Synthesis and characterization of Graphene Oxide and its reduction with different reducing agents

Karan Bansal*, Jagdeep Singh and A. S. Dhaliwal

Department of Physics, Sant Longowal Institute of Engineering and Technology, Longowal-148106, Punjab, India
*corresponding author e-mail: karban083@gmail.com

Abstract: - The present work reports the simplistic formation of graphene oxide (GO) and reduced graphene oxide (rGO) by oxidizing graphite powder with the 9:1 volume combination of concentrated sulfuric acid/ and ortho-phosphoric acid (H₂SO₄/H₃PO₄) in the company of KMnO₄ as an oxidant. The acid combination solution of H₂SO₄/H₃PO₄ produces the improved oxidized hydrophilic GO without any evolution of hazardous gases instead of only H₂SO₄, which differentiates this procedure from the Hummers’ method. Then, the synthesized GO is diminished to rGO by employing various reducers namely hydrazine hydrate, sodium borohydride and, ascorbic acid through the chemical route. The properties of synthesized materials have been investigated by diverse investigative systems that are X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Raman spectroscopy and, Energy Dispersive X-ray spectroscopy (EDS) which approved its high crystallinity and reduction of GO into rGO. EDS analysis confirms that the carbon to oxygen ratio is higher in rGO prepared by using hydrazine hydrate in comparison to rGO made by using sodium borohydride and ascorbic acid which reveals the good reducing capability of hydrazine hydrate. Hence, it may be concluded that the rGO synthesized by the reduction of GO in the presence of hydrazine hydrate is better as compared to others and it is expected that the synthesized material may be used for various applications.

1. Introduction

Graphene is the thinnest and strongest material having a two-dimensional (2D) structure with sp²-hybridized carbons [1-3]. The material based on graphene has been widely utilized in support of several advanced purposes namely Li-ion batteries, Supercapacitors, etc[4-15]. For the synthesis of GO, various synthesis methods in particular thermal reduction [16], chemical reduction [17], electrochemical reduction [18] have been used. In the chemical reduction technique for the oxidation of graphite, the Tour method is widely used because it is cost-effective and environmentally friendly [19]. Moreover, some modification in this process has been employed to develop the efficiency of the oxidation of graphite [20-21]. The properties and performance of synthesized material in the above-stated applications are dependent on the oxygen content [22-24]. The complete reduction of GO into reduced graphene oxide (rGO) and complete exclusion of oxygen from it is still a contest. To achieve this goal, some modification in the well-known reported method [25] has been carried out in the current design for the formation of rGO by using various reducing agents. To the best of our knowledge, the comparison of effects of various reducers to produce rGO from GO has been not available in the literature. Hence, the present studies related to the synthesis of graphene oxide by using graphite powder by Tour method and then reduced into rGO by various reductants such as ascorbic acid, sodium borohydride, Hydrazine
Hydrate. Furthermore, the properties of synthesized samples have been investigated by several diagnostic systems such as X-ray diffraction (XRD), Raman spectroscopy, Field Emission Scanning Electron Microscope (FESEM), and Energy Dispersive X-ray spectroscopy (EDS).

2. Synthesis of GO and rGO

2.1 Chemicals and materials
Graphite flake (natural, 325 mesh) along with a purity of 99.8% is purchased from Sigma Aldrich. Sulphuric acid (H₂SO₄), potassium permanganate (KMnO₄), barium chloride (BaCl₂), hydrogen peroxide (H₂O₂), Phosphoric acid (H₃PO₄), Hydrochloric acid (HCl) are obtained from Merck, India. Distilled water has been utilized during all the experiments.

2.2 Preparation of GO
GO has been synthesized by the Tour method [25-26]. Firstly, an acid solution having 9:1 (volume/volume ratio) of concentrated H₂SO₄ and H₃PO₄ has been prepared. Then, the mixture of 9 g of KMnO₄ (potassium permanganate) and 1 g of graphite powder (in 9:1 ratio) is added to the prepared acid mixture. After that, the reaction mixture is heated and stirred for 12 hours at 50 °C. After this time interval, the thick paste having greenish-black colour is formed and then cool down the reaction mixture at room temperature. Finally, the distilled water of quantity 500 millilitres is added into the reaction mixture for stopping this reaction. In order to decrease the ions of manganese to soluble manganese sulphate (MnSO₄) and manganese oxides, 20 millilitres of 30 wt.% hydrogen peroxide (H₂O₂) is added, as defined by the reaction given below [27]:

\[
2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O} \text{ (steam)} + 5\text{O}_2 \tag{1}
\]

With the addition of 30 weight percent of H₂O₂, bubbling occurs, and a clear pale colour appears that signifying a high level of oxidation. The reaction product is centrifuged by centrifugation at 4000 rpm and cleaned with distilled water and 5% HCl mixture again and again till the sulphate ions are completely removed. The verification of elimination of the metal sulphate ions has been done by applying barium chloride (BaCl₂) mixture. Finally, the product is dried up at 60 °C.

2.3 Reduction of Go with Ascorbic acid
Added 25 mg GO in 50 ml of Deionized water and sonicated it for 1 hour till a homogenous solution would be obtained. Maintained the PH value to 10-11 (by using 0.1 M of NaOH solution). Then added 100 mg of Ascorbic acid and stirred for 1 hour at 95 °C. Filtered out the solid product by using Whatman filter paper and cleaned with ethanol and distilled water. Then dried up in the oven at 60 °C.

---

**Figure 1.** (a) Shows the bright yellow colour when 30 wt.% H₂O₂ is added to the mixture. (b) the obtained solution of graphene oxide (GO) after centrifugation at 4000 rpm and rinsed with distilled water and 5% HCl mixture continually for removal of the metal sulphate ions.
2.4 Reduction of GO with sodium borohydride
Added 25 mg GO in 50 ml of Deionized water and sonicated it for 1 hour till a homogenous solution would be obtained. Maintained the PH value to 10-11 (by using 0.1 M of NaOH solution). Then added 200 mg of sodium borohydride (NaBH₄) and stirred for 1 hour at 95 °C. Filtered out the solid product by using Whatman filter paper and cleaned with ethanol and distilled water. Then dried up in the oven at 60 °C.

2.5 Reduction of GO with Hydrazine Hydrate
Added 25 mg GO in 50 ml of Deionized water and sonicated it for 1 hour till a homogenous solution would be obtained. Maintained the PH value to 10-11 (by using 0.1 M of NaOH solution). Added 4 ml Hydrazine Hydrate and stirred at 90 °C for 1 hour. Filtered out the solid product by using Whatman filter paper and cleaned with ethanol and distilled water. Then dried up in the oven at 60 °C.

3. Characterization

Bruker D8 advance X-ray diffractometer having Cu Kα radiation (λ = 1.54060 Å) has been used for noting X-ray diffraction (XRD) patterns to explore the crystallinity and structure of formed samples. The surface morphology of synthesized samples has been recorded by using a field emission scanning electron microscope (JSM-7610FPlus). To enhance the surface conductivity, the samples have been coated with gold by using a DII-29030SCTR smart coater. Furthermore, the elemental analysis has been carried out using Energy-dispersive X-ray spectroscopy (EDS). Renishaw In-Via confocal micro-Raman spectrometer with 488 nm argon-ion laser at room temperature has been used for noting the Raman spectra of synthesized materials.

3.1 X-ray diffraction
The XRD pattern of Graphite, GO and rGO synthesized by using different reducing agents have been presented in Figure 2. In the case of graphite, the diffraction peak is available at 26.7° with an interlayer spacing of 3.7 Å. Moreover, in the case of GO, the diffraction peak appears at 10.9° with an interlayer distance of 8.5 Å. The other small peaks around 43° in the case of GO are not observed which confirms that synthesized GO is not in limited order in mounded sheets [28]. The shifting in the position of the peaks in the case of rGO_AA, rGO_HH, rGO_SB is due to the decline in the interlayer gap owing to the expulsion of groups comprising oxygen in the reduction procedure. It can be too observed that the XRD spectrum of different reduced graphene oxide is not smooth and small peaks are noticed around 43° because there are some residuary functional units on the rGO that affects the rGO assembly [29].
3.2 Raman Spectra
The Raman spectra of Graphite, GO and rGO produced by utilizing distinct reducers, have been presented in Figure 3. In the case of graphite, the graphitic pattern (G band) occurs at 1575 cm\(^{-1}\) due to highly ordered graphite. Unlike peaks are noted at 1365 cm\(^{-1}\) and 1591 cm\(^{-1}\) in the case of graphene oxide which correspond to the D band and G band of the carbonic matter. The fraction of the intensity of D height and that of G height (I\(_D\)/I\(_G\)) are about 0.9 and 1.0 for GO and rGO synthesized by using various reducing agents, respectively. This (I\(_D\)/I\(_G\)) ratio confirms the mean dimension contraction of sp\(^3\) realms [30].
3.3 FESEM
In Figure 4, the micrograph of GO confirms its sheet-type structure with a magnification of 25,000x. The surface morphologies of synthesized rGO_AA, rGO_HH and rGO_SB confirm its wrinkled stacked layers structure [31]. In rGO, several edges are visible on it, and it is very essential for the interaction of synthesized material with other materials. It is noticeable, the complete change in the surface morphologies has been brought by the conversion of GO into rGO. The more wrinkled type of structure has been noted in the case of sodium borohydride as correlated to hydrazine hydrate and ascorbic acid.

![Figure 4](image)

**Figure 4** (a) FESEM image of GO at a magnification of 25,000x (b) FESEM image of rGO prepared by hydrazine hydrate. (c) FESEM image of rGO prepared by sodium borohydride. (d) FESEM image of rGO prepared by ascorbic acid.

3.4 Energy-dispersive X-ray spectroscopy (EDS).

The EDS spectra of synthesized rGO_AA, rGO_HH and rGO_SB is displayed in Figure 5. The carbon to oxygen ratio is a significant parameter that determines the oxygen content present in the sample. In the case of GO, the C:O fraction is about 2.53. The C:O fraction after the reduction of GO into rGO is about 9.99, 7.62 and 6.69 respectively, by employing a variety of reducers such as hydrazine hydrate, ascorbic acid, sodium borohydride. The higher C:O fraction in the case of hydrazine hydrate confirms its effectiveness in the reduction procedure.
4. Conclusion and Summary

Due to the simple synthesis and astonishing properties of graphene oxide, it is an auspicious material. Although the process of formation decides the Graphene oxide assembly. Here, the synthesis of graphene oxide by the Tour method is less hazardous, more efficient, and eco-friendlier than Modified Hummer’s method without the release of toxic gases. Further, reduction of graphene oxide was done using a different reducing agent and characterized by XRD, FESEM, Raman Spectra, and EDS. The qualities of graphene oxide are affected using different chemicals and reducers because they produce different types of impurities. The reduction GO into rGO is effective in the case of hydrazine hydrate as a reducing agent as indicated by the higher carbon to oxygen ratio. Hence, it may conclude that the rGO synthesized by the reduction of GO in the presence of hydrazine hydrate is better as compared to other reducing agents and it is expected that the synthesized material has improved properties and may be used for various advanced applications.

References

[1] Rao C N R, Sood A K, Subrahmanyam K S and Govindaraj A 2009 Graphene: The new two-dimensional nanomaterial Angew. Chemie - Int. Ed. 48 7752–77
[2] Geim A K 2009 Graphene: Status and prospects Science (80-. ). 324 1530–4
[3] Morozov S V., Novoselov K S, Katsnelson M I, Schedin F, Elias D C, Jaszczak J A and Geim A K 2008 Giant intrinsic carrier mobilities in graphene and its bilayer Phys. Rev. Lett. 100
[4] Singh J and Dhaliwal A S 2022 Electrochemical and photocatalytic degradation of methylene blue by using rGO/AgNWs nanocomposite synthesized by electroplating on stainless steel J. Phys. Chem. Solids 160 110358
[5] Choi J H, Lee J, Byeon M, Hong T E, Park H and Lee C Y 2020 Graphene-Based Gas Sensors with High Sensitivity and Minimal Sensor-to-Sensor Variation ACS Appl. Nano Mater. 3 2257-65
[6] Chen X and Tian Y 2021 Review of Graphene in Cathode Materials for Lithium-Ion Batteries *Energy and Fuels* **35** 3572–80

[7] Gao J, Wu H, Li A, Yue Y, Xie D and Zhang X 2019 Graphene Nanofluids as Thermal Management Materials: Molecular Dynamics Study on Orientation and Temperature Effects *ACS Appl. Nano Mater.* **2** 6828–35

[8] Singh J and Dhaliwal A S 2020 Plasmon-induced photocatalytic degradation of methylene blue dye using biosynthesized silver nanoparticles as photocatalyst *Environ. Technol. (United Kingdom)* **41** 1520–34

[9] Liu J, Cui L and Losic D 2013 Graphene and graphene oxide as new nanocarriers for drug delivery applications *Acta Biomater.* **9** 9243–57

[10] Zhou T, Zhou X and Xing D 2014 Controlled release of doxorubicin from graphene oxide based charge-reversal nanocarrier *Biomaterials* **35** 4185–94

[11] Han T H, Kim H, Kwon S J and Lee T W 2017 Graphene-based flexible electronic devices *Mater. Sci. Eng. R Reports* **118** 1–43

[12] Velasco A, Ryu Y K, Boscá A, Ladrón-De-Guevara A, Hunt E, Zuo J, Pedrós J, Calle F and Martinez J 2021 Recent trends in graphene supercapacitors: From large area to microsupercapacitors *Sustain. Energy Fuels* **5** 1235–54

[13] El-Kady M F, Shao Y and Kaner R B 2016 Graphene for batteries, supercapacitors and beyond *Nat. Rev. Mater.* **1**

[14] Su H and Hu Y H 2021 Recent advances in graphene-based materials for fuel cell applications *Energy Sci. Eng.* **9** 958–83

[15] Czerniak-Reczulska M, Niedzielska A and Jędrzejczak A 2015 Graphene as a Material for Solar Cells Applications *Adv. Mater. Sci.* **15** 67–81

[16] 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 N. Y.* **48** 1146–52

[17] De Silva K K H, Huang H H, Joshi R K and Yoshimura M 2017 Chemical reduction of graphene oxide using green reductants *Carbon N. Y.* **119** 190–9

[18] Shao Y, Wang J, Engelhard M, Wang C and Lin Y 2010 Facile and controllable electrochemical reduction of graphene oxide and its applications *J. Mater. Chem.* **20** 743–8

[19] Singh J and Dhaliwal A S 2018 Synthesis, characterization and swelling behavior of silver nanoparticles containing superabsorbent based on grafted copolymer of polyacrylic acid/ Guar gum *Vacuum* **157** 51–60

[20] HIRATA M, GOTOU T, HORIUCHI S, FUJIIWARA M and OHBA M 2004 Thin-film particles of graphite oxide 1:High-yield synthesis and flexibility of the particles *Carbon N. Y.* **42** 2929–37

[21] Nakajima T, Mabuchi A and Hagiwara R 1988 A new structure model of graphite oxide *Carbon N. Y.* **26** 357–61

[22] Bansal S A, Singh S, Srivastava A, Singh A P and Kumar S 2021 Covalent attachment of 2D graphene oxide (GO) sheets with poly allylamine (PAA) for enhanced mechanical performance: Theoretical and experimental study *Polymer (Guildf).* **213**

[23] Singh J, Kumar S and Dhaliwal A S 2020 Controlled release of amoxicillin and antioxidant potential of gold nanoparticles-xanthan gum/poly (Acrylic acid) biodegradable nanocomposite *J. Drug Deliv. Sci. Technol.* **55** 101384

[24] Singh J and Dhaliwal A S 2019 Novel Green Synthesis and Characterization of the Antioxidant Activity of Silver Nanoparticles Prepared from Nepeta leucophylla Root Extract *Anal. Lett.* **52** 213–30

[25] Higginbotham A L, Kosynkin D V., Sinitskii A, Sun Z and Tour J M 2010 Lower-defect graphene oxide nanoribbons from multiwalled carbon nanotubes *ACS Nano* **4** 2059–69

[26] Twinkle, Singh K, Bansal S A and Kumar S 2019 Graphene oxide (GO)/Copper doped Hematite (α-Fe2O3) nanoparticles for organic pollutants degradation applications at room temperature and neutral pH *Mater. Res. Express* **6**

[27] Shahriary L, Ghourchian H and Athawale A A 2014 Graphene-multiwalled carbon nanotube hybrids synthesized by gamma radiations: Application as a glucose sensor *J. Nanotechnol.*
[28] Stobinski L, Lesiak B, Malolepszy A, Mazurkiewicz M, Mierzwa B, Zemek J, Jiricek P and Bieloshapka I 2014 Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods J. Electron Spectros. Relat. Phenomena 195 145–54

[29] Krishnamoorthy K, Veerapandian M, Yun K and Kim S J 2013 The chemical and structural analysis of graphene oxide with different degrees of oxidation Carbon N. Y. 53 38–49

[30] Xue Y, Zhu L, Chen H, Qu J and Dai L 2015 Multiscale patterning of graphene oxide and reduced graphene oxide for flexible supercapacitors Carbon N. Y. 92 305–10

[31] Marcano D C, Kosynkin D V., Berlin J M, Sinitskii A, Sun Z, Slesarev A, Alemany L B, Lu W and Tour J M 2010 Improved synthesis of graphene oxide ACS Nano 4 4806–14