

Synthesis and Characterization of Graphene Oxide and Graphene Nanomaterial for Fuel Cell Applications

Christabel C. Ngetich, James M. Mutua, Patrick G. Kareru, Evan Murimi, and Kabini Karanja

Abstract—Nanotechnology and nanomaterials are key to bridging the energy supply and demand deficit in the world. Graphene, an allotrope of carbon, is the future nanomaterial for energy conversion and storage devices. The inability to produce large quantities and property optimized graphene hinders its widespread application in the energy sector. This paper describes the synthesis and characterization of graphene obtained by the chemical exfoliation of graphite. The improved Hummer's method that excludes the use of sodium nitrate is employed to synthesize graphene oxide (GO) which is further reduced to graphene using ascorbic acid. The resultant GO and graphene materials are characterized by Fourier Transform-Infrared (FT-IR) spectroscopy, ultraviolet visible (UV-vis) spectroscopy, and Scanning Electron Microscopy (SEM). The electrical conductivity of both GO and graphene is also analyzed. The FT-IR analysis of GO indicates the presence of oxygen containing functional groups with formation of C=O, C-H, C-O-C, and COOH chemical bonds showing that graphite is completely oxidized. Scanning electron microscopy is used to analyze the morphology and structure of graphite, GO, and graphene and the results show a decrease in number of layers in graphene compared to graphite and GO. The obtained graphene in this work forms a foundation material for application in energy conversion devices such as fuel cells.

Keywords—Graphene; Nanomaterial; Improved Hummer's Method; Chemical Exfoliation.

I. INTRODUCTION

THE global energy demand continues to increase as a result of economic, population, and industrial growth. The gap between the energy demand and supply has negatively impacted the environment and global economy and has promoted researchers and scientists to find alternative and long-lasting solutions to the energy crisis.

Nanoscience and nanotechnology promises a breakthrough to the future of energy sector through the development, synthesis, characterization, and utilization of nanomaterials with novel properties [1]. Carbon material has particularly been the center of interest in technology development due to its outstanding properties and its existence in different allotropic forms i.e.,

fullerenes, carbon nanotubes (CNTs), and graphene [2].

Graphene, also known as a "wonder material" is the building block of the other carbon allotropes has gained interest among researchers in various sectors such as medicine, electronics, and energy due to its outstanding properties [3]. However, one of the obstacles to widespread use of graphene is its high manufacturing costs. Graphene oxide (GO) is the oxidized form of graphene containing oxygen functional groups including carboxylic acid at the edges and hydroxyl and epoxy groups on its basal plane. GO is commonly used as the precursor material in the production of graphene due to its ease of functionalization and low manufacturing cost [4]. Thus, it is of importance to employ the right and economical approaches to obtain GO. Mechanical exfoliation of graphite with scotch tape is the most commonly used method that was first developed to obtain a few mono-layer of graphene [5]. The advantage of this method is that it can produce monocrystalline graphene films [6]. However, the low yield of graphene obtained limits the application of this method. Moreover, controlling the thickness and number of crystals has been found to be difficult. The chemical exfoliation of graphite is considered as one of the conventional techniques to produce GO in bulk with the Hummer's method developed by Hummers *et al.* [7]. This method involves the exfoliation of graphite into GO by dissolving it in a mixture of sodium nitrate (NaNO₃), potassium permanganate (KMnO₄) and concentrated Sulphuric acid (H₂SO₄). In as much as the Hummers' method has been found to be efficient and quicker in the synthesis of GO it still suffers from some issues such as the emission of toxic gases as well as low produced quantity of GO [8], [9]. An improved Hummers' method was reported by Marciano *et al.* [10], this approach replaces NaNO₃ with phosphoric acid (H₃PO₄) and a larger amount of KMnO₄ is used during the exfoliation process. The method has been found to produce highly oxidized GO [11]. Once GO has been obtained the next step is usually to reduce it to graphene using reducing reagents with hydrazine being the most commonly employed. Chen *et*

C. C. Ngetich, Department of Mechanical Engineering, JKUAT (phone: +2540729229362; e-mail: cchepngeno@jkuat.ac.ke).

J. M. Mutua, Department of Mechanical Engineering, JKUAT (e-mail: mutajay@eng.jkuat.ac.ke).

P. G. Kareru, Department of Chemistry, JKUAT (e-mail: pgkareru@eng.jkuat.ac.ke).

E. Murimi, Department of Mechatronic Engineering, JKUAT (e-mail: murimi.evan@eng.jkuat.ac.ke).

K. Kabini, Department of Mechatronic Engineering, JKUAT (e-mail: kkabini@eng.jkuat.ac.ke).

al. [12] recently employed hydrazine hydrate to chemically reduce GO to graphene with the results showing gradual removal of the oxygen-functional groups in GO with increase in hydrazine quantity. Other researchers [13]–[15], have also demonstrated the effectiveness of hydrazine hydrate in the reduction of graphene oxide to graphene. However, the major challenge with this reducing agent is its toxicity and explosive nature which makes it harmful to the environment. The toxic nature of hydrazine and metal hydrides has prompted research to find alternative ways to reduce GO by using reducing agents considered green including plant extracts [16]–[18], organic acids [19], and amino acids [20]. Among the green reducing agents, vitamin C (ascorbic acid) is considered effective and environmental friendly. In this work, the synthesis of GO and eco-friendly reduction of GO to graphene for fuel cell applications using ascorbic acid is reported. Graphene oxide is produced by chemical exfoliation of graphite using the Improved Hummers' method.

II. EXPERIMENTAL METHOD

A. Materials and Chemicals required

Graphite powder was purchased from Sigma Aldrich, the chemical reagents, i.e., Sulphuric acid (H_2SO_4 , 98%), Phosphoric acid (H_3PO_4 , 75%), Hydrochloric acid (HCl), Potassium permanganate ($KMnO_4$), Hydrogen peroxide (H_2O_2 , 30% wt.), and Ascorbic acid were purchased from a local supplier (Kobian Scientific, Kenya).

B. Synthesis and Purification of Graphene Oxide

Graphene oxide was synthesized via the chemical exfoliation of natural graphite using the Improved Hummer's method [10]. This method excludes $NaNO_3$ that is associated with the generation of toxic gases such as nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4).

Briefly, 2 g of natural graphite flakes was added to an acid mixture consisting of 54 ml concentrated sulfuric acid (H_2SO_4) and 6 ml phosphoric acid (H_3PO_4). The acid mixture was stirred in an ice bath for 30 minutes followed by the slow addition of 12 g of potassium permanganate ($KMnO_4$) to begin the oxidation process. The resulting mixture was then placed in a shaker set at $50^\circ C$ and allowed to continuously stir for 8 hours. After graphite was fully oxidized indicated by a brown colour, 10 ml of 30 % hydrogen peroxide (H_2O_2) was added slowly to stop the reaction of $KMnO_4$. This was followed by the addition of 100 ml of deionized (DI) water and the solution left to stand overnight. To purify the obtained GO solution, 10% HCl solution was prepared and used to clean GO using a vacuum filter. The obtained metal free GO solution was then divided into four separate 50 ml centrifuge tubes and further washed with DI water in 5 steps at a centrifugation speed of 6000 rpm for 10 minutes. Finally, the GO product was dried in the oven at $70^\circ C$ for 48 hours.

C. Synthesis and Purification of Graphene

The obtained GO in the previous step was used in the synthesis of graphene (rGO). The GO film was first added to 50 ml DI

water and sonicated using for 30 minutes forming GO dispersion of 50 ml. Next, 5 ml of ascorbic acid (ratio of 10:1 of GO to ascorbic acid) was added to the GO solution and stirred. The resulting mixture was then placed in a water bath sonicator with the temperature set to $25^\circ C$ and left for 1 hour. The color of the solution was noticed to change from brownish yellow to black. The obtained solution was then washed with DI water and centrifuged in two steps. The final product was then freeze-dried using a freeze dryer (Alpha 1-4 LD plus –Martin Christ model-101541, Germany) for 21 hours.

D. Characterization

The synthesized GO and graphene samples were characterized by Fourier Transform-Infrared Spectroscopy (FT-IR, Bruker, Ettlingen, Germany) to determine the functional groups present, Scanning Electron Microscopy (SEM, JEOL, Tokyo, Japan), and Ultraviolet-visible spectroscopy (UV-vis) using a UV-vis 1800 spectrophotometer (Shimadzu, Kyoto, Japan).

III. RESULTS AND DISCUSSION

Figure 1 (a) - (c) shows the obtained images of synthesized GO solution, freeze dried GO powder, and graphene respectively. The GO produced has a brownish color an indication that the graphite flakes were successfully exfoliated to GO. The freeze-dried GO sample was employed for characterization. After reduction of GO to graphene using ascorbic acid, the color was observed to change from brownish to black as shown in Fig. 1 (c). The color change being due to the removal of the oxygen-containing functional groups after reduction of GO which results in the repair of the pi-networks within the sheets.

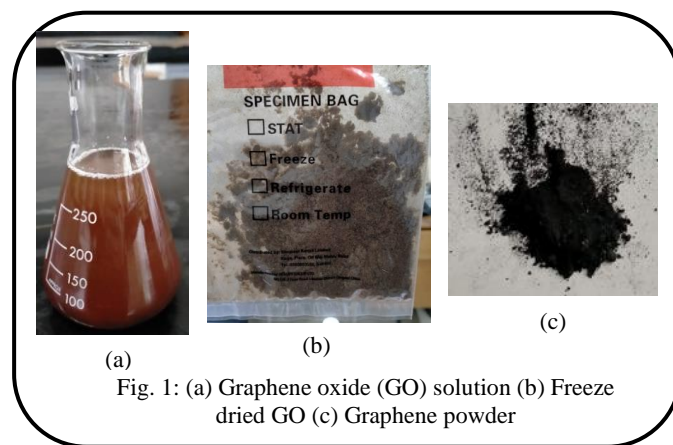


Fig. 1: (a) Graphene oxide (GO) solution (b) Freeze dried GO (c) Graphene powder

Low vacuum Scanning Electron Microscopy (SEM) with power 10 kV, was used to examine the morphologies of graphite powder, synthesized GO and graphene and the results are depicted in Fig. 1-3. The observed micrograph of graphite was obtained at a magnification of 300x and is as shown in Fig. 2. The image has a sheet like structure appearing to be densely packed characteristic of graphite material.

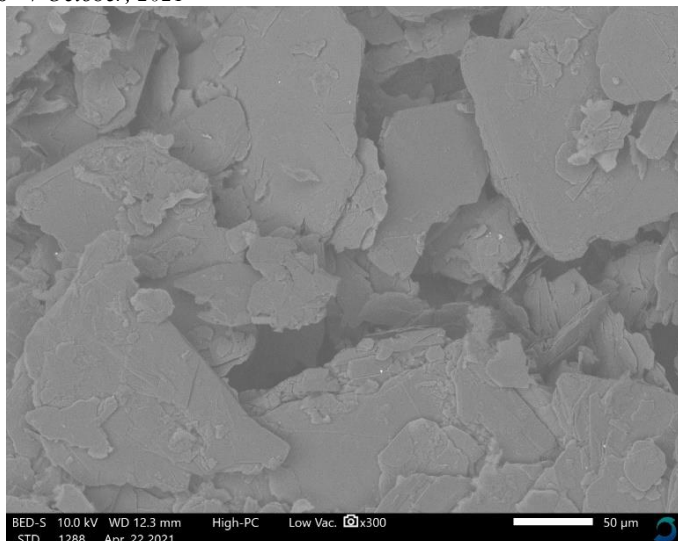


Fig. 2: SEM image of graphite

Figure 3 shows the observed SEM morphology of GO. In this case, a wrinkled sheet structure can be seen showing possible chemical exfoliation of graphite.

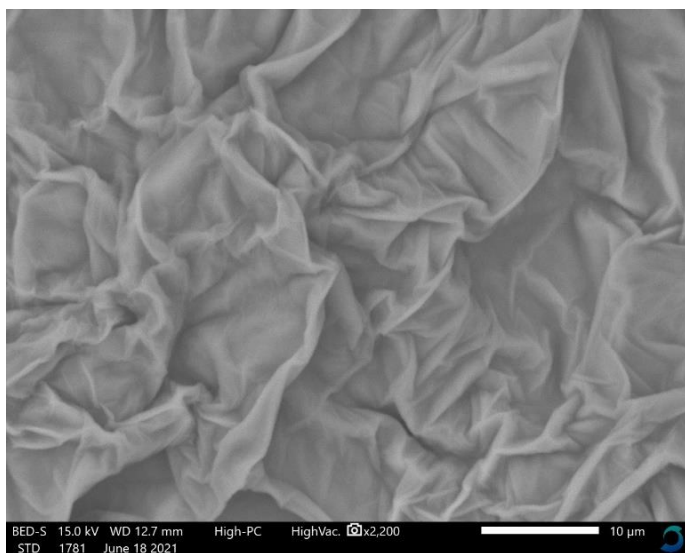


Fig. 3: SEM image of graphene oxide

Reduce graphene oxide's SEM micrograph (Fig. 4) shows thin sheets with irregular sizes. It is observed that after reduction of GO the particles agglomerate together which is due to the loss of the oxygen functional groups on GO surface.

Figure 5 exhibits the FT-IR spectra of graphite, GO, and graphene. The graphite FT-IR spectrum (Fig. 5 (a)) is a straight line with no visible peaks indicating that graphite is chemically inert [21].

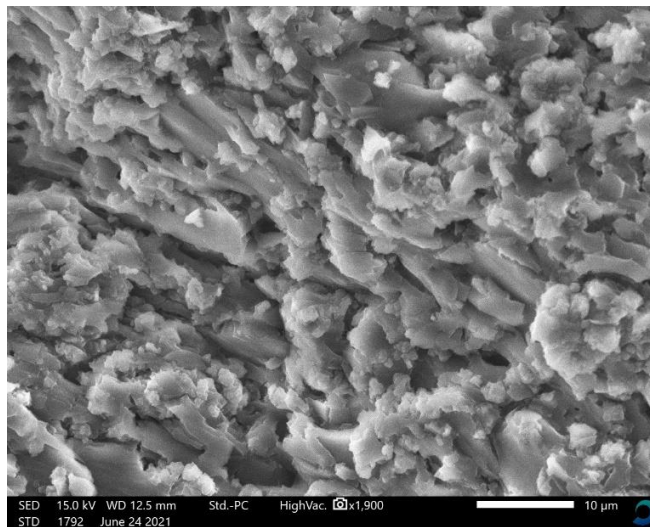


Fig. 4: SEM image of reduced graphene oxide

The obtained FT-IR spectrum of GO (Fig. 5 (b)) has broad peaks observed in the region 3271-3448 cm^{-1} . This is attributed to the O-H stretching vibrations. The peak at 1630.9 cm^{-1} is attributed to C=C groups while the peaks at 1400 cm^{-1} and 1119 cm^{-1} are assigned to OH and alkoxy C-O respectively. After reduction of graphene oxide, the peak at 1630.9 cm^{-1} is replaced by peak at 1590.7 cm^{-1} which indicates the restoration of the sp^2 carbon networks.

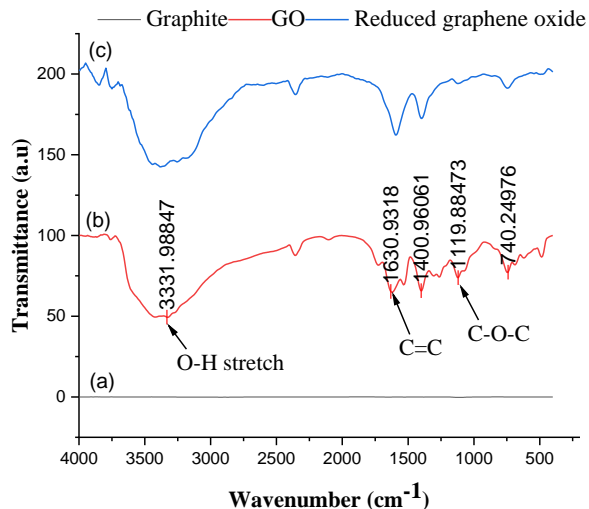


Fig.5: FT-IR spectra of graphite, graphene oxide and graphene

The optical properties of GO and graphene were evaluated using UV-vis spectroscopy. The obtained UV-vis spectra for GO and graphene is as depicted in Fig. 6. The absorption peak for GO dispersion was observed at 228 nm because of $n \rightarrow \pi^*$ transitions of C=O in the aromatic ring. By reducing GO to graphene using ascorbic acid, a redshift of the absorption peak to a wavelength of 262 nm is observed as depicted in the UV-vis spectra of graphene. This characteristic peak in graphene is due to $\pi \rightarrow \pi^*$ transition of C=C bonds in the aromatic ring. The absorption peak shift observed in graphene

is due to the restoration of the electronic configuration upon the reduction of GO.

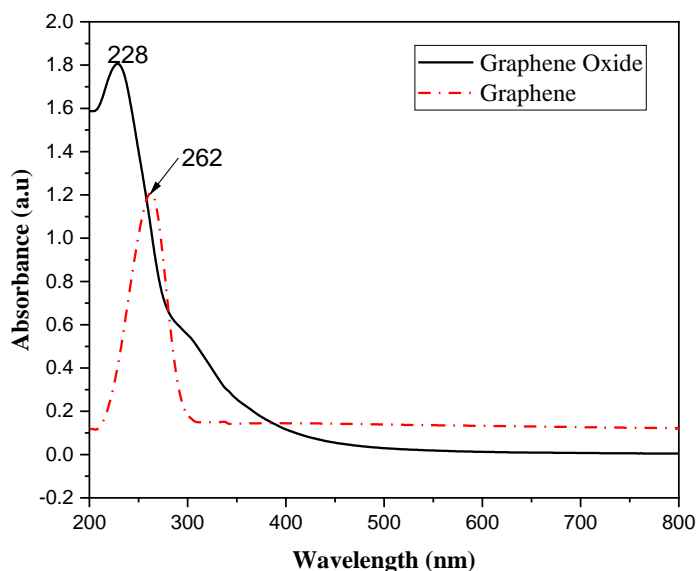


Fig. 6: UV-vis spectra of graphene oxide and graphene

The obtained UV-vis absorption values were further employed to calculate the optical band-gaps (E_g) of both GO and rGO. The optical band-gap was estimated using the Tauc plot. The Tauc equation [21] is defined as

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (1)$$

Where α the absorbance value obtained from the UV-vis spectrum, h is the Plank's constant, ν is the incident frequency, E_g is the optical band-gap, and A is a constant. The optical band-gaps are calculated by extrapolating a linear segment on the Tauc plot to intersect the x-axis. Figure 7 shows the obtained Tauc plot for GO. The optical band-gap was found to range from 3.20 - 4.21 eV. This large value of the band-gap shows that GO is an insulator due to the presence of the oxygen functional groups.

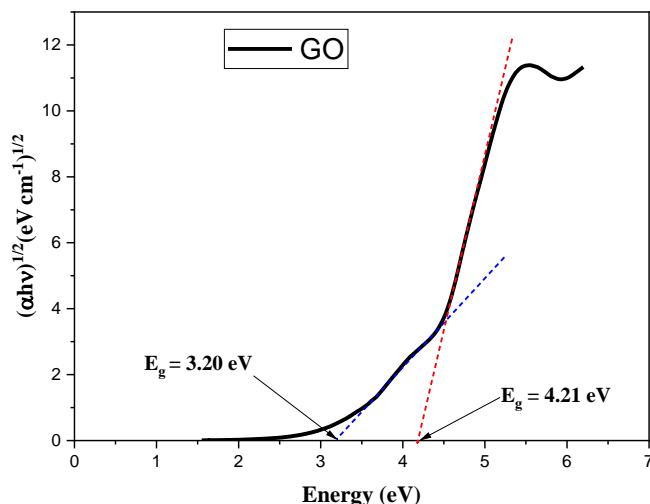


Fig. 7: Tauc plot for graphene oxide (GO)

Figure 8 shows the calculated optical band-gap of rGO from the Tauc plot. The optical band-gap is found to be in the range 0.8 – 2.7 eV. This value is lower when compared to that obtained for GO. The decrease in the optical band-gap is attributed to the reduction in the oxygen-containing functional groups when GO is reduced using ascorbic acid.

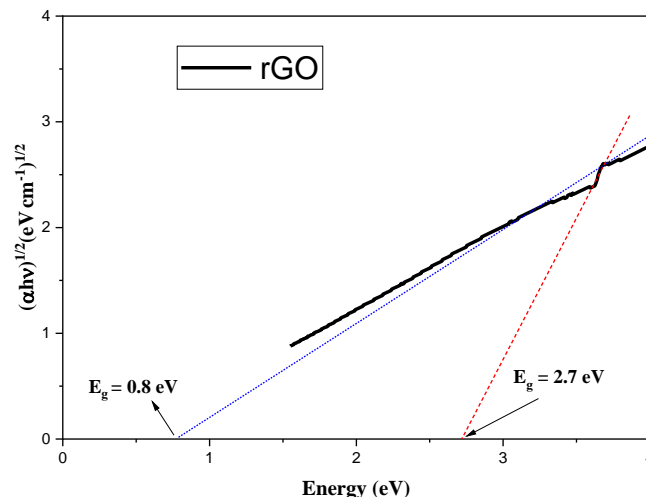


Fig. 8: Tauc plot for reduced graphene oxide (rGO)

Further to the characterization of GO and reduced graphene oxide and calculation of its optical band-gaps, the electrical properties were evaluated by measuring the electrical resistance of GO and rGO using a fluke 87V TRMS digital multi-meter (Everett, Washington, USA), with max range of ~ 1 K Ω . The electrical resistance of GO powder was found to range from 1.2 M Ω to 1.5 M Ω indicating that the material is an insulator which occurs due to the existence of the oxygen functional groups on the edges and basal planes of GO after exfoliation from graphite. The reduced graphene oxide had an electrical resistance of 100-500 Ω measured, which is low in comparison to the value obtained for the synthesized GO. To fabricate the parts of a fuel cell for instance the bipolar plates and the cathode electrode, a material with good electrical and thermal conductivity is required. The novelty of this study is pegged on being able to not only synthesize the GO using the improved Hummers' methods but also to characterize its properties with focused applications in fuel cell electrodes, bipolar plates, and potential replacement of the expensive Platinum catalyst. This will support R&D in fuel cell in developing countries besides contributing to the body of knowledge in demystifying graphene as a material of choice in energy storage and conversion systems.

IV. CONCLUSION

The vast and excellent properties of graphene allows for its use in widespread applications. However, one challenge has been its production in large-scale. In addition, some applications require the tailoring of fabricated graphene to improve on its properties. In this study, derivatives of graphene including GO and rGO were successfully synthesized via the chemical exfoliation of graphite using the improved Hummers' method. This approach proved to be efficient in the production of GO in

large-scale graphite. The resulting GO was reduced using ascorbic acid (10:1 ratio) that is mild and less toxic to form rGO. The synthesized GO and rGO were then characterized using SEM, FT-IR, and UV-vis characterization techniques. The obtained FT-IR shows the presence of oxygen-containing functional groups confirming the formation of GO. On the other hand, the obtained UV-vis spectra for GO and rGO shows absorption peaks at 228 nm and 262 nm with this redshift indicating the restoration of the electronic conjugation of rGO after reduction using ascorbic acid. An optical band-gap in the range of 3.20 – 4.21 eV is obtained while the optical band-gap for rGO is in the range of 0.8 – 2.7 eV. For fuel cell applications, low optical band-gaps are desirable as they indicate that the material is a semiconductor thus easy for it to be doped to further improve on its properties. The unique properties possessed by GO and reduced graphene oxide opens its endless possibilities for various applications especially in energy-conversion devices. Future experiments involves doping of the obtained rGO to improve its properties for application in a polymer electrolyte membrane fuel cell.

ACKNOWLEDGEMENT

The authors acknowledge the funding and support from Kenya Education Network (KENET), German Academic Exchange Service (DAAD), and Jomo Kenyatta University of Agriculture and Technology (JKUAT).

REFERENCES

- [1] S. Bayda, M. Adeel, T. Tuccinardi, M. Cordani, and F. Rizzolio, "The history of nanoscience and nanotechnology: From chemical-physical applications to nanomedicine," *Molecules*, vol. 25, no. 1, pp. 1–15, 2020.
- [2] M. C. dos Santos, M. C. Maynard, L. R. Aveiro, E. C. da Paz, and V. dos Santos Pinheiro, *Carbon-Based Materials: Recent Advances, Challenges, and Perspectives*. Elsevier Ltd., 2017.
- [3] J. H. Lee, S. J. Park, and J. W. Choi, "Electrical property of graphene and its application to electrochemical biosensing," *Nanomaterials*, vol. 9, no. 2, 2019.
- [4] R. Xing, Y. Li, and H. Yu, "Preparation of fluoro-functionalized graphene oxide via the Hunsdiecker reaction," *Chem. Commun.*, vol. 52, no. 2, pp. 390–393, 2016.
- [5] K. Novoselov *et al.*, "Electric Field Effect in Atomically Thin Carbon Films," *Science (80-.)*, vol. 306, no. 5696, pp. 666–669, 2004.
- [6] C. Cao, Y. Sun, and T. Filleter, "Characterizing mechanical behavior of atomically thin films: A review," *J. Mater. Res.*, vol. 29, no. 3, pp. 338–347, 2014.
- [7] W. Hummers and R. Offeman, "Preparation of Graphitic Oxide," *J. Am. Chem. Soc.*, vol. 80, no. 6, p. 1339, 1958.
- [8] Y. Hu, S. Song, and A. Lopez-Valdivieso, "Effects of oxidation on the defect of reduced graphene oxides in graphene preparation," *J. Colloid Interface Sci.*, vol. 450, pp. 68–73, 2015.
- [9] J. Sun *et al.*, "Fully Converting Graphite into Graphene Oxide Hydrogels by Preoxidation with Impure Manganese Dioxide," *ACS Appl. Mater. Interfaces*, vol. 7, no. 38, pp. 21356–21363, 2015.
- [10] D. Marcano *et al.*, "Improved synthesis of graphene oxide," *ACS Nano*, vol. 4, no. 8, pp. 4806–4814, 2010.
- [11] A. Adetayo and D. Runsewe, "Synthesis and Fabrication of Graphene and Graphene Oxide: A Review," *Open J. Compos. Mater.*, vol. 09, no. 02, pp. 207–229, 2019.
- [12] H. Chen *et al.*, "Preparation of chemically reduced graphene using hydrazine hydrate as the reduction agent and its NO₂ sensitivity at room temperature," *Int. J. Electrochem. Sci.*, vol. 15, no. 2, pp. 10231–10242, 2020.
- [13] S. Park, J. An, J. R. Potts, A. Velamakanni, S. Murali, and R. S.

- [14] Ruoff, "Hydrazine-reduction of graphite- and graphene oxide," *Carbon N. Y.*, vol. 49, no. 9, pp. 3019–3023, 2011.
- [15] N. Cao and Y. Zhang, "Study of Reduced Graphene Oxide Preparation by Hummers' Method and Related Characterization," *J. Nanomater.*, vol. 2015, pp. 1–5, 2015.
- [16] X. Wang, Z. Yang, F. Mei, Y. Zhou, J. Xu, and Y. Jiang, "One pot synthesis of Sb₂O₃/reduced graphene oxide composite anode material for sodium ion batteries," *Mater. Lett.*, vol. 280, p. 128565, Dec. 2020.
- [17] S. Thakur and N. Karak, "Green reduction of graphene oxide by aqueous phytoextracts," *Carbon N. Y.*, vol. 50, no. 14, pp. 5331–5339, 2012.
- [18] X. Jin, N. Li, X. Weng, C. Li, and Z. Chen, "Green reduction of graphene oxide using eucalyptus leaf extract and its application to remove dye," *Chemosphere*, vol. 208, pp. 417–424, 2018.
- [19] B. Sabayan, N. Goudarzian, M. H. Moslemin, and R. Mohebat, "Green synthesis and high efficacy method for reduced graphene oxide by zataria multiflora extract," *J. Environ. Treat. Tech.*, vol. 8, no. 1, pp. 488–496, 2020.
- [20] R. Krishna *et al.*, "Improved Reduction of Graphene Oxide," *Mater. Today Proc.*, vol. 2, no. 1, pp. 423–430, 2015.
- [21] J. Wang, E. C. Salihi, and L. Šiller, "Green reduction of graphene oxide using alanine," *Mater. Sci. Eng. C*, vol. 72, pp. 1–6, 2017.
- [22] J. Tauc, "Optical Properties and Electronic Structure of Amorphous Semiconductors," *Opt. Prop. Solids*, pp. 123–136, 1969.