

GREEN REDUCTION OF GRAPHENE OXIDE USING CHROMOLAENA ODORATA EXTRACT AND ITS CHARACTERIZATIONS

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Abstract

This study synthesizes reduced graphene oxide (rGO) by modifying Hummer's method using various concentrations of Chromolaena Odorata rGO1 to rGO4 extract as a reducing agent, replacing the use of environmentally toxic chemicals. XRD analysis of rGO4 showed a sharp peak at 26.5°, corresponding to the (002) plane with an interlayer spacing of 0.33 nm. Raman micro-spectroscopy analysis showed an ID/IG ratio, indicating the removal of oxygen-containing functional groups from the structure. EDS analysis showed a C:O ratio of 14:1. The FESEM images of rGO4 showed a large-area, stacked sheet structure that was smooth and ruffled. The FTIR analysis showed a decrease in O-H, C=O, and C-O functional groups. The UV-vis absorption spectrum of rGO4 showed an absorption wavelength of 286 nm, indicating the restoration of the electron conjugated system, resulting from a band gap energy of 1.89 eV. In addition, the electrochemical performance of the synthesized FTO/rGO electrode was investigated using cyclic voltammetry (CV). The results demonstrate the performance of rGO4, evident from a larger CV curve area and high symmetry.

Keywords: Chromolaena Odorata; Graphene oxide; Hummer's method; Reduced graphene oxide

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Introduction

Graphene oxide (GO), a derivative of graphene, is renowned for its remarkable physicochemical properties, making it a pivotal material in various scientific and technological applications (Ray, 2015). However, the production of reduced graphene oxide (rGO), a more conductive form of GO, typically involves the use of hazardous reducing agents, raising significant environmental concerns. Many researchers propose rigorous approaches to produce a new environmentally friendly reducing agent. Kindalkar *et al.* (2021) use *Syzygium samarangense* (rose apple) fruit extract as a reducing agent for graphene oxide. Akhavan *et al.* (2012) report green tea polyphenols in the presence of iron to reduce graphene oxide. Verma *et al.* (2022) investigate another reducing agent for graphene oxide.

The main chemical components extracted from this green reduction are flavonoids, saponins, tannins, and phenolic compounds. These compounds are known for their strong antioxidant properties, which make them effective reducing agents. The reduction mechanism involves the donation of electrons from these antioxidant compounds to the graphene oxide (GO), resulting in the removal of oxygen-containing groups and the restoration of the conjugate structure of graphene. This electron donation helps reduce GO to rGO by breaking the CO, C=O, and O-H bonds in GO, restoring the sp-hybridized carbon network typical of graphene. In the search for more environmentally friendly alternatives, natural extracts have emerged as viable candidates, offering a sustainable pathway to synthesize rGO while minimizing ecological footprints. *Chromolaena odorata*, a plant known for its medicinal and pesticide properties, represents an interesting possibility in this context. Its extract is rich in reducing compounds and provides an eco-friendly option for the reduction of GO. This study pioneers the use of *Chromolaena odorata* extract for the green synthesis of rGO and aims not only to mitigate the environmental hazards associated with traditional reduction methods but also to investigate the efficiency of plant-based reducing agents in the field of advanced materials science. This study focuses on the synthesis and reduction of GO and was carried out using a reducing agent prepared from *Chromolaena odorata* extract, which is considered an environmentally friendly approach. The different mass ratios of *Chromolaena odorata* the reduction process result from their different morphological, optical, and electrochemical properties. The morphological, electrochemical, and optical properties of the synthesized rGO are

carefully analyzed using X-ray diffraction (XRD Shimadzu: XRD-6000), Raman spectroscopy (DXR SmartRaman), Energy-dispersive X-ray spectroscopy, Field-emission scanning electron microscopy (JEOL: JSM7610F), Fourier transform infrared spectroscopy (FTIR: Nicolet 6700), UV-visible spectroscopy (Metash 5200), and Cyclic voltammetry (CV) (Autolab) provides comprehensive insights into the effectiveness of the natural extract as a reducing agent. Our results show remarkable changes in the morphological, optical, and electrochemical properties of rGO synthesized with *Chromolaena odorata* extract, demonstrating its potential as a sustainable alternative in the field of materials science. The implications of this study extend beyond the field of graphene synthesis and suggest broader applicability of natural extracts in nanotechnology and environmental chemistry.

Materials and Methods

Material

Graphite powder (100 μm), Sulphuric acid (H_2SO_4 , 96%), Sodium nitrate (NaNO_3 , 99%), Potassium permanganate (KMnO_4 , 99%), Hydrochloric acid (HCl, 37%), Hydrogen peroxide (H_2O_2 , 30%) and Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 95%) from Union science trading co., Ltd. *Chromolaena Odorata* were collected from the local area (Sakon Nakhon district, Thailand).

Preparation of GO Powder

A modified Hummers method, known for its environmental sustainability, was used to synthesize graphene oxide (GO). In the first step, a reaction mixture was formulated by combining 1 g of graphite, 1 g of sodium nitrate (NaNO_3), and 30 mL of concentrated sulfuric acid (H_2SO_4 , 96%) in a beaker and then placed in ice bath to maintain the reaction temperature at 0°C for 30 min at a stirring speed of 500 rpm. Potassium permanganate (KMnO_4), a strong oxidizing agent, was added to the cooled solution to facilitate the oxidation of graphite to graphene oxide. The reaction mixture was then heated to 35°C , resulting in a brownish mixture, indicating the progression of the oxidation reaction. The mixture was then transferred to a round bottom flask and further reacted at 80°C , the mixture was washed with 180 mL of deionized water to remove impurities and excess reagents. The solid product was separated by filtration and washed with a dilute hydrochloric acid solution to neutralize residual

reactants and adjust the pH. Deionized water was then applied until the pH = 7. The resulting material was then dried in an oven at 80°C for 12 h to remove moisture. Finally, the dried product was ground into a fine powder using a mortar and pestle, producing a black powder that was identified as graphene oxide (GO).

Preparation of Chromolaena Odorata Extract And Reduction of Graphene Oxide

Fresh *Chromolaena odorata* leaves were first cleaned of contaminants and air-dried, followed by thorough dehydration in a vacuum oven at 80°C for a period of 12 h. The dried leaves were then pulverized into a fine powder using a standard fruit blender at a speed of 26,000 rpm for 5 min. This powder was then successfully immersed in 95% ethanol at ratios of 1:10, 1:5, 1:4, and 1:3 (g/ml) for 12 h in a controlled environment. After maceration, the mixture was filtered with filter paper No. 102 and processed in a rotary evaporator at a speed of 100 rpm and a temperature of 45°C for 30 min. In the reduction process, four samples of graphene oxide (GO) powder weighing 3 g each were mixed with different concentrations of *Chromolaena odorata* leaf extract using a magnetic stirrer at 100 rpm for 15 min. The mixture was then subjected to ultrasonication at 20 kHz for 20 min, followed by further magnetic stirring at 100 rpm for 3 h. The pH of the mixture was adjusted to a neutral value of 7. The mixture was then ball milled at 300 rpm for 15 h. In the final step, all samples were calcined at 600°C in an argon atmosphere for one hour to produce reduced graphene oxide powder (rGO), as shown in Figure 1.

Preparation of rGO4 Paste

To prepare rGO paste, the amounts of rGO4 (0.05 g) and ethyl cellulose (0.05 g) were mixed in 10 mL of ethanol in a beaker with continuous stirring. 1 ml of terpinol was then added to the solution with vigorous stirring. Finally, the solution was dried in the oven to obtain the GO paste (Islam *et al.*, 2023).

Results and Discussion

X-ray Diffraction Characterization

The graphite (JCPDS 41-1487) shows a sharp and intense peak around 26.5, which corresponds to the (002) peak of graphite observed with a d-spacing of about 0.36 nm. This peak indicates the reformation of the ordered graphitic structure after the reduction process. The high intensity suggests that the reduction was effective and resulted in the restoration of the crystal structure typical of

graphene. Graphene oxide (GO) shows that the broad peak for GO indicates a larger interlayer distance compared to graphite due to the presence of oxygen functionalities. The peak is shifted to a lower angle (around 10°-15°), suggesting that the material is more disordered than graphite. Reduced graphene oxide (rGO1-rGO4) shows that the spectra for rGO1-rGO4 show different peak intensities and positions, indicating that different reduction degrees of GO were observed at a d-spacing of about 0.8 nm. In general, as the degree of reduction increases, the peaks become sharper and move to larger angles, indicating recovery of the graphite structure. rGO4 shows a peak closer to that of graphite, which could indicate a higher degree of reduction, thereby reducing the interlayer distance and arranging the structure more like the pristine graphene shown in Figure 2.

Raman Spectroscopy Characterization

Graphene oxide (GO) shows a fairly pronounced D-band, indicating a significant degree of disorder due to oxidation. The G band is present

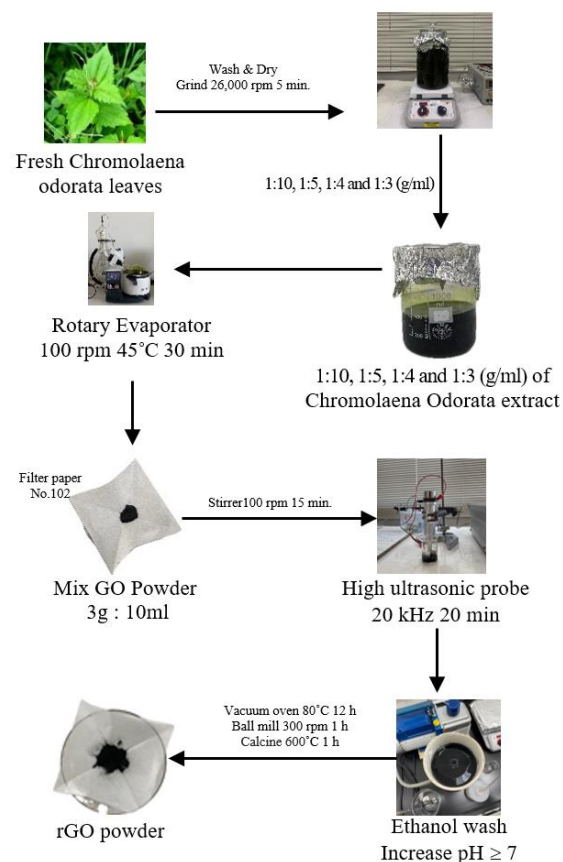


Figure 1. Schematic representation of reduced Graphene oxide (rGO)

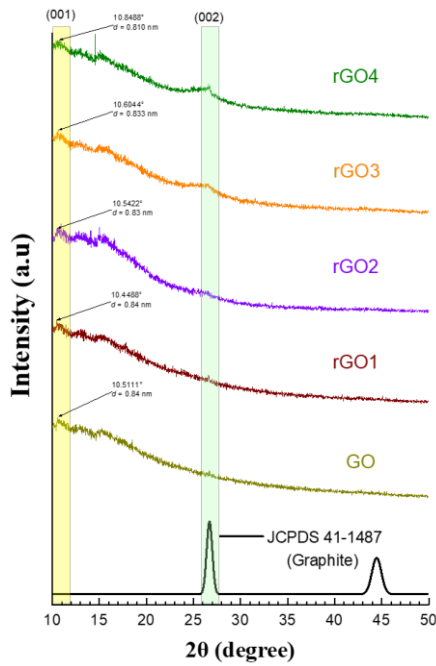


Figure 2. XRD spectra of Graphite, GO, and rGO1-rGO4

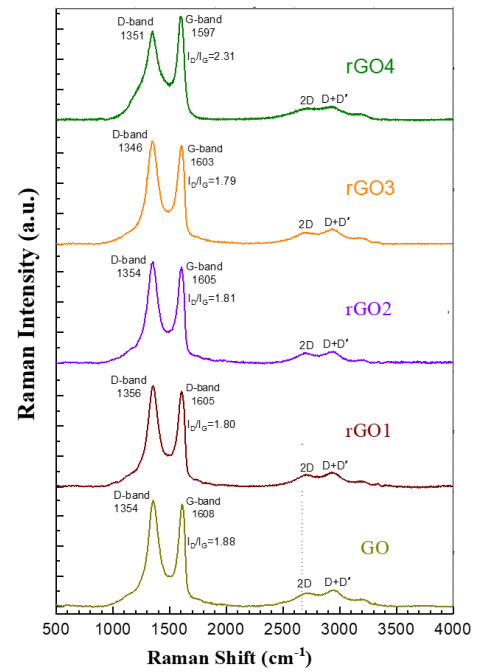


Figure 3. Shows Raman spectra of GO and rGO1-rGO4

but may be broader than in reduced samples, consistent with the presence of various oxygen functions that disrupt the sp^2 carbon network. The 2D band is either very weak or absent, which is typical for GO due to disruption of the graphite structure. Reduced graphene oxide (rGO1-rGO4) When changing from rGO1 to rGO4, the D-band intensity appears to decrease, indicating a reduction in defects and restoration of the graphite structure. The G band becomes sharper and shifts to a higher wavenumber, indicating an increase in graphite domains and recovery of the sp^2 network as the reduction proceeds. The 2D band is more prominent, especially in rGO4, suggesting a more characteristic structure of graphene with fewer layers and less disorder. The ratio of the intensity of the D-band to the intensity of the G-band (I_D/I_G) is shown in Figure 3 and Table 1.

Figure 4 shows the Raman spectrum of rGO4 with a D band at $1,351\text{ cm}^{-1}$ and a G band at $1,597\text{ cm}^{-1}$. Notably, the D-band shift indicates a significant reduction in oxidized functional groups and defects compared to graphene oxide (GO). However, based on the data in Table 1, it was found that the full width at half maximum (FWHM) of the G-band for rGO4 (77) is actually narrower than that of GO (82). This narrower G-band in rGO4 may indicate a more ordered graphite structure. Furthermore, the intensity ratio of D-band to G-band (I_D/I_G) for rGO4 is 2.31, reflecting a higher defect density compared to GO, which has a ratio of 1.88.

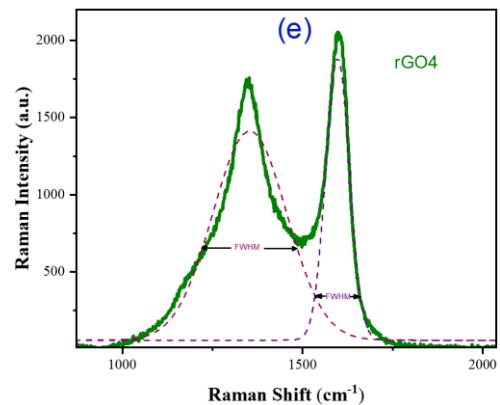


Figure 4. Shows the Full Width at Half Maximum (FWHM) data for (a) GO, (b) rGO1, (c) rGO2, and (d) rGO3

Table 1. Shows Parameters of Raman spectra for GO and rGO1-rGO4

Samples	D band	FWHM	G band	FWHM	I_D/I_G	I_G/I_{2D}
GO	1,354	162	1,608	82	1.88	1.00
rGO1	1,356	166	1,605	89	1.80	1.36
rGO2	1,354	169	1,605	91	1.81	0.79
rGO3	1,346	168	1,603	91	1.79	1.06
rGO4	1,351	241	1,597	77	2.31	0.75

The IG/I2D ratio of 0.75 further supports that rGO4 has fewer layers and may be close to a monolayer structure. These Raman features suggest an improvement in the graphitization process, although some remaining defects are likely caused by incomplete reduction or residual stresses. Further research is required to clarify these defects and their impact on the electrical performance of rGO4 in electronic applications.

Fourier Transforms Infrared Spectroscopy Characterization

Broad O-H stretch ($\sim 3,000$ - $3,700\text{ cm}^{-1}$), a broad peak due to hydroxyl groups and absorbed water molecules, indicating the highly oxidized nature of GO. C=O stretching ($\sim 1,720\text{ cm}^{-1}$) is a sharp absorption peak of carbonyl and carboxyl groups indicating the presence of significant oxidative functionalization. C-O (epoxy) stretching vibrations ($\sim 1,000$ - $1,300\text{ cm}^{-1}$) in this region are attributed to C-O stretching vibrations of epoxides and alcohols. Reduction of graphene oxide (rGO1-rGO4) in O-H. The intensity of the broad O-H stretching progressively decreases from rGO1 to rGO4, suggesting a decrease in hydroxyl and water content due to reduction. Decrease in C=O stretching: The peak intensity at $\sim 1,720\text{ cm}^{-1}$ decreases with increasing sample number (rGO1-rGO4), which correlates with the removal of oxygen-containing groups and the recovery of the conjugated graphene network. Changes in C-O stretching: The intensity and shape of the peaks associated with C-O stretching also change across samples, which is further evidence of the reduction of epoxide and other oxygen groups shown in Figure 5. Furthermore, The C-O stretching vibrations were expected in the range of $1,000$ - $1,300\text{ cm}^{-1}$, but they may not be visible in the FT-IR spectrum due to the overlap with other functional groups or the low concentration of these oxygen functionalities after the reduction process.

Energy Dispersive X-Ray Spectroscopy

The weight percentage (wt%) and the atomic percentage (at%) provide information about the relative abundance of carbon and oxygen. The element mapping shows the distribution of different elements in the sample. A uniform color distribution for carbon and oxygen would indicate a homogeneous distribution of the respective elements within the sample shown in Table 2. The ratio of the atomic weights of carbon and oxygen is 1.7, indicating the significant presence of the oxygen functional groups characteristic of GO. The poor electrical conductivity reflects interference with sp^2 binding by these groups. Due to the oxidation process, the mechanical

properties are significantly weakened compared to pure graphene. The high chemical reactivity is due to the presence of various oxygen functional groups.

rGO4 exhibits the highest electrical conductivity and strongest mechanical properties in the series, highlighting its superiority for applications that utilize these properties. The high C/O ratio indicates a material that closely resembles pure graphene, making it a potential candidate for high-end electronics applications. The stable chemical reactivity suggests that the reduction process has effectively deleted the majority of reactive oxygen functional groups, resulting in a material that potentially offers better environmental stability and a lower propensity for undesirable side reactions (Piñeiro-García *et al.*, 2021).

SEM Characterization

Figure 6(a) shows an overall view of the GO surface. The GO sheets exhibit a certain degree of

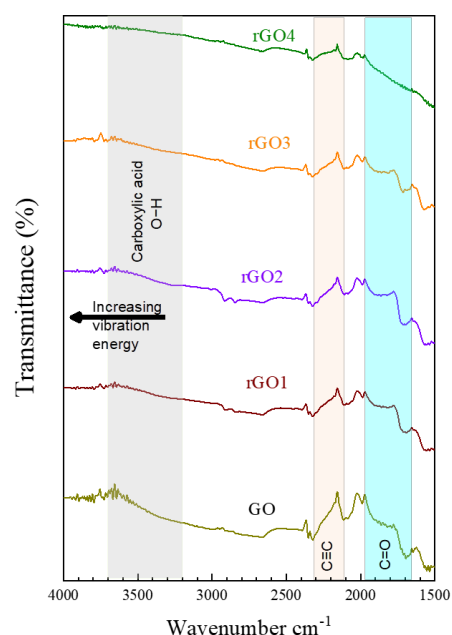


Figure 5. Shows The FT-IR spectra of GO and rGO1- rGO4

Table 2. Shows the C/O atomic ratio and typical properties of GO

Samples	C/O
GO	1.70
rGO1	3.24
rGO2	5.06
rGO3	6.27
rGO4	13.8

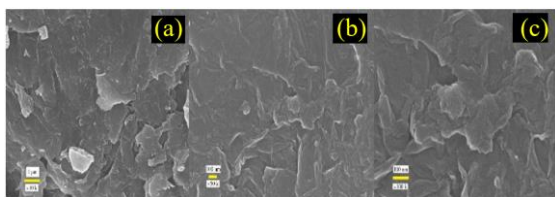


Figure 6. Shows SEM image of GO (a) 10k, (b) 50k, and (c) 100k

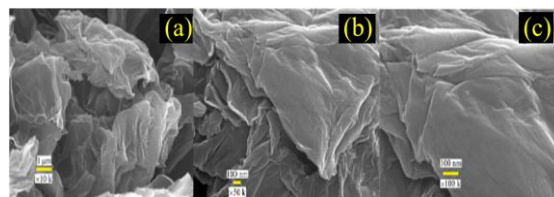


Figure 9. Shows SEM image of rGO3 (a) 10k, (b) 50k, and (c) 100k

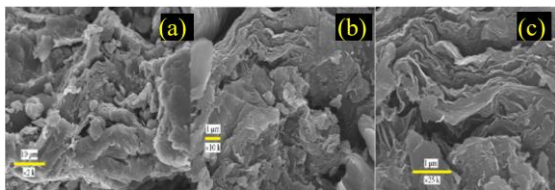


Figure 7. Shows SEM image of rGO1 (a) 2k, (b) 10k, and (c) 25k

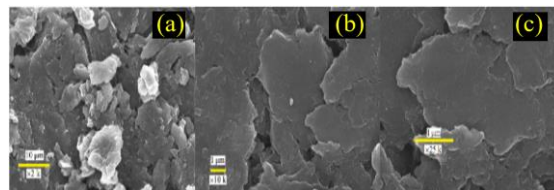


Figure 10. Shows SEM image of rGO4 (a) 10k, (b) 50k, and (c) 100k

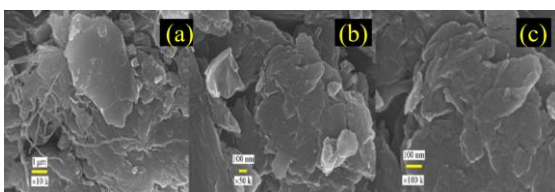


Figure 8. Shows SEM image of rGO2 (a) 10k, (b) 50k, and (c) 100k

folding and creasing, which is characteristic of these materials. There appear to be areas of overlap where individual leaves are on top of each other. Figure 6(b) shows more detailed structural features. The surface morphology includes ridges, folds, and some smoother areas, indicating variations in surface topography. Small particles and deposits can be seen, which could be residues from the synthesis or processing of the GO. In Figure 6(c), the fine details of the GO plate surface are visible at the highest magnification. The image captures the intricacies of the wrinkled texture, which may contribute to the material's properties, such as surface and mechanical strength. There could be nanoscale defects or variations visible in the GO sheets that could affect the electronic properties of the material.

Analysis of reduced graphene oxide (rGO) for rGO1, rGO2, rGO3, and rGO4. Figure 7(a) shows the low magnification that allows observation of the general surface morphology of rGO1. Large aggregated structures and some flake detachments are visible, with a heterogeneous surface showing areas of different textures, possibly due to partial

GO reduction. Figures 7(b) and 7(c) show a higher magnification of the surface of rGO1, revealing smaller structures, suggesting that the reduction process facilitates the exfoliation of the layer. Compared to GO, there is a noticeable reduction in surface roughness, which may indicate a decrease in oxygen-containing groups. For rGO2, rGO3, and rGO4 (Figures 8, 9, and 10), the magnifications provide insights into the gradual changes with increasing magnification levels of reduction. A trend towards smoother surfaces can be observed, particularly with rGO3 and rGO4. In Figures 8 and 9, the layers exhibit fewer wrinkles and a more uniform texture, indicating a restoration of graphene's hexagonal carbon lattice. Finally, the material in rGO4 (Figure 10) exhibits a significantly smoother surface with fewer features indicative of oxidation, suggesting the most extensive reduction in the series.

UV-Vis absorbance Spectroscopy

Figure 11 shows a tauc plot for graphene oxide (GO) (Romero *et al.*, 2017), which indicates a band gap energy (E_g) of about 4.2 eV. This value is typical of GO and contributes to the coverage, arrangement, and relative ratio of the epoxy and hydroxyl groups that disrupt π -conjugation (Yan *et al.*, 2009; Huang *et al.*, 2020). It is also consistent with the previous report by Verma *et al.* (2022). A band gap of GO and rGO was calculated to be 4.23 eV and 2.71, 2.80, 2.54, and 2.63 eV for the green reducing agent. The reduced graphene oxide (rGO1) has a slightly lower E_g of about 4.04 eV, indicating partial recovery of

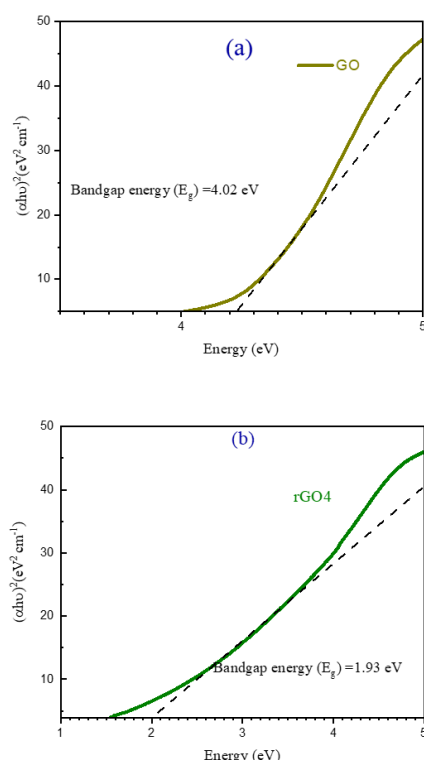


Figure 11. Shows band gap energy of (a) GO (b) rGO4

π -conjugation due to the removal of some oxygen functional groups during the reduction process (Tene *et al.*, 2023). For rGO2, a further reduction in the band gap is observed with an E_g of about 4.03 eV, indicating increased electronic conjugation and improvement in electrical properties. The band gap for rGO4 is significantly lower, about 1.93 eV, indicating substantial recovery of the graphene-like structure. Interestingly, rGO4 shows a deviation from previous trends with increased absorption at lower energies, implying a much smaller band gap. However, due to the scale limitations of the chart, the exact value cannot be determined from the chart. This pattern suggests a highly effective reduction process that brings the material's electrical properties closer to those of pure graphene. The observed band gap reduction in the samples suggests increased electron mobility and improved conductivity, potentially making these materials suitable for various electronic applications.

Cyclic Voltammetry

The electrochemical study was carried out to determine the successful reduction responsible for the conductivity of rGO. The rGO4 paste was coated by screen printing on fluorine-doped tin oxide-coated glass (FTO), which was used as an electrode. The electrochemical performance of rGO4 was

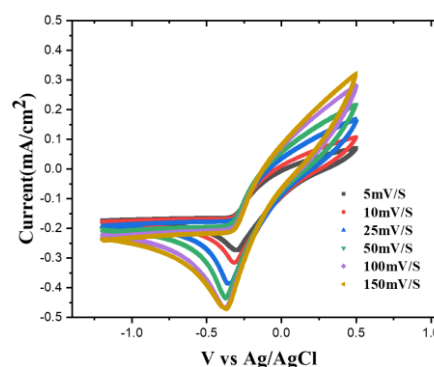
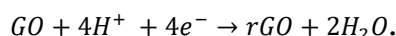


Figure 12. Shows band gap energy of (a) GO (b) rGO4

evaluated using the cyclic voltammetric curves. The electrochemical characterizations were carried out in 0.1 M H_2SO_4 electrolyte with graphite as a counter electrode and Ag/AgCl as a reference electrode in a three-electrode system at a scan rate of 5 to 150 mV/s and a potential window of -1 V to 1 V (Figure 12).

The rGO4 exhibits smooth CV curves and high symmetry at a larger current density, indicating higher electrochemical stability. The CV curves do not change with scan rate, indicating excellent electrochemical stability and reversibility of the electrode. One peak indicated the presence of a redox reaction. This can contribute to pseudocapacitance behavior. The equation represents the reduction of graphene oxide (GO) to reduce graphene oxide (rGO) is



Conclusions

In summary, green synthesis methods using *Chromolaena odorata* have been employed to reduce the toxicity of the reduction process, which was found to be an effective and cost-effective reducing agent for GO. EDS measurements showed a reduction and the distribution of all a sample. UV-visible spectra confirmed the reduction of GO in rGO. IR analysis showed the presence of oxygen functional groups, whose intensity decreased after reduction. In Raman's analysis, the high intensity of the D peak in GO indicates the presence of basal/edge defects; However, the characteristic 2D peak of graphene dominates in the rGO. Furthermore, the intensity ratio of D-band to G-band (I_D/I_G) indicates a successful reduction process and a decrease in defect density. In the rGO4 sample, the smallest energy gap

indicates a highly effective reduction process. The cyclic voltammetric curves exhibit smooth CV curves and high symmetry and pseudocapacitance behavior. Confirm the reduction responsible for the conductivity of rGO.

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References

- Akhavan, O., Kalaei, M., Alavi, Z.S., Ghiasi, S.M.A., and Esfandiari, A. (2012). Increasing the antioxidant activity of green tea polyphenols in the presence of iron for the reduction of graphene oxide. *Carbon*, 50(8):3015-3025. <https://doi.org/10.1016/j.carbon.2012.02.087>
- Huang, X.M., Liu, L.Z., Zhou, S., and Zhao, J.J. (2020). Physical properties and device applications of graphene oxide. *Frontiers of Physics* 15(3):33301. <https://doi.org/10.1007/s11467-019-0937-9>
- Islam, T., Hasan, M.M., Subrata S., and Ahammad, A.J.S. (2023). Intrinsic properties of GO/RGO Bilayer electrodes dictate their inter-/intra-layer intractability to modulate their capacitance performance. *ACS Omega*, 8(15):14013-24. <https://doi.org/10.1021/acsomega.3c00573>
- Kindalkar, V.S., Kumara, K., Shreesha, B., and Dharmaprakash, S.M. (2021). An eco-friendly approach for the reduction of graphene oxide using *Syzygium samarangense* fruit extract. *Materials Chemistry and Physics*, 261:124224. <https://doi.org/10.1016/j.matchemphys.2021.124224>
- Piñeiro-García, A., Vega-Díaz, S.M., Tristán, F., Meneses-Rodríguez, D., Labrada-Delgado, G.J., and Semetey, V. (2021). New insights in the chemical functionalization of graphene oxide by thiol-ene Michael addition reaction. *FlatChem*, 26:100230. <https://doi.org/10.1016/j.flatc.2021.100230>
- Ray, S.C. (2015). Chapter 2-Application and Uses of Graphene Oxide and Reduced Graphene Oxide. In: *Applications of Graphene and Graphene-Oxide Based Nanomaterials*, William Andrew Publishing, p. 39-55. <https://doi.org/10.1016/B978-0-323-37521-4.00002-9>
- Romero, U.A.M., Soto, M.Á.V., Jiménez, L.L., Quintana, J.Á., and García, S.A.P. (2017). Graphene derivatives: controlled properties, nanocomposites, and energy harvesting applications. In: *Graphene Materials - Structure, Properties and Modifications*. Kyzas, G.Z. and Mitropoulos, A.C. (eds). Intech, <https://doi.org/10.5772/67474>
- Tene, T., Guevara, M., Palacios, F.B., Barrionuevo, T.P.M., Gomez, C.V., and Bellucci, S. (2023). Optical properties of graphene oxide. *Frontiers in Chemistry*, 11:1-14. <https://doi.org/10.3389/fchem.2023.1214072>
- Verma, S., Das, T., Pandey, V.K., and Verma, B. (2022). Facile and scalable synthesis of reduced-graphene oxide using different green reducing agents and its characterizations. *Diamond and Related Materials*, 129:109361. <https://doi.org/10.1016/j.diamond.2022.109361>
- Yan, J.A., Xian, L., and Chou, M.Y. (2009). Structural and electronic properties of oxidized graphene. *Physical Review Letters*, 103(8):86802. <https://doi.org/10.1103/PhysRevLett.103.086802>