Journal of Applied Sciences and Nanotechnology, Vol. 2, No. 2 (2022)

Journal of Applied Sciences and Nanotechnology

Journal homepage: https://jasn.uotechnology.edu.iq/

A Physico-chemical Contribution to the Conventional Technique of Preparation Graphene Oxide

[1]Zainab Basim Abd*, [1]Nasser A. Habib, [2]Abbas Khammas

[1]Department of Applied Sciences, University of Technology – Iraq

[2]Nanotechnology and Advanced Materials Research Centre, University of Technology – Iraq

Article information

Article history:
Received: September, 24, 2021
Accepted: February, 08, 2022
Available online: June, 10, 2022

Keywords:
Graphene Oxide,
Hummers' Method,
Graphene Exfoliation,
Characteristics of GO

Corresponding Author:
Zainab Basim Abd
as.18.78@grad.uotechnology.edu.iq

Abstract

The modified Graphene Oxide (GO) synthesis methods used over the past sixty years is contributed mainly to improving its characteristics and increasing its advanced applications. Therefore, in this work, modifying Hummer's Method via oxidizing graphite flakes using one type of acid (H_2SO_4) was performed without any chemical agents. Also, ultra-sonication and filtration were implemented with optimal parameters (50 kHz frequency during 120 minutes at room temperature 30 ^oC) to prepare GO nanosheets. These procedures improved GO characteristics via analyzing; Particle size, X-ray diffraction pattern (XRD), Ultra-violet visible (UV-vis) absorption, and Scanning Electron Microscopy (SEM). The obtained results showed that the characteristics of GO nano-sheets had met the preparation requirements, such as reducing the average diameter of GO nano-sheets from 313 nm to 94 nm. Moreover, characterizing the diffraction angle of GO at 9.86^o and the optimal absorption by UV-vis achieved at 230 nm. The synthesis and exfoliation of GO nano-sheets were carried out with fewer impacts of toxicity using distilled water. Finally, this GO synthesis in the lab might be used to make a variety of nanocomposites.

DOI: 10.53293/jasn.2021.4296.1090, Department of Applied Sciences, University of Technology

1. Introduction

Graphene is a single layer (monolayer) of carbon atoms, tightly bound in a hexagonal honeycomb lattice. It is an allotrope of carbon in a plane of sp2-bonded atoms with a molecular bond length of 0.142 nm. Layers of graphene stacked on top of each other form graphite. The separate graphene layers in graphite are held together by Van der Waals forces, which can be overcome during the exfoliation of graphene from graphite [1, 5].

Several methods have been reported to produce graphene in small quantities, such as Chemical Vapor Deposition, Chemical peeling, Electrochemical peeling and Hammer method. Researchers seek to develop these methods; Hummer's Method is the most used technique for large amounts and low-cost production [6, 7]. In this method, a chemical process can be used (oxidation by acids) to generate graphite oxide. Local labs commonly use it as a reliable method of producing quantities of graphite oxide. Also, it can be revised to create a one-molecule-thick version of the substance known as graphene oxide. [8, 9] Hummer's Method was developed

in 1958 to produce graphite oxide. The production of graphite oxide was hazardous because of concentrated sulphuric, phosphoric and nitric acid [10-12].

The Staudenmeier–Hoffman–Hamdi (SHH) method [13-15] introduced potassium chlorate. However, this method had more hazards and produced one gram of graphite oxide to ten grams of potassium chlorate. Also, they did not use high temperatures to avoid the explosive risk of the (SHH) method. Nonetheless, after noting the risks, William and Richard created the above techniques. Their approach was similar to it involved adding graphite to a solution of concentrated acid. However, they simplified it to graphite, concentrated sulfuric acid, sodium nitrate, and potassium permanganate. The procedure starts with mixing graphite and sodium nitrate in sulfuric acid then cooled to 0 °C. $KMnO_4$ is then added to the solution and stirred. Adding water in increments until the final solution contains about 0.5% of solids to be cleaned of impurities and dehydrated with phosphorus pent-oxide [16].

Other groups have been focused on improving the Hummers' Method to make it more efficient and environmentally friendly. One such process is eliminating $NaNO_3$ from the process, and Nitrate elimination is also advantageous as it stops producing nitrogen dioxide and di-nitrogen tetraoxide [17-20]. Exfoliation of graphite to yield suspensions of individual graphite oxide sheets needs some additives and techno-tactics. [21]. Various synthesis methods are summarized in Table 1.

Table 1 Summary of GO synthesis methods

Method	**Year**	**Oxidants**	**Solvent**	**Reference**
Hofmann	1937	$KClO_3$	HNO_3, H_2SO_4	(Hofmann and Konig,1937)
Hummers	1958	$NaNO_3$, $KMnO_4$	H_2SO_4	(Hummers and Offeman,1958)
Modified Hummers	1999	$K_2S_2O_8$, P_2O_5, $KMnO_4$	H_2SO_4	(Kovtyhova et al.,1999)
	2010	$KMnO_4$	H_2SO_4,H_3PO_4	(J.Chen,B.Yao et 2013)

GO is another critical intermediate between graphite and graphene; it is structurally different but chemically similar to graphite oxide. It retains its precursor's oxygen functionalities; however, it primarily exists in single-layer graphene sheets. The oxygen functional group renders the GO hydrophilic and readily dispersed in water or a polar solvent to form stable colloidal suspensions. GO is usually achieved by mechanical stirring or ultrasonication methods in aqueous media. Although the ultrasonication method ensures a more efficient and faster exfoliation of the staked graphite oxide sheets, it often entails structural damages and breaks GO sheets into smaller fragments [22].

It is known that ultrasonic wave energy affects suspended solutions on a molecular level via high-power ultrasound's chemical and physical effects caused by high-power ultrasound. The dynamics of bubbles create this process due to the vibration called a cavitation phenomenon when ultrasonic waves irradiate the solution. [23]. it is worth mentioning that the cavitation behaviour is favoured at lower frequencies less than kHz because much more intensity is needed to induce cavitation by ultrasonic waves at higher frequencies. [24].

The typical ultrasonic devices such as ultrasonic probes are immersed into samples which can transfer much higher ultrasonic intensity to the pieces. The second type is called an ultrasonic bath, where the liquid container itself acts as an oscillating source [25].

This research demonstrates that GO can be synthesized using a modified approach of Hummer's Method. The innovation in this work is synthesis without using $NaNO_3$ and other acids and proceeding with a physical exfoliation technique by adjusting Ultra-sonic processing with a suitable device and setting. This method could reduce the cost and environmental impacts, and exfoliation techniques utilized carefully to gain high characteristics.

2. Experimental Procedure

Materials

Graphite powder with an average particles diameter (20 μm) was obtained from Sigma Aldrich by Evergreen Co. Ltd. Sulfuric acid (98%), and Hydrogen peroxide (30%) were obtained from R&J chemicals. Potassium permanganate (99.9%) and hydrochloric acid (36%) were provided, all other chemicals were used as received. Distilled water was used for washing the graphene solutions.

Preparation of Graphite Oxide

Graphite oxide was synthesized using 4 g of graphite (powder) oxidized by 200 ml of H2SO4 in a volumetric flask with continuous stirring for 4 hours. 15 g of KMnO4 was added to the mixture gradually and carefully. A mechanical magnetic stirrer was used for 60 hours to oxidize graphite completely (solution colour was converted from dark green to dark brown), as shown in figure 1 (step 1). Subsequently, 30 ml of H2O2 solution was added to terminate excess KMnO4 and oxidation process (the colour was altered to bright yellow). Graphite oxide was formed and washed three times with an aqueous HCl solution to remove SO42- ions. To remove Cl- ions from the variety, the mixture was washed with distilled water and deionized DI-H2O several times. These solutions were poured into filter tubes and washed repeatedly using a centrifugation technique with 9000 RPM, as demonstrated in figure 1 (step 2). At the third step, sonication for 30 minutes until it forms a paste-gel (pH-neutral) with a dark brownish colour.

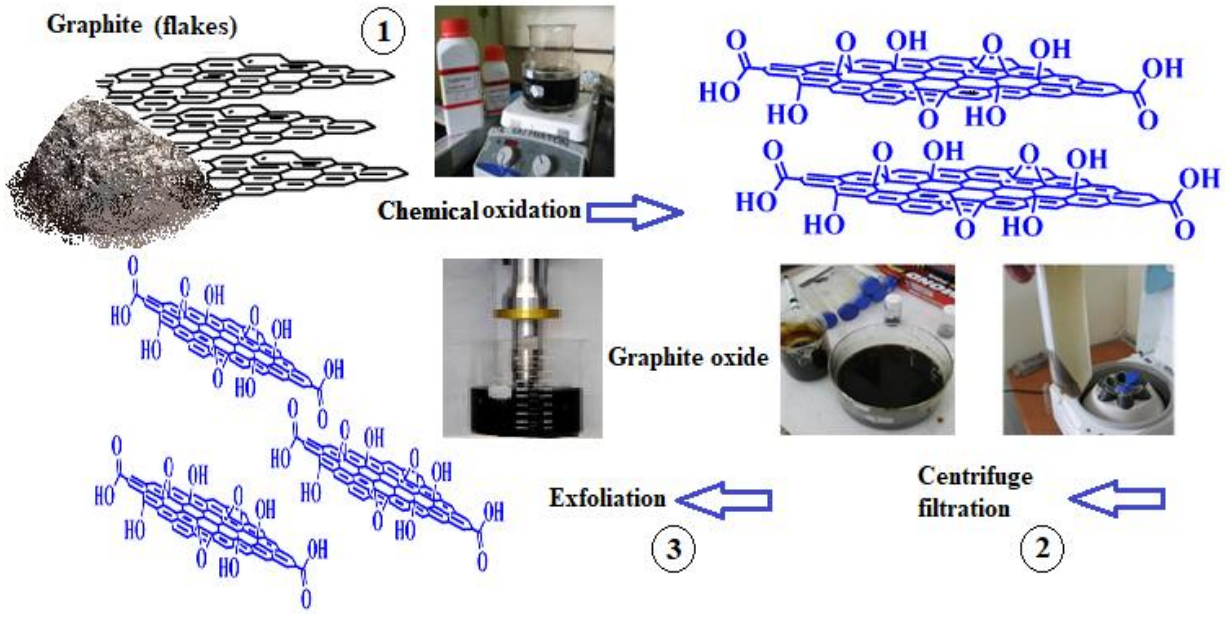

Figure 1: steps of synthesis graphite oxide using modified Hummer's technique

Preparation of Graphene Oxide nanosheets

The exfoliation process on graphite oxide layers was used by applying mechanical forces to its suspension solution, such as stirring and sonication techniques, as shown in figure 2. One gram of GO (thick liquid) was initially dispersed in distilled water using a magnetic stirrer to separate the agglomerated graphite oxide particles for 30 min and repeated at three temperatures (30, 40 and 50) ^{o}C. GO nanosheets precipitated at the bottom of the beaker; therefore, a probe-sonication technique was used to disperse the graphite oxide sheets. In this technique, the device's parameters such as power and frequency for three values (20, 30 and 50) kHz at 60 minutes room temperature with an average of 30^{o}C increase the exfoliated sheets. A water-bath sonication device was used to reduce the sediment particles and obtain the most considerable graphene oxide nanosheets (high yield nanoparticles) in the solution. The completion of dispersion of the GO occurred after three tries of sonication time (30, 60 and 120) min. as shown in figure 2, tube c. The final product of GO was a thick solution of GO. Some of it dried in a vacuum dryer at 80^{o}C and pressure of 70 cm Hg.

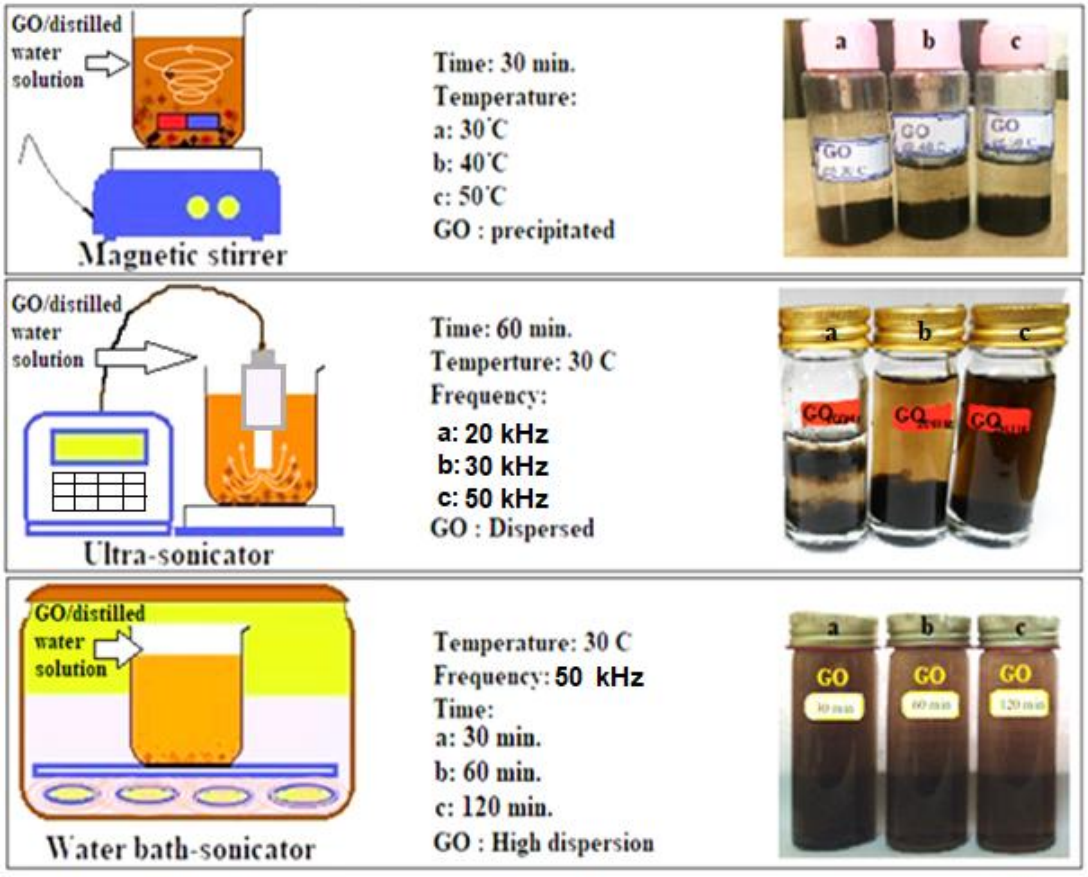

Figure 2: Mechanical techniques to produce GO.

3. Results and Discussion

been performed under optimal parameters The justification for using mechanical methods is to exfoliate graphite oxide layers into nanosize sheets, as performed in section 2.2. A series of devices was used according to the physical techniques and based on the device efficiency, so the obtained results showed different sizes, as shown in figure 2. Firstly, the magnetic stirrer device exhibited the microparticles suspended in the aqueous solution were few despite utilizing different temperatures. It is attributed to the Van der Waals forces' dominance and the mechanical force's inability to overcome these forces to separate the accumulated graphite layers. Therefore, the second technique (probe sonication device) was used because it has an advantage in its work mechanism. It generates high-energy ultrasound waves that create tiny micro-bubbles waves that penetrate the GO layers with the support of the distilled water medium (OH group). The process has of power; with 200 watts, a frequency of 50 kHz, and a time of 60 minutes at an ambient laboratory temperature of 30 (±2) ^{o}C. Thus, this method largely

transcends Van der Waals forces, reduces the quantity of precipitated particles, and increases the suspended GO nanoparticles in the solution from 20 kHz to 50 kHz as shown in figure 2 (tubes a, b and c). However, incomplete GO exfoliation with microparticles of GO in the bottom of the tubes led to repeat the process with the third technique. Three jars of GO solutions were placed in Bath-sonication equipment for (30, 60 and 120) minutes to invest the combination of the type of ultrasound waves that have been created in the bath in addition to the sonication time. This technique was suggested to avoid sedimentation problems and obtain a high yield of nano-particles. Moreover, this device enhanced the dispersion of the agglomerated GO nanosheets in the aqueous medium. It was found that very few deposited particles in the tubes were achieved at time 120 min. Characterization of the best sample has been analyzed using nanosized particles and other tests.

3.1. Particle Size of GO Nanosheets

The particles size distribution was analyzed using *BrookHaren* (NanoBrook 90plus USA). The raw data were normalized determine GO particles' average size and range. In figure 3, curves between the intensity and diameter (nm), particles sizes of the first technique figure 3-a were 313 nm, where the particles size in the second instrument was 134 nm, as shown in figure 3-b. It is attributed to the type of sonication, where the water bath sonicator provides gentile and harmonic ultra-sonic waves with a reasonable and practical force higher than Van der Waals forces. This process assists in exfoliating the layers of GO carefully compared to the probe-sonicator type based on the amount of GO nanosheets. In addition, using an extended period (120 min) with monitoring the temperature within an average of 30 ^{o}C enhanced the number of nanosize particles. However, the range of nanosized particles includes 50-500 nm size. Practically, in a typical local lab with limited facilities, these results are considered a promised outcome. Therefore, the best way to collect a high percentage of nanoparticles is to use nanoparticles paper filters (100 nm) under vacuum. It has been performed to raise the effective diameter to 94 nm, as shown in figure 3-c.

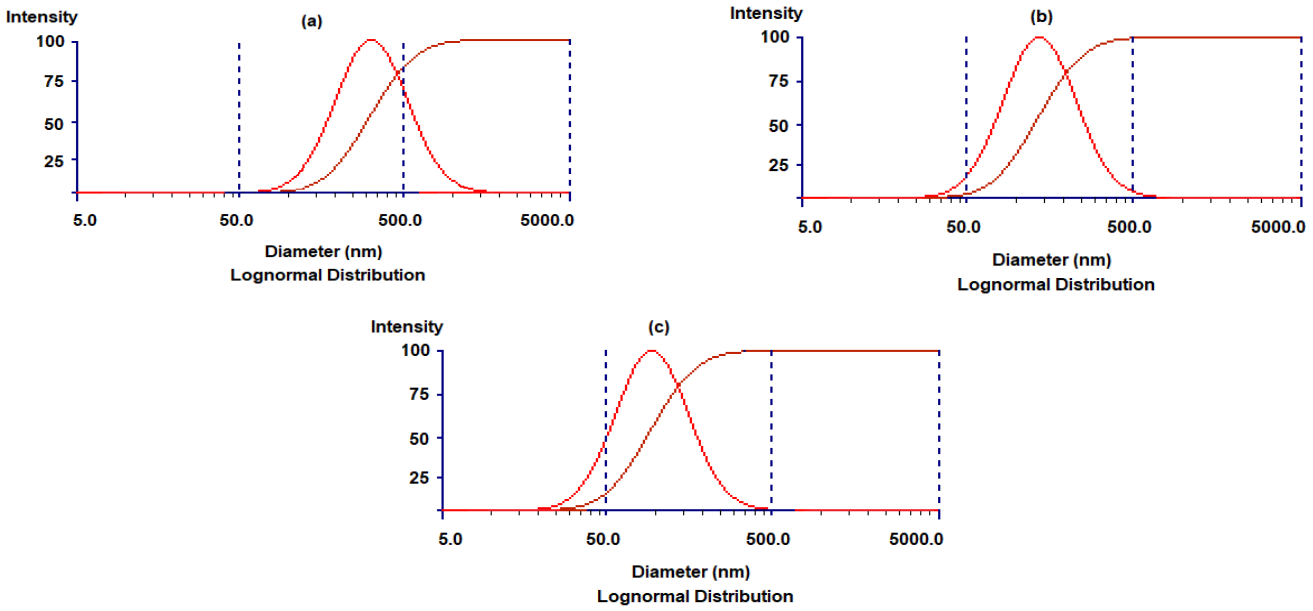

Figure 3: Particle nanosize distribution of GO analysis, (a) with prob-sonicator, (b) with water bath sonicator and (c) with a paper filter with (100 nm)

3.2. X-Ray Analysis

The crystalline structure analysis to a sample of GO was characterized using (XRD-6000 /SHIMADZU) under conditions of the voltage of 40 kV. Based on the diffraction pattern, the average spacing between layers of atoms was calculated by determining the orientation of a single particle crystal. Figure 4 shows a sharp diffraction peak (002) of pure graphite is found around $2\theta=25.78^{o}$. The typical diffraction peak (001) of GO was observed at $2\theta=9.86^{o}$, which is mainly due to the oxidation of graphite, corresponding to the highly organized layer structure with an interlayer distance (d) of 0.393nm for graphite and 0.895nm for GO using Bragg's law, $n\lambda = 2\ d\ Sin\theta$. This interlayer space indicates successes in exfoliation treatment using physical process (sonication) and chemical treatment (oxidation). The interlayer spacing of graphite oxide increases due to large covalently bounded oxygen-containing functional groups on the graphene sheets during the oxidation process.

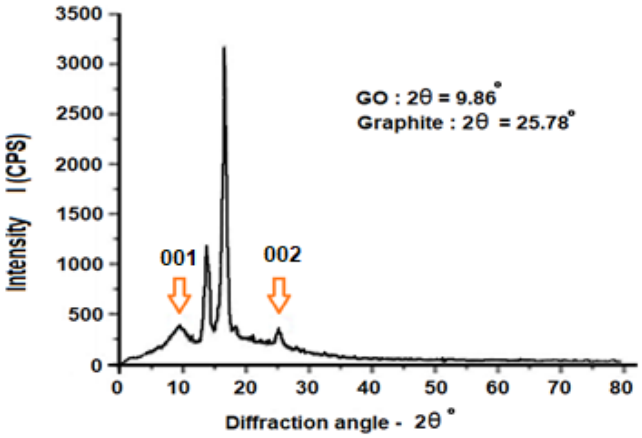

Figure 4: XRD Pattern of GO

3.3. UV/Vis Test

Ultraviolet-visible spectra (UV/Vis) test was performed using Brookhaven (Nano Brook Zeta plus USA). As UV-Vis Spectroscopy is a quantitative technique, it is used to measure the graphene suspension solution that absorbs light to determine the wavelength of GO. In figure 5, UV-Vis of GO has an absorption peak at 230 nm, shifting to 270 nm in graphene. Also, based on sonication time, absorption was greater than at 60 min sonication, which indicates that the surface area increased and absorbed more radiation when the sonication time reached 120 min. It is the optimal time to get a high rate of GO particles in the solution at the suitable adjusted sonication process.

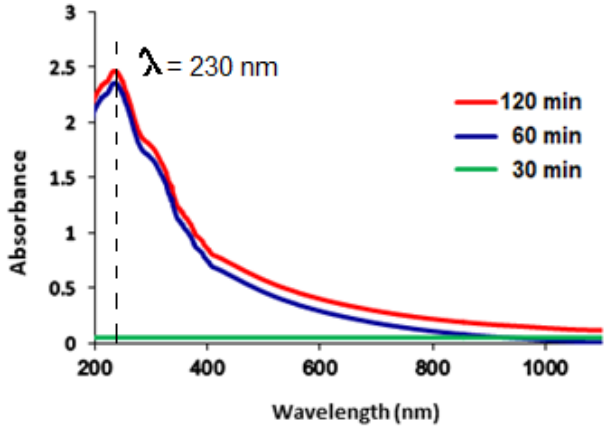

Figure 5: UV-vis test of GO at different sonication time

3.4. SEM Analysis

Scanning electron microscopy (SEM) type Inspect F50 FE-SEM was used to analyze GO nanosheets microimages of a dry sample by scanning the surface. It includes fragile and huge wavy layers of GO with a few graphite oxide particles as shown in figure. 6-a at 7000 x magnification with a scale of 10µm. The morphology of the sample surface of GO was observed at 50000 x with a scale of 2μm, the feature of GO Nanosheets as demonstrated in figure 6-b. The selected micro spot was magnified to nanoscale as shown in figure 6-c at 190000 x magnification with 500nm. Several GO sheets have been appeared obviously in figure 6-c and measured in figure 6-d at 380000 x with a scale of 200 nm. Despite some imperfections, some graphene flakes can identify under FE-SEM. However, filtration of the GO solution using a filter with nanoporous could reduce the bulk and micro-particles in addition to any impurities. The size range of the sheets was between 48.92nm to 172.8nm. It is attributed to that oxidation of graphite was performed entirely.

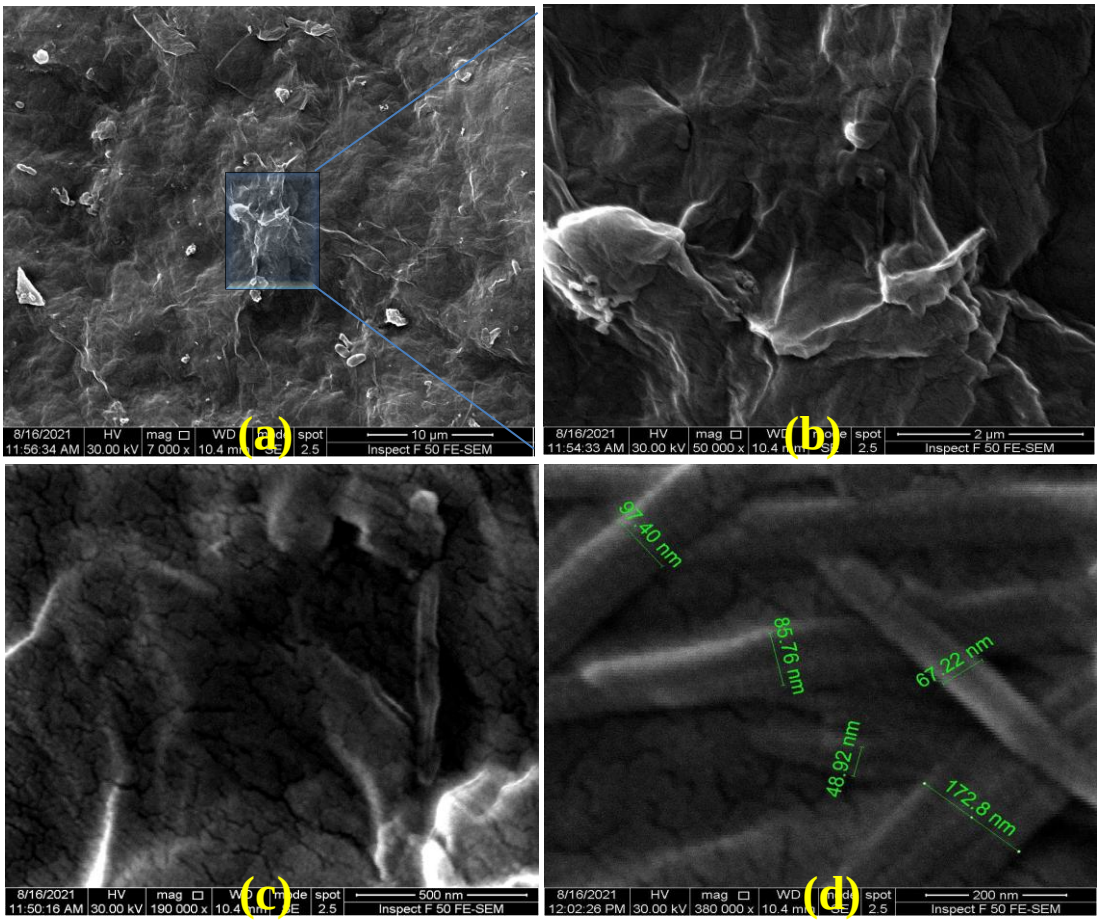

Figure 6: SEM micro-nano images of GO sheets at the scale of (a) 10 µm, (b) 2 µm, (c)500 nm and (d) 200 nm.

4. Conclusion

Hummer's Method has been successfully modified and improved to synthesize GO. The change was thought to be a simple and delicate way to make advanced GO nanosheets. The novelty of the current research can be described by reducing the danger and effects of acidic solutions on the environment, where it concludes that a solution of H_2SO_4 containing $KMnO_4$ can oxidize graphite to graphite oxide with a high yield of exfoliated sheets without using $NaNO_3$ or any chemical agents. Moreover, the best conditions of the exfoliation process were achieved using the proper ultra-sonication device with the filtration. The result showed that using an optimal frequency of 20 kHz during 120 minutes at room temperature (30 ^{o}C) provided a high yield of GO nanosheets gained with 94 nm size. Furthermore, this methodology kept the GO characteristics as characterized by X-ray and UV-vis tests. It is found that the UV-vis absorption of GO increased due to the increase in the surface area of the nanosheets after two hours. This evidence shows that GO nanosheets have been well

prepared. Thus, the prepared GO in this modified method has a high yield of nanosheets with low cost and offers a unique specification of GO for several applications.

Acknowledgement
The authors would like to express their gratitude to the staff of the Center for Research in Nanotechnology and Advanced Materials at the University of Technology for their cooperation in most of the tests. We also appreciate the use of instrumentation in the Materials Properties Laboratory/Department of Applied Sciences.

Conflict of Interest
The authors declare that they have no conflict of interest.

References
[1] Ch.H. Lui, Li.Liu , K.F.Mak, G .W.Flynn and T.F.Heinz, "Ultraflat graphene", *Nature*, vol. 462, p. 339-341, 2009.
[2] D.C.Marcano، D.V.Kosynkin، J.M.Berlin, A.Sinitskii, Z.Sun, A.Slesarev، L.B.Alemany and W.Lu, J.M.Tour, "Improved synthesis of graphene oxide," *AscNano*, vol. 4, no. 8, p. 4806-4814, 2010.
[3] S.H. Ali , A.M.Abdul Hussein and M.K. Abd Mohammed , " Structural Properties of Multi-layer Graphene (MLG) Films Prepared by Flame Technique in Open Environment" , *Iraqi A.S.J* ,vol.34, no.1 , p.129-135, 2016 .
[4] H.T. Hussein ,U.M. Nayef, A.M. Abdul Hussien , " Synthesis of Graphene on Porous Silicon for Vapor Organic Sensor by Using Photoluminescence", *Optik*, vol.180,p.61-70,2018.
[5] N. A. Habib, B.W.Chieng, N. Mazlan, U. Rashid,R. Yunus, and S. Abdul Rashid," Elastomeric Nanocomposite Based on Exfoliated Graphene Oxide and Its Characteristics without Vulcanization", *Hindawi*,vol.2017,p.1-11, 2017.
[6] J. Chen, B. Yao, Ch. Li and Ga. Shi, "An improved Hummers method for eco-friendly synthesis of graphene Oxide", *Carbon*, vol.64, p.225-229, 2013.
[7] A.Adetayo and D.Runsewe,"Synthesis and Fabrication of Graphene Oxide", *J.composite material*, vol.9, no.2, p.207-229, 2019.
[8] N. Ucar, I. O.Yuksek, M. V. Olmez, E. Can and A. Onen " The effect of oxidation process on graphene oxide fiber properties", *Materials Science-Poland*, vol.37, no.1, p.83-89, 2019.
[9] R. Ikram, BM.Jan and W. Ahmad, "An overview of industrial scalable production of graphene oxide and analytical approaches for synthesis and characterization", *JMR&T*, vol.9, no.5, p.11587-11610,2020 .
[10] A. T.Smith, A.M.Lachance,S.Zeng, B.Liu and L.Sun, "Synthesis, properties and application of graphene oxide / reduced graphene oxide and their Nanocomposite ", *Nanomaterialscience*, vol.1, no.1, p.31-47, 2019.
[11] W.S.Humers and R.E.Offeman, "preparation of Graphitic oxide, "*Am.chem.Soc*, 80, p.1339, 1958.
[12] R. Ikram, BM.Jan and W. Ahmad, "An overview of industrial scalable production of graphene oxide and analytical approaches for synthesis and characterization," *JMR&T*, vol.9, no.5, p.11587-11610 ,2020 .
[13] K.Ojha, O.Anjaneyulu and A.K.Ganguli, "Graphene-based hybrid materials: synthetic approaches and properties ", *current science*, vol.107, no.3, p.397-418, 2014.
[14] R. Ikram, BM.Jan and W. Ahmad, "An overview of industrial scalable production of graphene oxide and analytical approaches for synthesis and characterization," *JMR&T*, vol.9, no.5, p.11587-11610,2020 .
[15] U. Hofman and E. Koenig, "Studies on Graphit Oxide", *journal for inorganic and general chemistry*, vol.234, no.4, p.311-336, 1937.
[16] R.K.Singh, R.Kumar and D.P.Singh " Graphene oxide: strategies for synthesis, reduction and frontier application, "*RSC*, vol.6, no.69, p.64993-65011, 2016.
[17] N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, Th. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, and A. D. Gorchinskiy, "Layer-by-Layer Assembly of Ultrathin Composite Films from Micron-Sized Graphite Oxide Sheets and Polycations", *Chemistry of Materials*, vol.11, no.3, p.771-778, 1999.
[18] J. Chen, B. Yao, Ch. Li and Ga. Shi, "An improved Hummers method for eco-friendly synthesis of graphene oxide," *Carbon*, vol.64, p.225-229, 2013.
[19] NI.Zaaba, K.L.Foo, V.Hashim, S.J.Tan, Wei-Wen.Liu and C.H.Voon, "Synthesis of graphene oxide using modified hummers method" *solvent Influence, Procedia Engineering*, vol.184, p.469-477, 2017.
[20] T.Soltani and B.K.Lee, "Low intensity-ultrasonic irradiation for highly efficient, eco-friendly and fast synthesis of graphene oxide," *pubmed*, vol.38, p.693-703, 2017.

[21] J. Chen, B. Yao, Ch. Li and Ga. Shi, "An improved Hummers method for eco-friendly synthesis of graphene oxide," *Carbon*, vol. 64, p.225-229, 2013.
[22] S. Park and R.S.Ruoff, " Chemical methods for the production of graphenes", *Nature Nanotech*, vol.4, p.217-224, 2009.
[23] A. Shah, " Industrial applications of ultrasound review high power ultra-sound ", *IEEE*, vol.22, no.2, p.60-71, 1975.
[24] D. Peters, " Ultrasound in materials chemistry", *J. Mater. Chem*., vol. 6, no.10, p.1605-1618, 1996.
[25] K. Suslick, "Applications of ultrasound to materials chemistry", *Annu. Rev. Mater. Sci*., vol. 29, p.295-326,1999.