Green Synthesis of Reduced Graphene Oxide Using Ascorbic Acid

Hayder A. Hessain, J. J. Hassan[*]

Physics Department, College of Science, University of Basrah, Basrah, Iraq

Abstract

A green and low-cost method was used to prepare graphene oxide (GO) and reduced graphene oxide (rGO) by chemical exfoliation of graphite powder by modified Hummers method, followed by reduction using ascorbic acid. X-ray diffractometry (XRD) and field emission scanning electron microscopy (FE-SEM) were used to analyze the structure and morphology of the synthesized materials. Fourier transform infrared spectroscopy (FTIR) and ultraviolet-visible spectroscopy were used to identify the formation of the GO and rGO.

Keywords: graphene oxide, reduced graphene oxide, XRD, SEM, ascorbic acid.

التحضير الصديق للبيئة للكرافين اوكسايد المختزل بواسطة فيتامين سي

حيدر عادل حسين ،جلال جبار حسن[*]

قسم الفيزياء، كلية العلوم، جامعة البصرة، البصرة، العراق

الخلاصة

تم تحضير أوكسيد الكرافين (GO) واكسيد الكارافين المختزل (rGO) بطريقة مبسطة وغير مكلفة بواسطة التقشير الكيميائي لمسحوق الغرافيت باستعمال طريقة هيومر (Hummers Method) ثم اختزال محلول أوكسيد الكرافين المحضر بطريقة صديقة للبيئة باستعمال فيتامين C . تم تحليل التركيب البلورية وهيئة السطح للمادة المحضرة باستعمال جهاز حيود الاشعة السينية (XRD) والمجهر الالكتروني الماسح (FE−SEM). من خلال تقنية التحليل الطيفي بالأشعة تحت الحمراء (FTIR) ومطياف الاشعة المرئية وتحت الحمراء (UV−Vis) تم تشخيص تكون الكرافين اوكسايد والكرافين اوكسايد المختزل.

1. Introduction

Research on the monolayer sheets of graphene oxides (GO) has been very extensive because of their remarkable properties and multiple applications [1]. In addition, GO is the basis for the synthesis of reduced graphene oxide (rGO), which is considered as the most similar structure to the graphene material. Graphene is well known as a single sheet of graphite that is composed of planar sp_2 hybridized carbon atoms [2, 3]. Recently, the graphene family has gained an increasing interest of scientists and engineers because of its extraordinary properties. These properties included the good electrical conductivity (room-temperature electron mobility of 2.5×10^5 cm^2 V^{-1} s^{-1}) [4], high Young's modulus (~ 1.0 TPa) [5], large theoretical surface area (2630 m^2 g^{-1}) [6], high intrinsic mobility (200000 cm^{2}v^{-1}s^{-1}) [7], optical transmittance ($\sim 97.7\%$) [8] and thermal conductivity (~ 5000Wm^{-1}K^{-1}) [9]. Graphene oxide has broad applications in diverse fields, including the

---

*Email: j.j.hassan@uobasrah.edu.iq

manufacturing of various electronic devices such as flexible displays, supercapacitors, and transistors [10]. Furthermore, GO is also used in other applications, such as organic electronics, photodetectors, storage, fuel cells, water filtration, and drug delivery[11]. On the other hand, several types of chemical and physical processes were reported for the preparation of grapheme, including chemical exfoliation, mechanical exfoliation, and chemical vapor deposition [12, 13]. The basic differences between these different methods are related to the quality and cost of their products. However, the most effective processes for the production of graphene in large scale are the exfoliation of graphite to GO, followed by the reduction of the resulting product. On the other hand, GO has recently emerged as one of the carbon nanomaterials which shows properties similar to graphene and received an increasing attention due to its low cost, easy access, and widespread ability to convert to graphene. It is made of graphite crystals that have been oxidized to intersperse the carbon layers with oxygen molecules. The graphene oxide nanosheet is similar to graphene, but it contains oxygen functional groups at its ends, such as phenolic hydroxyl, carboxylic, and epoxide groups. GO was prepared by the oxidation process of graphite powder or flakes using strong oxidant agents and concentrated acids. Many scientists, such as Brodie [14], Staudenmaier [15], Hummer [16], and Tour [17] developed many processes to synthesis GO. On the other hand, the preparation of rGO from GO can be achieved by the disposal of the defects resulting from the oxidation process, where the goal of the reduction process is to obtain a graphene-like material in properties and structure. There are many methods for the reduction of GO, such as the thermal [18], optical [19], and chemical methods [20]. Among these methods, the chemical is the most popular and depends on many types of reducing agents, such as the strong alkaline hydrazine [21], hydroquinone, sulfur-containing compounds [22], sodium borohydride [23], hydrohalic acids [24], and green agents such as ascorbic acid[25]. In this work, we performed an oxidation process using the hummers method to produce GO, followed by an antioxidant process using the green chemical ascorbic acid to obtain rGO.
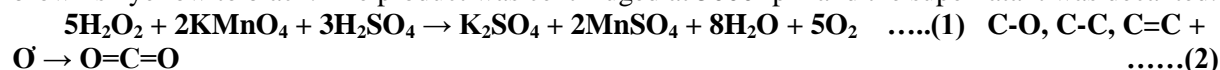
2. Experimental part
2.1 Materials
3. Potassium permanganate ($KMnO_4$, Merck), pure graphite powder (50 micrometer), sulfuric acid (H_2SO_4, 99.9%) (GCC), hydrogen peroxide (H_2O_2, 30%), Riedel-de Haen) and sodium nitrate ($NaNO_3$) with high purity were used without additional purification.

3.1 Synthesis of graphene oxide
Graphene oxide was prepared from the natural pure graphite powder by the oxidation method (Hummer method) [26, 27]. In this method, a mixture of graphite powder (1g) and $NaNO_3$ (1g) was kept at 0 °C using water ice surrounding the reaction vessel. Subsequently, concentrated H_2SO_4 (50 mL) was added to the mixture with strong stirring for 3 hours, followed by gradually adding potassium permanganate (6 gm) with stirring. The water ice was removed after one hour and the solution was kept at 35°C for 3 days to allow the oxidation reaction of graphite. The color of the mixture changed from dark purplish green to dark brown. Then, the mixture was placed inside an ultrasound bath for 10 min for the peeling of the graphite sheets. Later, the mixture was cautiously diluted with 100 mL distilled water. Then, 10 mL of 30% hydrogen peroxide H_2O_2 solution was added with continuous stirring for 2 hours to end the oxidation process. The color of the mixture changed to bright yellow indicating a high oxidation level of graphite. Finally, the washing process was performed to remove all residual contamination from the product. Ascorbic acid was used to capture the oxygen ions from GO and convert it to rGO [28]. A mixture of 50 ml of GO solution and 0.1 M ascorbic acid was prepared, heated at 70 °C on the heating plate, and stirred for 2 hours. The color of the solution changed from brownish yellow to black. The product was centrifuged at 5000 rpm and the supernatant was decanted.

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 \quad …..(1)$$

$$C\text{-}O, C\text{-}C, C=C + \dot{O} \rightarrow O=C=O \quad ……(2)$$

3.2 Characterization
Crystal structure of GO and rGO was characterized by X-rays diffraction (XRD). The X-ray was generated by copper (Cu) target with CuKα wavelength of 1.5443 Å, voltage of 40 KV, and 20 mA. The sample was scanned at 2θ in the range of 10°- 80°. The surface morphology of the prepared GO and rGO was examined by the FE-SEM (model FEI nanosem nova 450). Optical properties of samples were recorded by the Shimadzu 1800 UV-Vis spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) was performed to study the chemical composition and to identify functional groups in a molecule over the wave number range of 400-4000 cm^{-1} using the KBr Disc method.

4. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD)

XRD is a helpful test to determine crystalline structures and interlayer distances of materials using the Bragg angle. XRD patterns of graphite, GO, and rGO are compared and shown in Figure-1. The XRD pattern of GO shows a strong and sharp diffraction peak at 2θ = 10.783 with an interlayer distance of 0.820 nm (001) [29]. This peak is related to the insertion of oxygen atoms between graphite layers that result from the oxidation process of graphite powder. In addition, one can notice the broad and low intensity peak at 2θ = 24.96. On the other hand, after reduction of GO, the 002 peak gradually disappeared, whereas the broad diffraction peak was observed in 2θ =24.96 (d = 3.56 Å), which matches the date card of graphite (JCPDS Card NO.75-1621) [30]. This shift in the interlayer spacing is due to the reduction of the GO, where the reduction makes the rGO packing tighter than that of GO due to the removal of most of oxygen atoms. In addition, the grain size was found to be 20.68 nm, as calculated by the following Scherrer equation.

$$D = \frac{K\lambda}{\beta Cos(\theta)}$$ ……………(1)

where:

D is the mean size of the ordered crystalline, K is a dimensionless shape factor with a value of about 0.9 but varies with the actual shape of the crystallite, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and Θ is the Bragg angle.

Table 1- XRD parameters for graphene oxide (GO) and reduced graphene oxide (rGO).

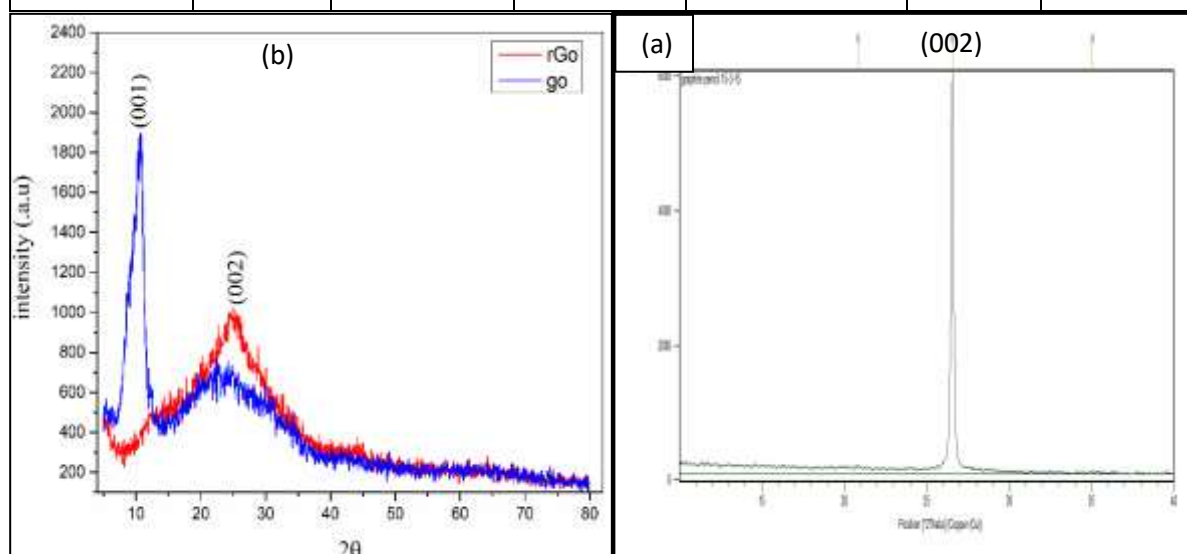|	POS [$^0 2\theta$]	FWHM [$^0 2\theta'$]	d-spacing [A0]	Height [cts]	D nm	Miller Index
GO	10.78	0.393	8.2045	1343	20.68	(001)
rGO	24.6	10.9	3.6059	350	-----	(002)

Figure 1- XRD patterns for (a) graphite powder, (b) graphene oxide (GO) (c) reduced graphene oxide (rGO).

3.2 UV-Vis absorption analysis

The absorption spectra of graphene oxide and reduce graphene oxide were analyzed by their suspension with water. The highest absorption peak was found at 226 nm due to the π–π* transition of the atomic C–C bonds [31], with a shoulder peak at ~300 nm which is attributed to n–π* transitions of the carboxyl (C=O) group [32] and the large non-oxidized graphite layers. The reduction of GO using ascorbic acid shifted the rGO peak to the highest absorption peak from 226 nm to 260 nm due to the removal of most of the oxygen functional groups.
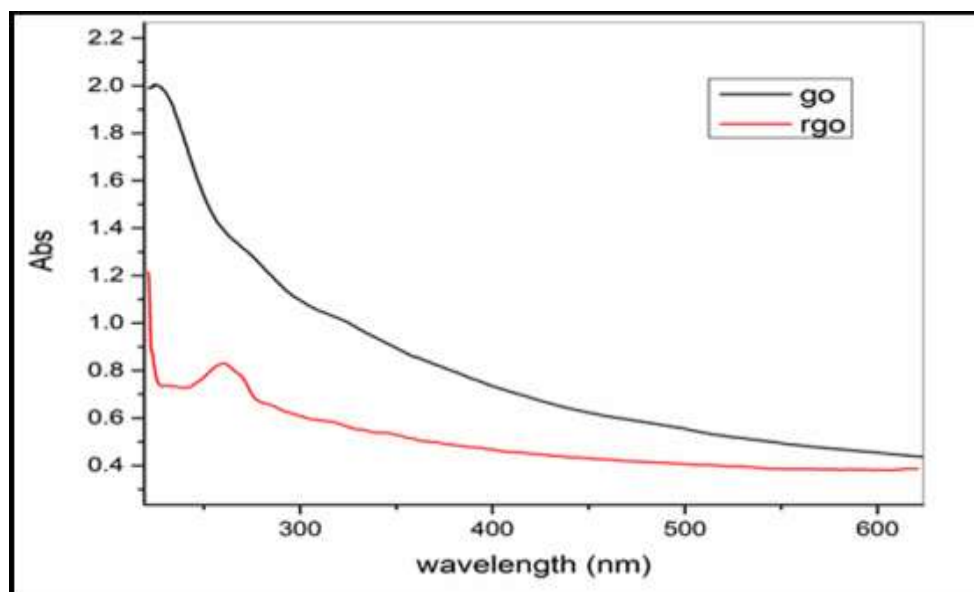
Figure 2- UV-vis spectra of GO (graphene oxide) and rGO (reduced graphene oxide).

3.4 Fourier-transform infrared spectroscopy (FTIR)

Figure-3 shows the FTIR spectra of the GO and rGO, respectively. As related to GO, we can observe a broad peak at 3418 cm^{-1} that is attributed to O-H stretching vibration and the water content of the sample [32]. Also, in the medium frequency zone, we observe the stretching carbonyl groups C=O at 1724 cm^{-1} with a peak at 1630 cm^{-1} that matches the C=C group [33]. Additionally, the peak at 1200 cm^{-1} corresponds to the stretching vibration of C–O–C [34]. On the other hand, in rGO spectra, we observe that some of the peaks decreased dramatically such as the peaks at 1637 cm^{-1} attributed to the C=O of epoxy group, most of them being vanished.
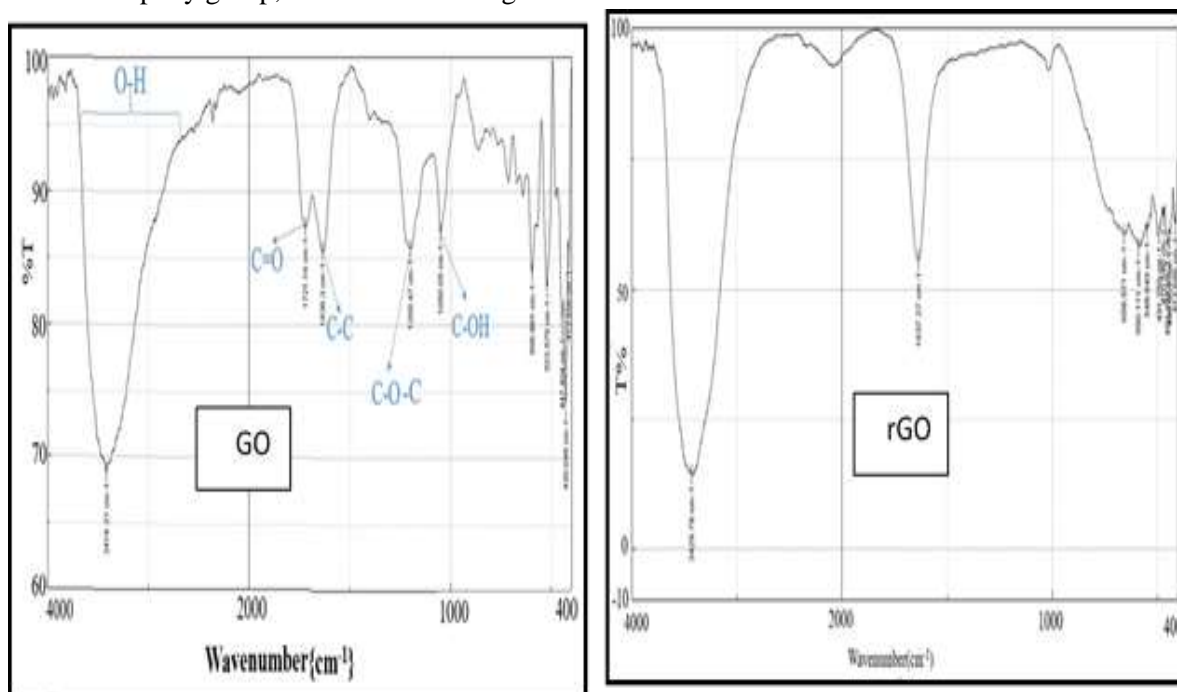

Figure 3- FTIR spectra of graphene oxide (GO) and reduced graphene oxide rGO.

3.5 Field Emission Scanning Electron Microscope (FE-SEM)

The surface morphology of GO and rGo was analyzed by the FE-SEM. The SEM images of plane GO and rGO are shown in Fig. 4. Most of these sheets are converted to smaller sizes with particles in multiple forms, such as spherical or semispherical, with very sharp edges and flat surfaces [35]. The dark gray areas consist of several layers of sheets along with kinked and wrinkled areas. After the

reduction of graphene oxide, different forms were obtained, such as the sphericaland semispherical with transparent and thin layers [36].
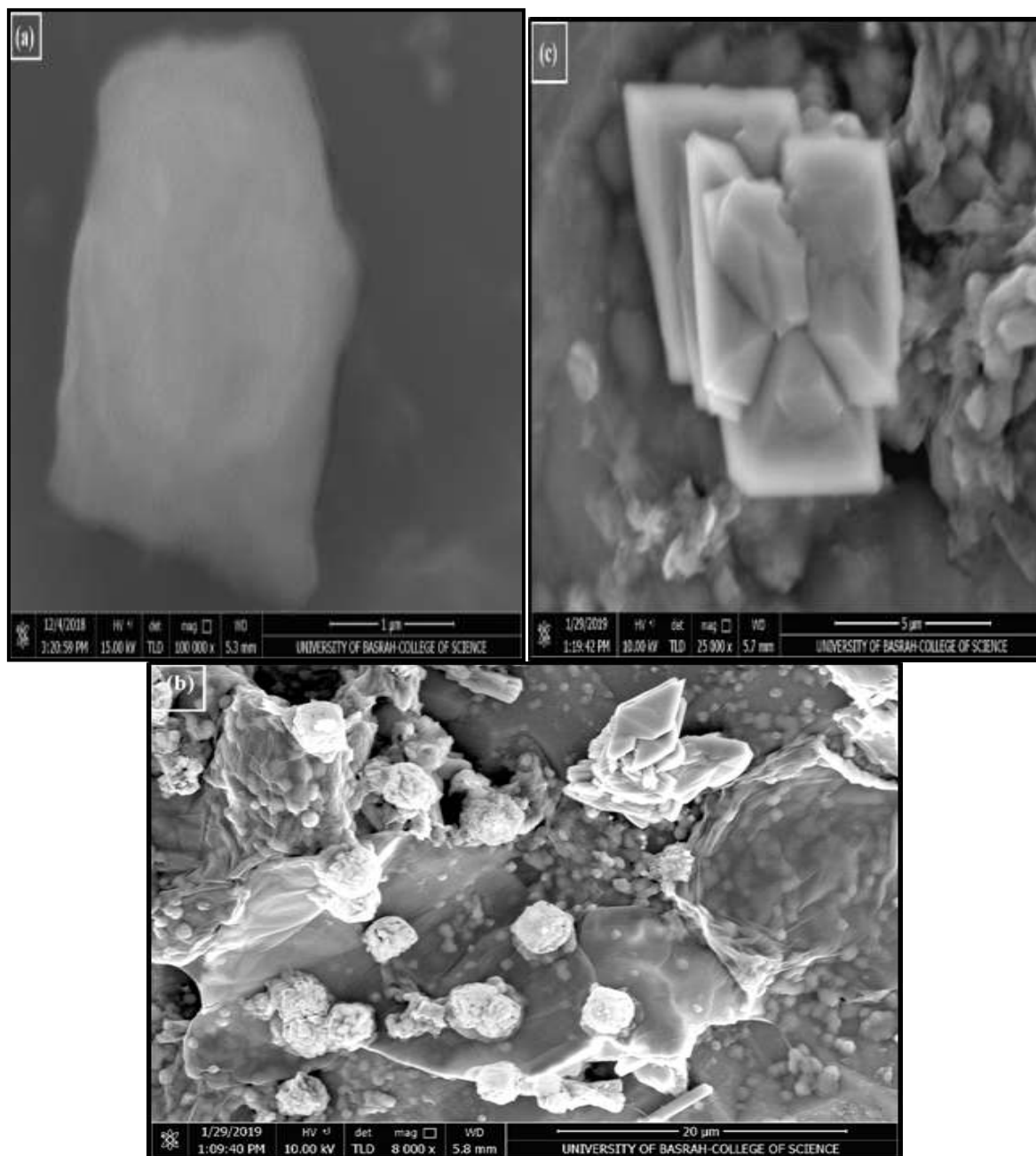

Figure 4- FESEM images of prepared (a) GO and (c,d) rGo.

Conclusion

In conclusion, graphene oxide (GO) was prepared successfully by chemical exfoliation of graphite powder using modified Hummer method. Then, GO was chemically reduced to rGO using ascorbic acid as a green reducing route. Both GO and rGO consisted of multiple layers of graphene sheets. The comparison between the FTIR spectra of GO and rGO showed that the chemical reduction is extremely effective in reducing GO to rGO.

ACKNOWLEDGMENTS

References

1. Bykkam, S., Rao, K.V. and Thunugunta, T. **2013**. Synthesis and characterization of graphene oxide and its antimicrobial activity against klebseilla and staphylococus. . *International Journal of Advanced Biotechnology and Research* **4.1** : 142-146.
2. Liu, S. **2011**. Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress. *ACS nano,*. **5**(9): 6971-6980.
3. Paredes, J. **2008**. Graphene oxide dispersions in organic solvents. *Langmuir*, **24**(19): 10560-10564.
4. Alam, S.N., Sharma, N. and Kumar, L. **2017**. Synthesis of graphene oxide (GO) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rGO). *Graphene,*. **6**(01): 1.
5. Lee, C. **2008**. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *science* **321**(5887): 385-388.
6. Zhu, Y. **2010**. Graphene and graphene oxide: synthesis, properties, and applications. *Advanced materials.* **22**(35): 3906-3924.
7. Bolotin, K.I. **2008**. Ultrahigh electron mobility in suspended graphene. *Solid state communications* **146**(9-10): 351-355.
8. Khan, Q.A. **2017**. Characterization of reduced graphene oxide produced through a modified Hoffman method. *Cogent Chemistry,*. **3**(1): 1298980.
9. Balandin, A.A. **2008**. Superior thermal conductivity of single-layer graphene. *Nano letters,*. **8**(3): 902-907.
10. Fan, T. **2015**. Controllable size-selective method to prepare graphene quantum dots from graphene oxide. *Nanoscale research letters,*. **10**(1): 55.
11. Abdolhosseinzadeh, S., Asgharzadeh, H. and Kim, H.S**. 2015**. Fast and fully-scalable synthesis of reduced graphene oxide. *Scientific reports,*. **5**: 10160.
12. Andrijanto, E. **2016**. "Facile synthesis of graphene from graphite using ascorbic acid as reducing agent.*" AIP Conference Proceedings.* **1725**(1). AIP Publishing,
13. Whitener Jr, K.E. and Sheehan, P.E**. 2014**. Graphene synthesis. *Diamond and related materials*. **46**: 25-34.
14. Brodie, B.C., *XIII.* **1859**. On the atomic weight of graphite. *Philosophical Transactions of the Royal Society of London,*. **149**: 249-259.
15. Starodub, E., Bartelt, N.C. and McCarty, K.F**. 2010**.Oxidation of graphene on metals. *The Journal of Physical Chemistry* C **114**(11): 5134-5140.
16. Yu, H. **2016**. High-efficient Synthesis of Graphene Oxide Based on Improved Hummers Method. *Scientific Reports,*. **6**: 36143.
17. Marcano, D.C. **2010**. Improved synthesis of graphene oxide. *ACS nano,*. **4**(8): 4806-4814.
18. Chen, W., Yan, L. and Bangal, P**.R. 2010**. Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves. *Carbon*. **48**(4): 1146-1152.
19. Lim, C.H.J. **2017**. Photoreduction of graphene oxides using a femtosecond laser: photothermal and photochemical contributions. Instead of Conference on Lasers and Electro-Optics/Pacific Rim. *Optical Society of America.* p. s1604
20. Guex, L.G. **2017**. Experimental review: chemical reduction of graphene oxide (GO) to reduced graphene oxide (rGO) by aqueous chemistry. *Nanoscale*. **9**(27): 9562-9571.
21. 21. Park, S. **2011**. Hydrazine-reduction of graphite-and graphene oxide. *Carbon.* **49**(9): 3019-3023.
22. Chen, W., Yan, L. and Bangal, P. **2010**.Chemical reduction of graphene oxide to graphene by sulfur-containing compounds. *The Journal of Physical Chemistry* C. **114**(47): 19885-19890.
23. Yang, Z.-z. **2015**. A simple method for the reduction of graphene oxide by sodium borohydride with CaCl2 as a catalyst. *New Carbon Materials,*. **30**(1): 41-47.
24. Kim, D. **2012**. Simple and cost-effective reduction of graphite oxide by sulfuric acid. *Carbon,*. **50**(9): 3229-3232.
25. Fernández-Merino, M.J. **2010**. Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions. *The Journal of Physical Chemistry* C,. **114**(14): 6426-6432.
26. Zaaba, N. **2017**. Synthesis of graphene oxide using modified hummers method: *solvent influence. Procedia engineering,*. **184**: 469-477.

27. Nanda, S.S., D.K. Yi, and Kim, K. **2016**. Study of antibacterial mechanism of graphene oxide using Raman spectroscopy. *Scientific reports*. **6**: 28443.

28. Zhu, X. **2012.** Reduction of graphene oxide via ascorbic acid and its application for simultaneous detection of dopamine and ascorbic acid. *Int. J. Electrochem. Sci,*. **7**: 5172-5184.

29. Loutfy, S.A. **2017**. Synthesis, characterization and cytotoxic evaluation of graphene oxide nanosheets: in vitro liver cancer model. Asian Pacific journal of cancer prevention*: APJCP,*. **18**(4): 955.

30. Zhang, J., Yang, H., Shen, G., Cheng, P., Zhang, J. and Guo, S. **2010**. Reduction of graphene oxide via L-ascorbic acid. *Chemical Communications*, **46**(7): 1112-4.

31. Krishnamoorthy, K. **2012**. Antibacterial activity of graphene oxide nanosheets. *Science of Advanced Materials*. **4**(11): 1111-1117.

32. Shahriary, L. and Athawale, A.A. **2014**. Graphene oxide synthesized by using modified hummers approach. *Int J Renew Energy Environ Eng,*. **2**(01): 58-63.

33. Bagri, A. **2010**. Structural evolution during the reduction of chemically derived graphene oxide. *Nature chemistry,*. **2**(7): 581.

34. Thakur, S. and Karak, N. **2012**. Green reduction of graphene oxide by aqueous phytoextracts. *Carbon,*. **50**(14): 5331-5339.

35. Loryuenyong, V. **2013**. Preparation and characterization of reduced graphene oxide sheets via water-based exfoliation and reduction methods. *Advances in Materials Science and Engineering,*.

36. Jaroensil, K., Thongpool, V. and Niamlang, S**. 2016**. Effect of Ascorbic acid Concentration on Electrical Conductivity of reduced Graphene oxide. 3rd International conference on Innovative Engineering Technologies (ICIET'2016) August 5-6, Bangkok (Thailand).