

Preparation and Characterization of graphene oxide nanosheets (GONS) from Graphite tailings recovered from drilling mold.

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ABSTRACT/RESUME

Abstract: Graphite is a stack of carbon layers where carbon atoms form hexagons in a honeycomb structure. Graphene on the other hand is a single atom thick layer which offers unique physical, chemical and biological properties compared to graphite.

Recycling graphite waste and converting it into graphene or graphène oxide may offer many economic, environmental and health benefits, and may also be used in many applications.

Graphite has been used widely in iron-steel, chemical, and nuclear industries for electrical, mechanical and other applications (e.g., metallurgy, pencil, coatings, lubricants and paint), and especially, most of the mold materials of drilling are made of graphite.

The major goal of this study is to produce recycled graphène oxide from graphite waste recovered from the drilling mold by using Hummer's method.

In this study, graphite-based tailings recovered from drilling mold were collected from local waste collection companies after the sieving and cleaning processes, the resulting graphite is exfoliated in a single layer using a chemical exfoliation process.

We herein present a simple, fast, efficient and environmentally friendly technique to prepare graphene oxide (GO) from graphite residues recovered from the drilling mold by using Hummer's method.

Complete characterizations of the properties of GO films have been performed. SEM and Raman analyzes showed that the GO sheets prepared in this study had a double-layered and multilamellar structure. X-ray diffraction (XRD) was chosen to measure the crystal structure of our materials.

A Fourier transform infrared (FT-IR) spectrum analyzer was used to certify the presence of oxygen-containing functional groups in GO films. The chemical structure of the GO sheet was described in this study. Discussion and references for further research on graphene are provided.



I. Introduction

As ahead of schedule as 1947, Wallace [1] first proposed the idea of graphene and considered the

electronic properties of graphene utilizing tight-restricting model. It is presumed that graphite is a

semiconductor without actuation energy, due to the little part of valence band of graphite reached out to the conduction band, in which information set up an establishment for the utilization of the actual properties of graphite. In any case, since a very long while, the investigation of graphene is still remaining at the degree of hypothesis [2]. Until 2004, Novoselov and Geim [3] in the University of Manchester first and foremost isolated the single graphene from graphite through straightforward mechanical stripping technique. Graphene was increasing more and more consideration in different spaces of science and innovation because of its momentous physicochemical properties. As a one-particle thick, two-dimensional gem, graphene has been considered as essential structure block for all sp² graphitic materials including fullerenes, carbon nanotubes, and graphite [3]. Attributable to the extraordinary two-dimensional structure, graphene had numerous exceptional properties not the same as carbon materials, including a high explicit surface region (hypothetically 2630 m²/g for single-layer graphene) [4], unprecedented electronic properties and electron transport abilities [5,6], and high warm conductivity ($\approx 5000 \text{ W m}^{-1} \text{ K}^{-1}$) [7, 8]. Presently, numerous strategies had been investigated to plan graphene. Novoselov and Geim [6] initially noticed a solitary layer of graphene from exceptionally arranged pyrolytic graphite using micromechanical shedding strategy. It is a basic method to plan graphene, yet the yield of graphene was low, and you can't accomplish excellent mechanical creation. Srivastava et al. [9] arranged "petal" graphite sheet with $\sim 20 \text{ nm}$ thickness by synthetic fume affidavit (CVD). Indeed in spite of the fact that thickness of graphite sheet arranged by CVD method altogether diminished than at any other time, more impurities Ni component in graphite sheet was another new issue. Dissolvable stripping strategy [10] is another methodology that arose lately. Its guideline is obliterating Van Der Waals Force between the graphite layers in a dissolvable to acquire graphene sheets. Strategy for dissolvable stripping didn't annihilate the construction of the graphene and introduced no surface imperfections in the graphene sheet.

Be that as it may, the low yield of graphene was still. Redox strategy [11,12] is the most famous technique to plan graphene and graphite oxide. During the oxidation measure, graphite gem was treated with solid oxidizing specialists and conveyed oxygen-containing practical gatherings into graphite oxide sheet. After warm or ultrasonic treatment, the oxygen-containing practical gatherings were eliminated and acquired the graphene sheet. Creation of graphene can be high utilizing redox strategy, and presentation of utilitarian gatherings in the oxidation interaction gave benefits of joining the compound to improve

the similarity of framework composite. Consequently, redox strategy was appropriate for the arrangement of graphene-based composite materials. At last, substance construction of GO sheet was likewise depicted in this examination. In outline, to transform graphene applications into reality, one should create the material. The redox strategy is viewed as an extremely encouraging approach to plan graphene, furthermore, graphite oxide (GO), as moderate result of planning measure impacts the nature of graphene. Thusly, investigation for properties of graphite oxide is fundamental and inescapable. Considering these issues, this examination effectively combined graphene oxide (GO) by the adjusted Hummers technique, as the antecedent for planning graphene. The infinitesimal morphologies of GO sheets were described by scanning electron microscopy (SEM) and Raman analyses. The designs of the GO sheets were estimated by Fourier-change infrared spectra analyzer (FT-IR) and X-ray diffraction (XRD). An UV spectrometer (UV-VIS) was utilized to gauge the optical assimilation properties of the GO sheet. An essential analyzer X-Ray fluorescence spectrometer (XRF) was utilized to break down the components in the GO sheet, including C and O.

II. Materials and methods

II.1. Chemicals and Materials.

A graphite drilling mold from drilling mold. NaNO₃, H₂SO₄, KMnO₄, H₂O₂, HCl chemicals were purchased from Sigma Aldrich. The experimental solution is double distilled water.

II.2. Synthesis of Graphene Oxide (GO).

Graphene oxide was synthesized by Hummers method through oxidation of graphite [13].

Graphite flakes (2 g) and NaNO₃ (2,5 g) were mixed in 108 mL of H₂SO₄ (98%) in a 1000 mL volumetric flask kept under at ice bath (0-5°C) with continuous stirring. The mixture was stirred for 2 hrs at this temperature and potassium permanganate (15 g) was added to the suspension very slowly.

The rate of addition was carefully controlled to keep the reaction temperature lower than 15°C. The ice bath was then removed, and the mixture was stirred at 35°C until it became pasty brownish and kept under stirring for 2 days. It is then diluted with slow addition of 100 ml water. The reaction temperature was rapidly increased to 98°C with effervescence, and the color changed to brown color. Further this solution was diluted by adding additional 200 ml of water stirred continuously. The solution is finally treated with 15 ml H₂O₂ to terminate the reaction by appearance of yellow color. For purification, the mixture was washed by rinsing and centrifugation with 5 % HCl and then deionized (DI) water several times. After filtration

and drying under vacuum at room temperature, the graphene oxide (GO) was obtained as a powder.

II.3. Characterization

The infinitesimal morphologies of tests were portrayed by scanning electron microscopy (SEM; Quanta FFG 250.) The designs of materials were estimated by Fourier-change infrared spectra analyzer (FT-IR; JASCO V 770) and X-beam diffraction (XRD; D8 Advance Eco diffractogram Bruker). UV spectrometer (UV-VIS; Agilent V770) was utilized to gauge the optical retention properties of GO. Thermo gravimetric analyzer (TA Instruments, SDT600) was utilized to decide the warm security of tests. Essential analyzer (EA; German Elementar Analysensysteme inc., D-63452 Hanau) .X-Ray Fluorescence Spectrometer (ZSX Primus II) were utilized to examine elementals in GO sheet and Raman Spectroscopic (HORIBA Scientific).

III. Results and Discussion

III.1. The Morphologies of GO Sheet.

From Figure 1 we can see that the pictures of our items show the unique type of graphene oxide and affirm the presence of homogeneity in the minuscule design.

These examining electron microscopy pictures show wide, flawless OG sheets snared on top of one another. Perception of Figure 1 shows the presence of folds and islands of the multi-facet graphene oxide

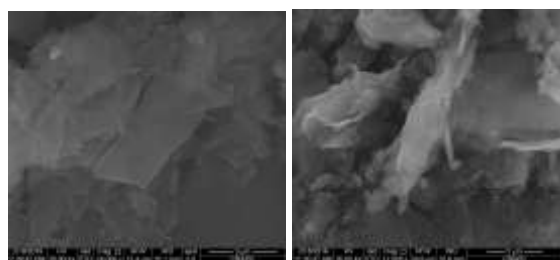


Figure 1. SEM of GO sheet

III.2. The Structures of GO Sheet.

XRD investigation was utilized to decide the normal translucent properties of the GO sheet. Results are showed in Figure 2. Concerning the verification of the crystallographic structure of GO given in literature [23,24], the characteristic 2 θ peak of graphene oxide appeared at 10.34 ° corresponds to a d-spacing of approximately 8.546 Å that is consistent with the interlayer space of graphene oxide sheets reported in the literatures, due to the existence of oxygen-rich groups on both sides of the sheets and water molecules trapped between the sheets.

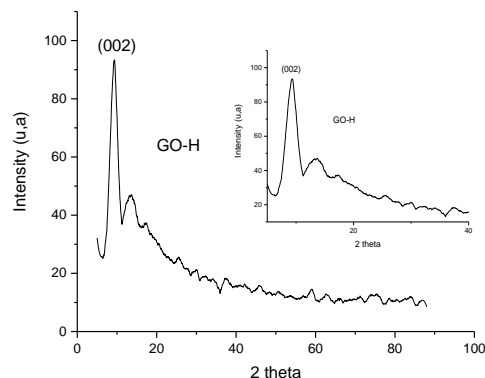


Figure 2. The XRD of GO sheet.

FTIR spectra examination was performed to research the structure and useful gatherings of the materials, as appeared in Figure 3. The GO sheet showed clear adsorption groups for the carboxyl C=O (1723 cm⁻¹), fragrant C=C (1621 cm⁻¹), epoxy C-O (1220 cm⁻¹), alkoxy C-O (1043 cm⁻¹), and hydroxy -OH (3391 cm⁻¹) gatherings. The show of oxygen-containing utilitarian gatherings, for example, C=O and C-O, further affirmed that the graphite in fact was oxidized into GO and was steady with the literary works [14,15]. The show of C=C bunches showed that even graphite had been oxidized into GO; the primary design of layer graphitewas still retained. The results of XRD and FT-IR synthesis both further demonstrated the successful synthesis of GO sheet

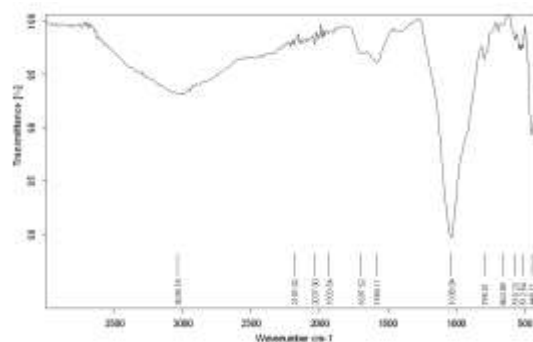


Figure 3. The FT-IR patterns of GO sheet.

III.3. The Optical Ingestion Properties of GO Sheet.

The examination of UV-VIS diffuse reflectance spectra of the GO sheet was appeared in Figure 4. The optical absorption spectra of suspended GO showed a characteristic peak at 265 nm. This peak was attributed to the $\pi-\pi^*$ transitions of the C-C aromatic bond.

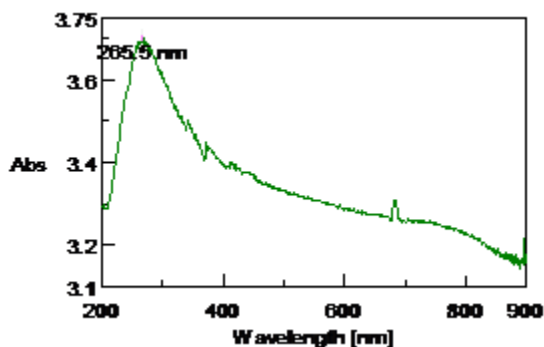


Figure 4. The UV-VIS spectra of GO sheet

III.4. Raman Characterization

In Raman spectroscopy, groups D and G are typically situated at 1350 cm^{-1} and 1574 cm^{-1} , individually. The presence of D and G groups affirms the arrangement of graphene with less deformities and a translucent design (Figure 5). What's more, an increment in the power of the D-line around 1355 cm^{-1} shows an extensive decrease in the size of the sp^2 spaces in the plane because of the oxidation measures and the arrangement of graphene nanofiles having a design translucent profoundly situated.

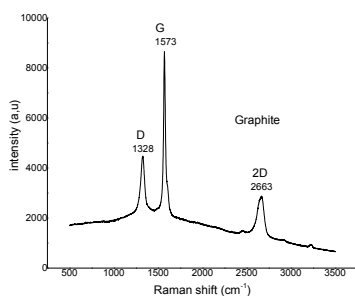


Figure 5. Raman spectrum of graphite (peak D at 1328 cm^{-1} , peak G at 1573 cm^{-1} and peak a 2D at 2663 cm^{-1})

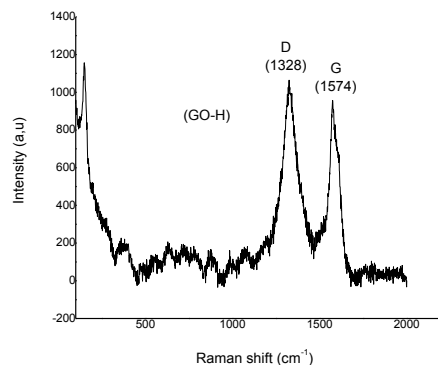


Figure 6. Raman spectrum of GO– (peak D at 1328 cm^{-1} , peak G at 1574 cm^{-1})

The ID/IG proportion, which has been approved as a proportion of the between imperfection distance in graphene, isn't solid when applied to GO and Rgo [16,17]. Ferrari and Robertson characterized an amorphization direction, wherein the ID/IG proportion of carbon (sp^2) would increment with the spread of the deformities, corresponding to the square of the crystallite size [18]. Along these lines, they characterize a progress between carbons which have a crystallite size not exactly $\sim 2\text{ nm}$, which ought to submit to the Ferrari - Robertson relationship, and those with bigger crystallites, which comply with the Tuinstra - Koenig relationship. The intermittence in the connection to structure is ascribed to the bending of aromaticity at exceptionally high deformity densities.

Kurniasari have shown that if the deformity power proportion (ID/IG) increments, inferring the increment of imperfection number [19].

The decline of the proportion of the forces of the D and G groups (ID/IG proportion) (table 1) and the removal of their situation towards lower frequencies show a less broad graphitic space, ascribed to an increment in the level of confusion of the sp^2 bonds, and an increment in the quantity of sp^3 bonds in the design. The lower the proportion ID/IG is lower (graphite) this outcomes in an expansion in the thickness of imperfections [20].

Table 1. The XRF results of graphite GO sheet.

Sample	D position (Cm^{-1})	D Intensity (u.a)	G position (Cm^{-1})	G Intensity (u.a)	ID/IG
Graphite	1328	4411	1573	8565	0.52
GO	1328	1009	1574	936	1.08

III.5. The X-Ray fluorescence spectrometer (XRF) of GO Sheet.

The results of the XRF are listed in Table-2. The O contents of the graphene oxide and graphite are 52.3 and 31.1 %, respectively. It can be expected that the O contents of the graphene oxide increased due to treatment of partial oxygen containing functional groups.

Table 2. The XRF results of GO sheet.

Sample	C wt. %	O wt %	others wt %
Graphite	50.1	31.1	18.8
GO	26.5	52.3	21.2

III.6. Structural Analysis of Graphene Oxide (GO).

Graphene oxide (GO) was a special part of graphene research. It can be considered as a precursor of the union of graphene by other compounds. The schematic design of graphite oxide (GO) is shown in Figure 6.

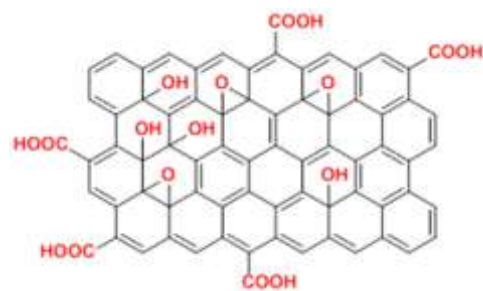


Figure 6. The schematic structure of graphite oxide (GO).

It is demonstrated that GO sheet can be viewed as the consolidated design of oxygen-containing utilitarian gatherings, like C–O, C=O, and –OH, upheld on the outside of a solitary layer graphene sheet [21]. The expansion of oxygen-containing utilitarian gatherings changed the design and properties of GO sheet. Contrasted and single-layer graphene, from one viewpoint, the presence of oxygen-containing practical gatherings undoubtedly extraordinarily expanded inadequacy of GO sheet. This may lead to some misfortune in electrical conductivity [21], which perhaps restricts the immediate use of GO in numerous spaces. On the other hand, the presence of these oxygen-containing useful gatherings likewise gave expected benefits to utilizing GO in various different applications. For instance, the polar oxygen utilitarian gatherings in GO sheet render it emphatically hydrophilic, which gave GO great dispersibility in numerous solvents, especially in water [22, 23]. This additionally given the conditions to incorporate composite materials. Simultaneously, these practical gatherings

can be filled in as destinations for compound change or functionalization of GO sheet, to handily apply in numerous different viewpoints.

IV. Conclusion

In summary, we have successfully demonstrated the extraction of graphite from drilling mold and it's conversion to GO using Hammer's method. The SEM investigations showed fruitful arrangement of GO movies on minute morphology. The presence of oxygen-containing gatherings and trademark tops in FT-IR, and XRD investigation further decided the fruitful readiness of GO sheets. At long last, XRF demonstrated the part of O components in GO movies was about 52.3%; components of C, and others components additionally observed. With this new graphene oxide synthesis process, a virtuous recycling route opens up for the used graphite waste produced each year.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

V. References

- Wallace, P. R. "The band theory of graphite," *Physical Review*, vol. 71, no. 9, pp. (1947) 622–63.
- Oshima, C.; Itoh, A.; Rokuta, E.; Tanaka, T.; Yamashita, K.; and Sakurai, T. "Hetero-epitaxial-double-atomic-layer system of monolayer graphene/monolayer h-BN on Ni(111)," *Solid State Communications*, vol. 116, no. 1, (2000) 37–40.
- Novoselov, K. S.; Geim, A. K.; Morozov, S. V. "Electric field in atomically thin carbon films," *Science*, vol. 306, no. 5696, (2004) 666–669.
- Stoller, M. D.; Park, S.; Yanwu, Z.; An, J.; and Ruoff, R. S. "Graphene-based ultracapacitors," *Nano Letters*, vol. 8, no. 10, pp. (2008) 3498–3502.
- Novoselov, K. S.; Geim, A. K.; Morozov, S. V. "Two-dimensional gas of massless Dirac fermions in graphene," *Nature*, vol. 438, no. 7065, (2005) 197–200.
- Novoselov, K. S.; Jiang, Z.; Zhang, Y. "Room-temperature quantum hall effect in graphene," *Science*, vol. 315, no. 5817, (2007) 1379.
- Balandin, A. A.; Ghosh, S.; W, Bao. "Superior thermal conductivity of single-layer graphene," *Nano Letters*, vol. 8, no. 3, (2008) 902–907.
- Ghosh, S.; Calizo, I.; Teweldebrhan, D. "Extremely high thermal conductivity of graphene: prospects for thermal management applications in nanoelectronic circuits," *Applied Physics Letters*, vol. 92, no. 15, (2008) Article ID 151911.
- Srivastava, S. K.; Shukla, A. K.; Vankar, V. D.; and Kumar, V. "Growth, structure and field emission characteristics of petal like carbon nano-structured thin films," *Thin Solid Films*, vol. 492, no. 1-2, (2005) 124–130.
- Hamilton, C. E.; Lomeda, J. R.; Sun, Z.; Tour, J. M.; and A. R.; Barron, "High-yield organic dispersions of unfunctionalized graphene," *Nano Letters*, vol. 9, no. 10, (2009) 3460–3462.

11. Guo, S.; and Dong, S. "Graphene nanosheet: synthesis, molecular engineering, thin film, hybrids, and energy and analytical applications," *Chemical Society Reviews*, vol. 40, no. 5, (2011) 2644–2672.
12. Rao, C. N. R.; Subrahmanyam, K. S.; Ramakrishna Matte, H. S. S.; Maitra, Moses, U. K.; and Govindaraj, A. "Graphene: synthesis, functionalization and properties," *International Journal of Modern Physics B*, vol. 25, no. 30, (2011) 4107–4143.
13. Chen, J.; Yao, B.; Li, C.; and Shi G. "An improved Hummers method for eco-friendly synthesis of graphene oxide," *Carbon N. Y.*, vol. 64, no. 1, (2013) 225–229.
14. Zhang, Y.; Pan, C. "TiO₂/graphene composite from thermal reaction of graphene oxide and its photocatalytic activity in visible light," *Journal of Materials Science*, vol. 46, no. 8, (2011) 2622–2626.
15. Shen, J.; Shi, M.; Yan, B.; Ma, H.; Li, N.; and Ye, M. "Ionic liquid assisted one-step hydrothermal synthesis of TiO₂-reduced graphene oxide composites," *Nano Research*, vol. 4, no. 8, (2011) 795–806.
16. Kotchey, G. P. the Enzymatic Oxidation of Graphene Oxide, *ACS Nano* (2011) 2098–2108.
17. Stankovich, S. Synthesis of graphene-based nano sheets via chemical reduction of exfoliated graphite oxide, *Carbon* 45(2007) 1558–1565.
18. Ferrari, A.; Robertson, C. Interpretation of Raman spectra of disordered and amorphous carbon, *J. Phys. Rev. B* 61 (2000) 14095–14107
19. Kurniasari. IOP Conf : Photoluminescence of Reduced Graphene Oxide Prepared from Old Coconut Shell with Carbonization Process at Varying Temperatures, *Materials Science and Engineering* 196 (2017)
20. Lucchese, M.; Staval, M.; Ferreira, F.; Vilani, F.; Moutinho, E.; Achete, C. *Carbon* 48 (2010) 1592–1597.
21. Dreyer, D. R.; S.; Park, C. W.; R., Bielawski.; and Ruoff, R.S. "The chemistry of graphene oxide," *Chemical Society reviews*, vol. 39, no. 1, (2010) 228–240.
22. Park S.; and Ruoff, R. S. "Chemical methods for the production of graphenes," *Nature nanotechnology*, vol. 4, no. 4, (2009) 217–224.
23. Szabo, T.; Berkesi, O.; and Dekany, I. Free-Green Synthesis and Dynamics of Reduced Graphene Sheets via Sun Light Irradiation, *Carbon*, 43, (2005) 3186–3189.
24. Titelman, G.I.; Gelman, V.; Bron, S.; Khalfin, R.L.; and Cohen, Y. *Carbon*, (2019) 508–515.

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