cooper, Benjamin D'Anjou, Nageswara Ghattamaneni, Benjamin Harack, Michael Hilke, Alexandre Horth, Norberto Majlis, Mathieu Massicotte, Leron Vandsburger, Eric Whiteway, and Victor Yu , "Experimental review of graphene", *ISRN Condensed Matter Physics*, 2011.
- [2] Changu Lee, Xiaoding Wei, Jeffrey W. Kysar and James Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene". *Science*, 2008.
- [3] Lee GH, Cooper RC, An SJ, Lee S, van der Zande A, Petrone N, Hammerberg AG, Lee C, Crawford B, Oliver W, Kysar JW and Hone J, "High-strength chemical-vapor-deposited graphene and grain boundaries", *Science*, 2013.
- [4] Sukang Bae, Hyeongkeun Kim, Youngbin Lee, Xiangfan Xu, Jae-Sung Park, Yi Zheng, Jayakumar Balakrishnan, Tian Lei, Hye Ri Kim, Young Il Song, Young-Jin Kim, Kwang S. Kim, Barbaros Özyilmaz, Jong-Hyun Ahn, Byung Hee Hong and Sumio Iijima , "Roll-to-roll production of 30 inch graphene films for transparent electrodes", *Nat.Nanotechnol.*, 2010.
- [5] Xia J, Chen F, Li J and Tao N, "Measurement of the quantum capacitance of graphene", *Nat.Nanotechnol.*, 2009.
- [6] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene", *Rev Mod Phys*, 2009.
- [7] B.C Brodie, " On the atomic weight of graphite", *Phil. Trans*, 1859.
- [8] L Staudenmaier, "Verfahren zur darstellung der graphitsaure", *Nanoscale*, 1898.
- [9] W.S. Hummers and R.E. Offman, "Preparation of graphitic oxide", *J. Am. Chem.Soc.*, 1958.
- [10] Shivangi Kosta, Prema Bansal and Niroj Kumar Sahu, "Improved oxide ion of graphite by optimizing the oxidation time and concentration of oxidizing agent for cellular sensing", *SSN*, 2016.
- [11] Marwa Fathy, Aya Gomaa, Fatma A. Taher, Magda M. El-Fass, Abd El-Hady and B. Kashyout, "Optimizing the preparation parameters of go and rgo for large-scale production" *J Mater Sci*, 2016.
- [12] Harish V Kumar, Steven Woltornist, Steven Woltornist and Douglas H. Adamson , "Fractionation and characterization of graphene oxide by oxidation extent through emulsion stabilization", *Carbon*, 2015.
- [13] Daniela C. Marcano, Dmitry V. Kosynkin, Jacob M. Berlin, Alexander Sinitskii, Zhengzong Sun, Alexander Slesarev, Lawrence B. Alemany, Wei Lu and James M. Tour, "Improved synthesis of graphene oxide", *ACS Nano*, 2010.
- [14] Shuge Peng, Xinjie Fan, Shuang Li and Jun Zhang, "Green synthesis and characterization of graphite oxide by orthogonal experiment", *J Chil Chem Soc*, 2013.