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Synthesis of Graphene Oxide (GO) by Modified Hummer's Method with Improved Oxidation through Ozone Treatment

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Summary: Graphene Oxide (GO) is one of the common members of the graphene family owing to its unprecedented and unique properties. These properties attract researchers to use GO in several potential applications such as a transparent electrode in light-emitting diodes (LED), biosensors and solar cells, etc. In this work, GO was produced through the oxidation of graphite by potassium permanganate using modified Hummer's method and this was followed by ozone treatment. The crystallographic structure, chemical properties, surface morphologies, and optical properties of before and after treatment of GO were determined by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and UV- visible spectroscopy. The FTIR observation confirmed the formation of GO from graphite flakes. XRD results showed peak at11.6° with a different interlayer spacing of 0.7nm and 0.8nm for GO and ozone-treated graphene oxide (O-GO) respectively. While for both GO and O- GO all the peaks were at the same position. Further, SEM micrographs of GO exhibited the multilayered graphene oxide with variable thickness. While the rough surface of O- GO suggests the reduction of GO particle size due to ozonation. Ultraviolet-visible spectra of GO at 223.2 nm was noted which is attributed to atomic C- C bonds but O- GO exhibited the peak shift at 232.7 nm thereby suggesting a higher surface area.

Keywords: Graphene oxide, Modified Hummer's method, Nanomaterials, Oxidation, Crystal structure, Ozone treatment.

Introduction

Graphene is two dimensional and a monoatomic layer of graphite that consists of sp^2 hybridized carbon atoms, arranged in honeycomb crystal lattice [1]. The Vander Waal bond holds the graphene layers together by a weak attractive force. The length between the graphene layers is 0.341nm [2]. Graphene is available in several forms such as; graphene oxide, graphon, reduced graphene oxide, fluoro-graphene, doped graphene, graphyne and graphdiyne. However, graphene oxide (GO) is the most relevant and researched of these derivatives since it is less costly and easier to make than other forms of graphene. GO may be easily added into the variety of polymers and other materials to increase the tensile strength, elasticity, conductivity, and other properties of composite materials. [3]. GO is a complex system, containing two- dimensional graphene sheets covalently bonded by OH, carbonyl, or epoxy functional groups. In the presence of an oxygen functional group, graphene oxide disperses in water and is considered hydrophilic [4]. One of the most interesting properties of GO is that; it is p- type semiconductor material whose optical bandgap is approximately equal to 3.06 eV which could be called photo-catalyzer material in the photoluminescence domain [5]. The GO is always considered as an electric charge insulator due to the disturbance ofsp^2 hybridized bonding structures. When an oxidizing agent is added with GO, it interrupts its electrical conductivity; hence, highly oxidized GO is considered a good semiconducting material [6]. Due to these excellent properties, GO has many potential applications in different fields such as; biosensors owing to its high electrical and chemical activity [7]. In one study [8], GO was functionalized with folic acid and was used as an anti-cancer drug for finding human breast cancer cells. This study proved the GO as a low toxic material and can be used to kill tumor cells. GO is also used for the fabrication of transparent conductive film, which is used for coating sensitive devices such as chemical sensors, solar cells, flexible electronic devices, touch screen devices, and liquid crystal displays [9]. Synthesis of GO has been researched in the past few years. Since in 1958, B.C Brodie an English Chemist was among the first who introduced a method for synthesis of GO. He mixed

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slurry of graphite in potassium chlorate ($KClO_3$) and added enough fuming nitric acid (HNO_3) [10]. In 1898, Staudenmaier improved the Brodie method by oxidizing graphite in the combined solution of sulfuric acid (H_2SO_4), fuming nitric acid (HNO_3), and gradually added potassium chlorate ($KCLO_3$) in the mixture. Due to this small change, the highly oxidized GO was produced [11]. After 60 years of Staudenmaier, Hummers developed a new method for GO synthesis. He used potassium permanganate ($KMnO_4$) and sodium nitrate ($NaNO_3$) in concentrated sulfuric acid (H_2SO_4) solution [12]. Hummer's method has attracted more attention because of its high efficiency and safety in the reaction process [4]. The modified hummer approach provides a number of benefits over previous methods, like: the number of flaws in the basal plane is minimized. A greater quantity of oxidized graphite is offered. When compared to other approaches, the degree of reduction gives a similar amount of conductivity. When compared to the Brodie, Staudenmaier, and Hummers methods, this approach produces the highest yield. Toxic gases are not produced during the processing, which is environmentally beneficial. When compared to graphite oxide produced by the Brodie and Staudenmaier processes, the result has a more ordered structure [3]. After the synthesis, graphene oxide is treated with ozone to improve structural functionalization and control. Low ozone levels are utilized in ozone treatment since they are less effective in terms of health and do not create as much pollution as moderate levels [13].

In this work, GO was synthesized using a modified Hummer's process, and the resulting GO was then treated with ozone. It shows that ozone treatment is performed for a long contact period (4 hr) at a low ozone level (100 ppm), which significantly modifies the GO band gap. When compared to previously develop structural modification methods, this technique stands out for its ease of use and high level of control. As a consequence, it is now possible to enhance the electrical properties of GO for various applications. Ozone-induced structural alterations in sp^2 nanocrystalline regions in GO are caused by GO oxidation in band-gap changes. This model is confirmed by XRD, FTIR, and SEM analysis of the GO particle.

Experimental

Materials

In this study, the following chemicals were utilized as shown in Table 1 along with their purity and supplier information.

Methods

Synthesis of Graphene Oxide: To prepare GO and O- GO, the quantities of reactant were doubled as compared to modified Hummer's method (MdTanviret *al* 2017) to obtain a sufficient quantity of GO. This is because half of GO is needed to be treated with ozone. All the reactants were mixed in a 1000ml reactor and the process ended on the production of GO as per steps depicted in Fig 1.

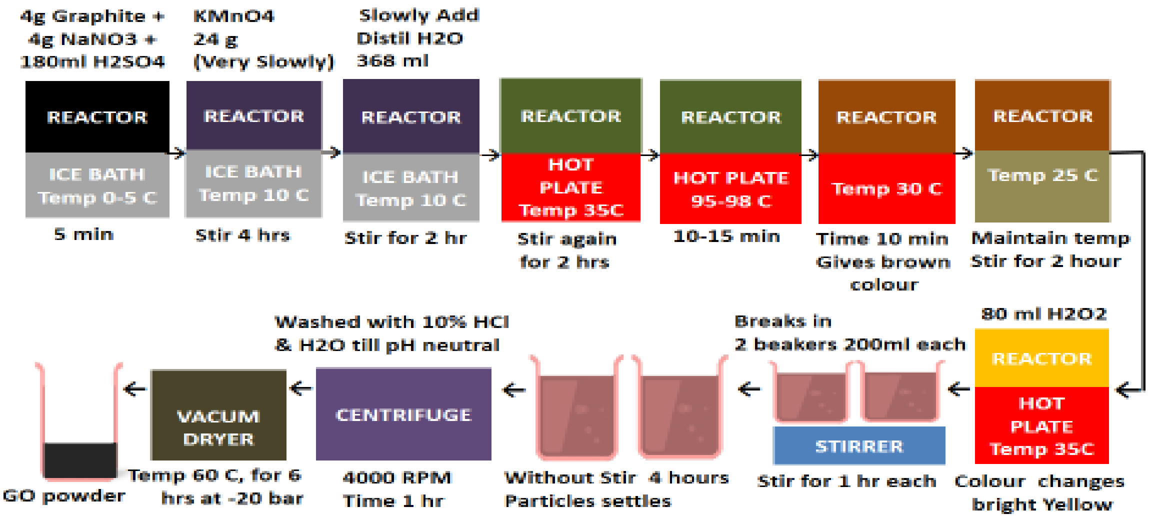

Fig. 1: Schematic process flow diagram for the synthesis of graphene oxide through the process of modified hummer's method.

Table-1: Shows the chemicals / reagents utilized in this study.

S.No.	Name	Purity	Supplier
1	Graphite powder < 45 µm	extra pure 99.9%	Sigma-Aldrich (Spain)
2	Sodium nitrate ($NaNO_3$)	99.3%	Merck (Darmstadt, Germany)
3	Sodium Hydroxide (NaOH)	99.5%	Fluka (Germany)
4	Sulphuric acid (H_2SO_4)	98%	Sinopharm Chemical Reagent Co., Ltd
5	Potassium-permanganate (KMnO4)	99.5%	Sigma-Aldrich (Spain)
6	Hydrogen peroxide (H_2O_2)	30%	Merck (Darmstadt, Germany)
7	Hydrochloric acid (HCl)	35%	Sigma-Aldrich (Spain)
8	De-ionized water	≤ 3 µs	Milli-DI® Water, Model: C7684

After the successful follow-up of these steps and exfoliation of the graphite layers, GO powder is produced.

Ozone Treatment of GO: The synthesized GO by modified Hummer's method was treated with ozone. In this method, as prepared GO (1.6 g) was spread in Pyrex glass tray of size 10''× 8'' and placed in a box with maintained with an ozone concentration of 100ppm, monitored by ozone sensor (Jiahuan Ozone, Model NO:MO009) for 4 hours and the sample was mixed after each hour during the reaction. The Lab developed an ozone generator operated with UV-light at 185 nm, fed with clean air produced from a clean air system at a flow rate of 400 ml/min for four hours as per Fig 2. After completion of the given time the samples was mixed completely and send for further characterization.

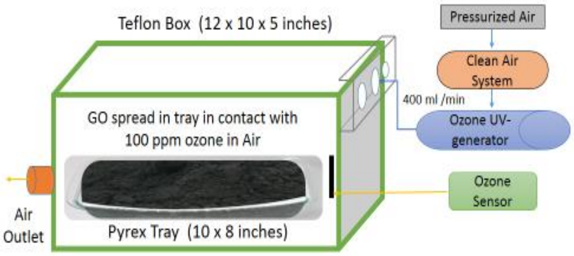

Fig. 2: The schematic diagram for process showing the ozone treatment of GO.

Characterization

Instrumentation: Fourier transform infrared (FTIR)Bruker Tensor 27 spectrometer (Bruker, Karlsruhe, Germany) was used and the spectra were recorded in the range of 400-4000 wavenumber /cm^{-1}, scanning electron microscope (SEM) (Hitachi S-4800, Japan) was utilized for capturing the micrographs at high resolution, X-ray diffraction (XRD; Philips PC-APD) with Cu Kα radiation (λ= 1.5418 Å) operating at 40 kV, 60 mA was used to analyze the samples in terms of formation of GO, UV-vis Spectrometer (Evolution 300, Thermo Fischer) for utilized to analyze the absorption spectra of graphene oxide. Ozone (O_3) analyzer model number 49i (Thermo Fisher Scientific Inc., US) alab-developed UV-ozone generator (at a wavelength of 185 nm) was used to treat the graphene with ozone.

Results and Discussions

X- Rays Diffraction analysis

XRD is a very useful procedure for the determination of the structure of crystalline substances and provides complete information about the dimension of the unit cell. It is also used for measuring average d-spacing between the layers, orientation of single crystals [14]. X- Rays diffraction patterns obtained for GO and O-GO nanomaterials prepared by Modified Hummer's method and ozone treatment are shown in Fig 3. The diffraction of GO indicates a strong and sharp peak at 2θ= 11.6°, which is represented by a black line and correlated with (001) plane. This points out that GO product is sufficiently oxidized after chemical oxidation and exfoliation. The d- spacing between GO layers is observed at about 0.7 nm [15-17]. This large d- spacing among GO layers is because of the formation of oxygen-containing functional groups like; carboxyl, epoxy, and hydroxyl groups. Similarly, O- GO is represented by a red line. The d- spacing for the O- GO raised to 0.8 nm after the ozonation process, the possible reason could be the further attachment of oxygen to GO. The interlayer spacing obtained for GO and O- GO are 0.7 nm and 0.8 nm respectively, which is similar to the earlier reported d- spacing range of GO as 0.8nm and 1.31nm [18].

Fourier Transform Infrared Spectroscopy Analysis

FTIR is a process adopted to create an infrared spectrum of emission and absorption of solid, liquid, gas and is also used for quantitative investigation of unknown structures. It is a simple method to recognize the presence of a specific functional group in the materials [19]. The FTIR spectra of synthesized GO and O-GO through the Modified Hummers method are shown in Fig 4. In the given Fig, the black line shows the graph of GO, which has peaks at 1049cm^{-1} and 1230 cm^{-1}. These peaks are associated to the stretching and bending vibration of C-O, and C-O-C respectively, confirming the presence of oxide. The peak located at 1616 cm^{-1} and 1720 cm^{-1} respectively are associated to the aromatic C= C and C= O of carboxylic and carbonyl groups, situated at the corners of GO sheets. The broad peak between 2900 cm^{-1} and 3580 cm^{-1} were ascribed to OH stretch of C- OH groups and water absorbed in GO. This broad peak contributed by OH, provides the implication of the hydrophilic property of GO [20, 21]. In given Fig 4, the brown line indicates the FTIR spectra of O- GO. All the peaks are at the same position, but the only change in the transmittance with increase peak height, that indicates the higher oxidation of O-GO than GO. The OH steep curve of O- GO, confirmed the enhanced hydrophilic property. In nutshell, O- GO is more oxidized and more hydrophilic than GO

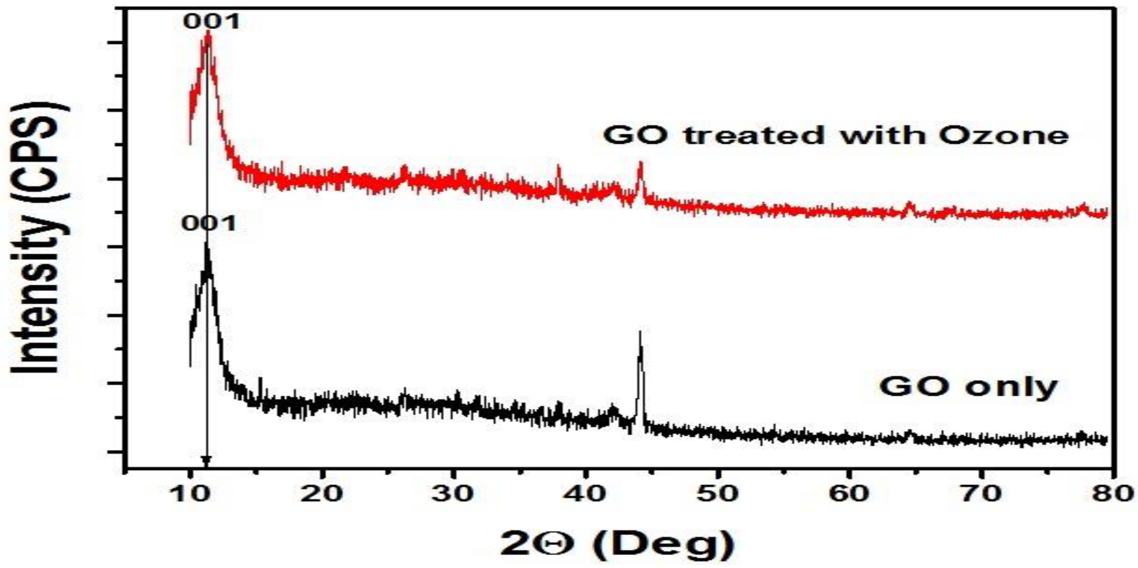

Fig. 3: XRD spectra of GO, black curve represents the GO without ozone treatment and the red curve represents GO treated with ozone.

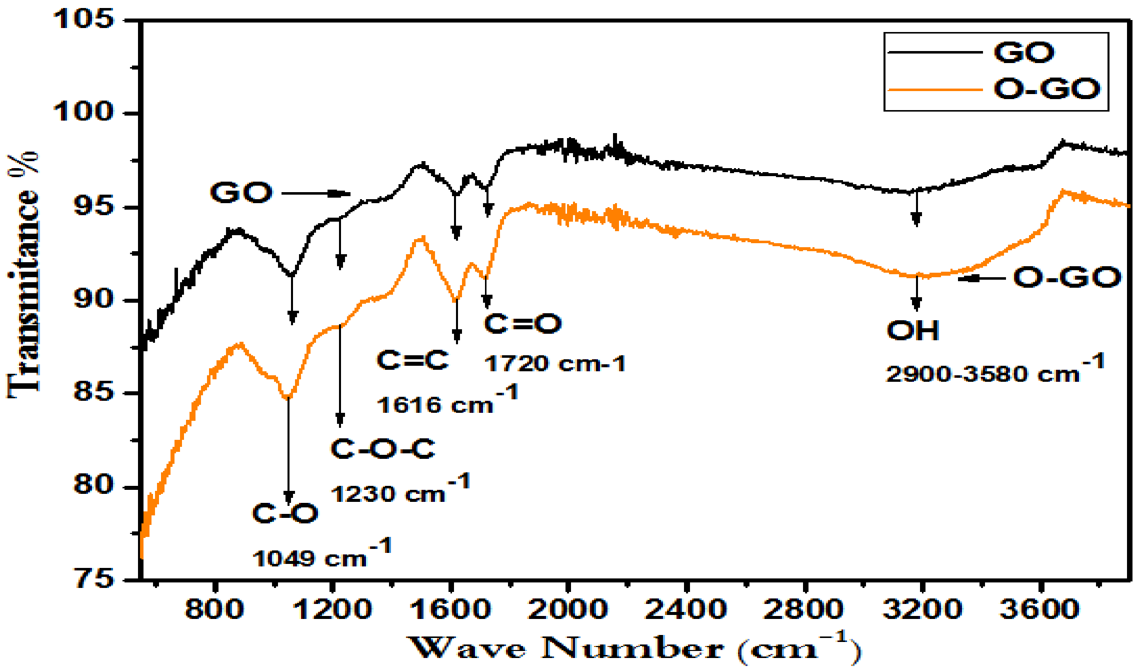

Fig. 4: FTIR spectrum of GO and O- GO: The GO is denoted by black line and O-GO as brown line. Here transmittances of C-O bond at wave number 1049 cm^{-1}, C-O-C at 1230 cm^{-1} and C=O at 1720 cm^{-1} have been slightly decreased by O-GO. Similarly, OH steep also increased in O-GO as compared to GO.

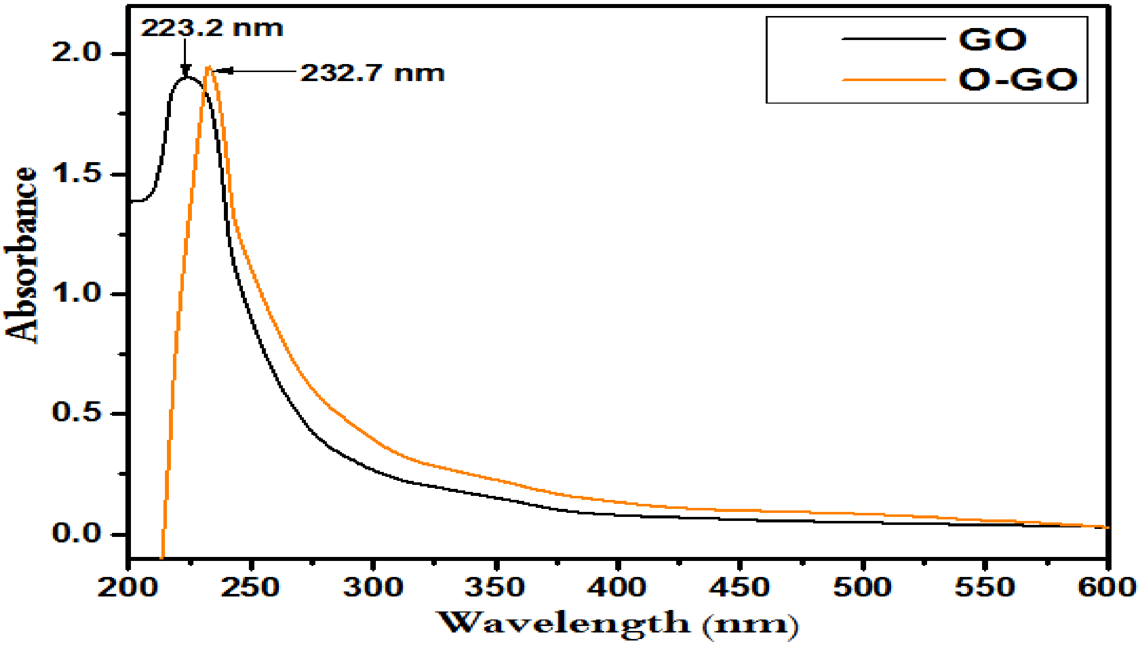

Fig. 5: Uv- visible spectra of GO (Black) and O- GO (Brown) showing absorbance peaks at 223.2 nm and 232.7 nm respectively.

Ultraviolet- visible Spectroscopy

Uv- visible spectroscopy was used to verify the dispersibility of GO and O- GO in water. From Fig 5, the black line represents GO sample without ozone treatment absorption characteristics, typical to only one layer GO suspensions, containing peak at 223.2nm which is associated to $\pi \rightarrow \pi^*$ transformation of sp^2 hybridized carbon atoms [22, 23]. However, in given Fig 5, the other sample O- GO brown line that is GO treated with ozone at 100ppm for 4 hours, has a clear shift of peak at 232.7nm, represented by orange color line, which might be anticipated the reduction of particles size inevitably increases the surface area of O- GO.

Scanning Electron Microscopy

SEM is an advanced instrument, used to observe the surface structure of the samples [4]. It is considered as a powerful instrument used to characterize magnetic, electrical and crystallographic properties of the sample and also provide information about the size, shape and arrangement of the atoms on the surface of the sample [24]. In Fig 6(a), the SEM image of GO without ozone treatment is represented, where the graphene sheets are less oxidized and therefore planer layers are uniform. Similarly in Fig 6(b) GO is treated with ozone (100 ppm) for 4hrs within xa concentrated ozone atmosphere. The morphology of O- GO samples which reflects a highly disordered nature that varies with thickness [25]. However, O- GO initiates from increased proton hopping, caused by higher content of oxygen-containing functional groups in the basal planes and edges of O- GO. In addition, the morphology changes in GO that is due to ozonation process, which also reveals that O- GO cause high level of oxidation [26]. The SEM image of our O- GO clearly shows the sample surface become rough as compared to GO sample that predicts reduction of GO particles, which ultimately results in increase of surface area.

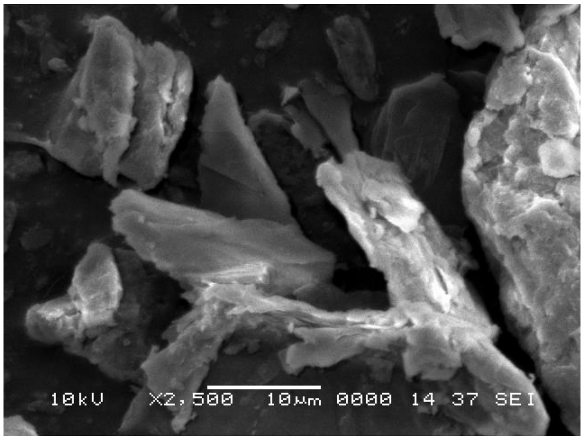

Fig. 6: (a):SEM image of graphene oxide (GO) before ozone treatment with direct magnification of 2500X.

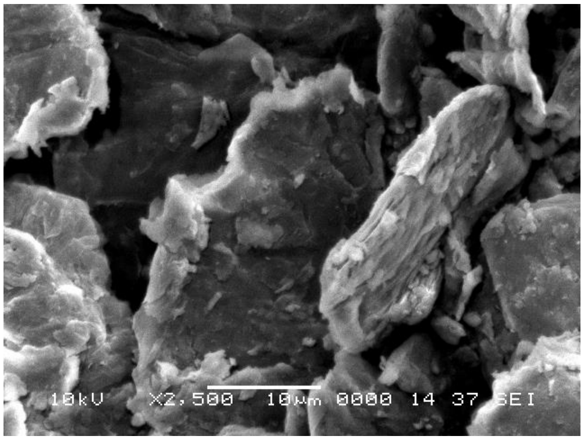

Fig. 6: Scanning electron micrograph of the graphene oxide (GO) after ozone treatment with direct magnification of 2500X.

Conclusions

GO was successfully synthesized through modified Hummer's method thereafter as-prepared GO was treated with ozone. The various characterization techniques confirm the success of modified Hummer's method in the production of GO. Treatment of GO with ozone was also helpful in enhancing the required properties of GO. Results suggest the larger d- spacing of O- GO than that of GO d- before treatment. The existence of different oxygen-containing functional groups was also confirmed. In addition, the absorption peak of O- GO is also greater than that of GO, which exhibits the enhanced surface area of O- GO. Thus, O- GO was more oxidized than that of GO counterpart that make the O-GO more of a hydrophilic nature.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. J. Li, X. Zeng, T. Ren and E. V. Heide, "The Preparation of Graphene Oxide and Its Derivatives and Their Application in Bio-Tribological Systems". *Lubricants*; **2**: 137 (2014).
2. P. L. de Andres, R. Ramírez, and J. A. Vergés, "Strong covalent bonding between two graphene layers". The American Physical Society; 77: 045403-5 (2008) (accessed on 27 December 2021).
3. A. N. Banerjee, "Graphene and its derivatives as biomedical materials: future prospects and challenges". *Interface Focus*; **8**: 1- 22 (2018).
4. D. F. Báez, H. Pardo, I. Laborda, J. F. Marco, C. Yáñez and S. Bollo, "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide". *Carbon*; 45(7): 1558–1565 (2007).
5. E. Dadvar and A. Heidari, "A Review on Separation Techniques of Graphene Oxide (GO)/ Base on Hybrid Polymer Membranes for Eradication of Dyes and Oil Compounds: Recent Progress in Graphene Oxide (GO)/ Base on Polymer Membranes-Related Nanotechnologies". *Clinical Medical Reviews and Case Reports*; **5**: 1-20 (2018).
6. P. B. Arthi G and B.D. Lignesh, "A Simple Approach to Stepwise Synthesis of Graphene Oxide Nanomaterial". *Journal of Nanomedicine& Nanotechnology;* **6**: 1- 4 (2015).
7. D. F. Báez, H. Pardo, I. Laborda, J. F. Marco, C. Yáñez and S. Bollo, "Reduced Graphene Oxides: Influence of the Reduction Method on the Electrocatalytic Effect towards Nucleic Acid Oxidation". *Nanomaterials*; **7**: 1- 15 (2017).
8. X. Yang, Y. Wang, X. Huang, Y. Ma, Y. Huang, R. Yang, H. Duana and Y. Chen, "Multi-functionalized graphene oxide based anticancer drug-carrier with dual-targeting function and pH-sensitivity". *Journal of material chemistry*;**21**: 3448- 3454 (2010).
9. P. Matyba, H. Yamaguchi, G. Eda, M. Chhowalla, L. Edman and N. D. Robinson, "Graphene and mobile ions: the key to all-plastic, solution-processed light-emitting devices". *ACS Nano*; **4**: 637- 642 (2010).
10. B. C. Brodie, "On the Atomic Weight of Graphite". *Philosophical Transactions of the Royal Society of London*; **149**: 249-259 (1859).
11. S.A. Abro, A.D. Chandio, A.S. Alaboodi, and I.A.Channa, "Design, Development and Characterization of Graphene Sand Nano-Composite for Water Filtration: Nano-Composite for Water Filtration", *Pakistan Journal of*

Scientific and Industrial Research; **63**:2:118-122 (2020).

12. W. S. Hummers, J.R., and R. E. Offman, “Preparation of Graphitic Oxide”. *Journal of the American Chemical Society*; **80**: 1339- 1339 (1957).
13. M.T Hasan, B. J. Senger, C. Ryan, M. Culp, R. Gonzalez-Rodriguez, J. L. Cofer and A. V. Naumov, “Optical Band Gap Alteration of Graphene Oxide via Ozone Treatment”. *Scientific Reports*; **7**: 1- 8 (2017).
14. B.D. Cullity, “Elements of X–ray diffraction”. 2nd Ed. *Addison–Wesley*; p. 1- 547 (1978). (accessed on 1 dec 2021).
15. S. Stankovich , D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y.J. Yue Wu, “ Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide”. *Carbon;* **45**: 1558- 1565 (2007).
16. M. F. Zainuddin, N. H. N. Raikhan, N. H. Othman and W. F. H. Abdullah “Synthesis of reduced Graphene Oxide (rGO) using different treatments of Graphene Oxide (GO)”. *Materials Science and Engineering*;**358**: 1- 6 (2018).
17. M. Ghorbani, H. Abdizadeh, M. R. Golobostanfard, “Reduction of Graphene Oxide via Modified Hydrothermal Method”. *Procedia Materials Science*; **11**: 326 – 330 (2015).
18. F. Yang, M. Zhao, Z. Wang, H. Ji, B. Zheng, D. Xiao, L. Wu and Y. Guo, “The role of ozone in the ozonation process of graphene oxide: oxidation or decomposition”. *RSC Advances*; **4**: 58325–58328 (2014).
19. C. Berthomieu and R. Hienerwadel, “Fourier transform infrared (FTIR) spectroscopy”. *Photosynth Res*; **101**:157–170 (2009).
20. T. Zhang, D. Zhang and M. Shen, “A low-cost method for preliminary separation of reduced graphene oxide nanosheets”. *Materials Letters*; **63**: 2051- 2054 (2009).
21. X. Liu, X. Wang, J. Li and X. Wang, “Ozonatedgraphene oxides as high efficient sorbents for Sr(II) and U(VI) removal from aqueous solutions”. *Sci China Chem*; 1-9 (2016).
22. Z. Tang, L. Zhang, C. Zeng, T. Lina and B. Guo, “General route to graphene with liquid-like behavior by non-covalent modification”. *Soft Materials*;**8**: 9214- 9220 (2012).
23. S. Xu , L. Yong and P. Wu, “One-pot, green, rapid synthesis of flower-like gold nanoparticles / reduced graphene oxide composite with regenerated silk fibroin as efficient oxygen reduction electrocatalysts”. *ACS Applied Material. Interfaces*; **5**: 654- 562 (2013).
24. J. I. Goldstein and H. Yakowitz, “Practical Scanning Electron Microscopy, Electron and Ion Microprobe Analysis”. *Plenum Press*, NY 975; 1-582 (1975).
25. Y. C. Cheng, T. P. Kaloni, Z. Y. Zhu, and U. Schwingenschlogl, “Oxidation of graphene in ozone under ultraviolet light”. *Applied Physics Letters*; 101(**7**): 073110-4 (2012).
26. W. Gao, G. Wu, M. T. Janicke, D. A. Cullen, R. Mukundan, J. K. Baldwin, E. L. Brosha, C. Galande, P. M. Ajayan, K. L. More, A. M. Dattelbaum* and P. Zelenay*, “Ozonated Graphene Oxide Film as a Proton-Exchange Membrane”. *Angewandte Communications*; **53**: 3588 –3593 (2014).