Risalah Fisika
Volume 5, Number 2, 2025 pp. 47-56
e-ISSN: 2548-9011
DOI: 10.35895/rf.v5i2.34

Towards Green Reduction of Reduced Graphene Oxide: A Comparative Study of Hydrazine and Ascorbic Acid Post Modified Hummer's Synthesis

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ARTICLE INFO

Article history:
Received 17 June 2025
Revised 28 June 2025
Accepted 08 July 2025
Available online 10 July 2025

ABSTRACT

The production of reduced graphene oxide (rGO) traditionally relies on hazardous reducing agents like hydrazine, which poses significant environmental and health risks. This study conducted a comparative analysis of the reduction of graphene oxide (GO), synthesized via a modified Hummer's method, using toxic hydrazine versus a green alternative, ascorbic acid. The resulting rGO from both methods was characterized using X-Ray Diffraction (XRD) and Fourier-Transform Infrared (FTIR) spectroscopy to evaluate structural and chemical changes, while waste profiles and process efficiencies were also compared. The results demonstrated that both hydrazine and ascorbic acid effectively reduced GO, as confirmed by the disappearance of the GO (001) peak and the emergence of the rGO (002) peak in XRD patterns, alongside a significant reduction of oxygen-containing functional groups in FTIR spectra. However, a critical difference was observed in their environmental impact; hydrazine generated a toxic, carcinogenic effluent and caused nitrogen doping, while ascorbic acid produced a benign, non-toxic waste stream. It was concluded that despite challenges such as process optimization and purification, ascorbic acid presents a vastly superior and more sustainable pathway for rGO synthesis for most applications, successfully balancing reduction efficiency with environmental responsibility.

Keywords: *Reduced graphene oxide; Green reduction; Ascorbic acid; Hydrazine; Hummer's method*

ABSTRAK

Produksi *reduced graphene oxide* (rGO) secara tradisional bergantung pada agen pereduksi berbahaya seperti hidrazin, yang menimbulkan risiko lingkungan dan kesehatan yang signifikan. Penelitian ini melakukan analisis komparatif terhadap reduksi *graphene oxide* (GO), yang disintesis melalui metode Hummer termodifikasi, menggunakan hidrazin yang beracun versus alternatif ramah lingkungan, yaitu asam askorbat. Karakterisasi rGO yang dihasilkan dari kedua metode dilakukan menggunakan Difraksi Sinar-X (XRD) dan Spektroskopi Inframerah Fourier-Transform (FTIR) untuk mengevaluasi perubahan struktural dan kimia, serta membandingkan profil limbah dan efisiensi proses. Hasil penelitian menunjukkan bahwa hidrazin dan asam askorbat secara efektif mereduksi GO, yang dibuktikan dengan hilangnya puncak GO (001) dan munculnya puncak rGO (002) pada pola XRD, serta penurunan signifikan gugus fungsi mengandung oksigen pada spektrum FTIR. Namun, perbedaan kritis teramati pada dampak lingkungannya; hidrazin menghasilkan limbah cair yang beracun dan karsinogenik serta menyebabkan *doping* nitrogen, sementara asam askorbat menghasilkan aliran limbah yang aman dan tidak beracun. Disimpulkan bahwa meskipun terdapat tantangan seperti optimalisasi proses dan pemurnian, asam askorbat menawarkan jalur sintesis rGO yang jauh lebih unggul dan berkelanjutan untuk sebagian besar aplikasi, dengan berhasil menyeimbangkan efisiensi reduksi dan tanggung jawab terhadap lingkungan.

Kata kunci: Oksida grafen tereduksi; Reduksi hijau; Asam askorbat; Hidrazin; Metode Hummer

1. INTRODUCTION

Graphene, a two-dimensional monolayer of sp^2-hybridized carbon atoms arranged in a hexagonal lattice, has garnered immense scientific interest due to its extraordinary properties. These include exceptional mechanical strength, high thermal conductivity, superior electrical conductivity, and a remarkably large theoretical specific surface area. However, the large-scale production of pristine graphene through methods like mechanical cleavage or chemical vapor deposition is often complex, time-consuming, and economically challenging for many applications (Ribeiro et al., 2024).

Reduced graphene oxide (rGO) has emerged as a viable and scalable alternative. It is typically produced by the chemical reduction of graphene oxide (GO), an oxidized form of graphite. This process allows for bulk production and chemical modification, making rGO suitable for a wide array of applications (Hu & Gao, 2023). These applications span diverse fields, including its use as electrode materials in batteries and supercapacitors, components in biosensors, conductive fillers in nanocomposites, and elements in optoelectronic devices. The properties of rGO, while not always matching those of pristine graphene, can be tailored by controlling the reduction process, making it a versatile material.

Graphene oxide is the foundational precursor for rGO synthesis. It is characterized by a graphite-like layered structure that is heavily decorated with oxygen-containing functional groups. These groups, primarily hydroxyl (-OH) and epoxide (C-O-C) groups on the basal planes, and carbonyl (C=O) and carboxyl (-COOH) groups at the sheet edges, are introduced during the aggressive oxidation of graphite.[1] The presence of these polar functional groups renders GO hydrophilic, allowing it to be readily dispersed in water and other polar solvents. This dispersibility is a significant advantage for solution-based processing and chemical functionalization (Ribeiro et al., 2024).

However, these oxygen-containing groups disrupt the sp^2 conjugated network of carbon atoms, converting many carbon atoms to an sp^3 hybridized state. This structural change makes GO electrically insulating (Jo et al., 2019). To restore the graphene-like properties, particularly electrical conductivity, GO must underGO a reduction process. This reduction aims to remove the oxygen functional groups and re-establish the sp^2 carbon network, thereby transforming insulating GO into conductive rGO (Hu & Gao, 2023).

The chemical reduction of GO has traditionally relied on potent, but often hazardous, reducing agents. Hydrazine (N_2H_4) and its derivatives have been among the most effective and widely used reductants due to their ability to achieve a high degree of deoxygenation. However, hydrazine is highly toxic, carcinogenic, and poses significant environmental and health risks (De Silva et al., 2017). The handling and disposal of hydrazine and its byproducts add complexity and cost to the rGO synthesis process, undermining its sustainability.

This has spurred a significant research effort towards developing "green" reduction methodologies. These approaches prioritize the use of non-toxic, environmentally benign reagents and sustainable processes, aligning with the principles of green chemistry. Ascorbic acid (Vitamin C), a naturally occurring antioxidant, has emerged as a promising green alternative to hydrazine, offering effective reduction capabilities with minimal environmental impact.[7] This report undertakes a comparative study, evaluating the traditional, highly effective but toxic hydrazine against the green alternative, ascorbic acid, for the reduction of GO.

It is important to recognize that the "greenness" of rGO synthesis is not solely determined by the choice of reducing agent. The initial synthesis of GO, typically via methods like the Hummer's method, itself involves strong oxidizers and acids, generating considerable waste and having its own environmental footprint (Ribeiro et al., 2024). A truly holistic green approach must consider the entire lifecycle, from the raw graphite to the final rGO product. While this report focuses specifically on the reduction step, this broader context is crucial for a comprehensive understanding of sustainable rGO production. The selection of a greener reductant is a significant step, but it is part of a larger challenge in developing entirely eco-friendly graphene-based materials.

2. METHOD

2.1. Materials

The key reagents and their roles in this research are generally understood such Graphite as The carbonaceous starting material, Sulfuric Acid (H_2SO_4) that acts as an intercalating agent, facilitating the penetration of oxidants between graphite layers, and serves as the reaction medium, Potassium Permanganate ($KMnO_4$) that have strong oxidizing agent that responsible for introducing oxygen-containing functional groups onto the graphite structure, Sodium Nitrate ($NaNO_3$) to promote interlayer spacing and assist in the initial stages of oxidation, Hydrogen Peroxide (H_2O_2) added at the end of the reaction to reduce residual $KMnO_4$ and manganese dioxide (MnO_2) to soluble manganese sulfate ($MnSO_4$), effectively terminating the oxidation process, Hydrochloric Acid (HCl) used during the washing phase to remove metallic impurities, particularly manganese ions. The use of concentrated HCl can also promote partial reduction of the GO, especially during subsequent drying steps (Jo et al., 2019).

2.2. Synthesis of Graphene Oxides

While numerous variations exist, a typical modified Hummer's procedure, drawing from examples such as those in (Jo et al., 2019), generally involves the following steps: (1) Dispersion of graphite powder (and $NaNO_3$, if used) in concentrated H_2SO_4, usually in an ice bath to manage the initial exothermic reactions and maintain a low temperature (e.g., below 20°C). (2) Slow, portion-wise addition of $KMnO_4$ to the stirred suspension while carefully controlling the temperature to prevent overheating and potential runaway reactions.39 specifically advises keeping the temperature below 20°C during this addition. (3) The reaction mixture is then typically stirred at a slightly elevated temperature (e.g., 35-50°C) for a period ranging from a few hours to tens of hours to allow the oxidation to proceed. For example, (Jo et al., 2019) mentions stirring at 50°C for 2 hours. (4) The reaction is quenched by the slow addition of deionized (DI) water, which is a highly exothermic step requiring careful control, often followed by the addition of H_2O_2 to terminate the oxidation and reduce excess permanganate species, indicated by a color change to bright yellow or brownish-yellow. It explicitly warns about the danger during water addition. (5) The resulting graphite oxide suspension is then subjected to extensive washing and purification steps. This typically involves repeated centrifugation or filtration with dilute HCl solutions to remove metal ions (e.g., Mn2+) and subsequently with DI water to remove residual acids and salts until the pH of the supernatant is neutral.

The details of the washing protocol, particularly the concentration and volume of HCl used, can have unintended consequences. As noted in the research, washing with concentrated HCl can initiate a degree of partial reduction of the GO. This means that the material isolated as "GO" and used as the precursor for the dedicated reduction step might already possess a slightly lower oxygen content than immediately after oxidation. This pre-reduction could influence the stoichiometric calculations for the main reducing agent and potentially lead to an overestimation of its efficiency if not properly accounted for.

2.3. GO Reduction by reducing agents

2.3.1. Hydrazine (N^2H^4)

Hydrazine (N_2H_4), often used in the form of hydrazine hydrate ($N_2H_4 \cdot H_2O$), is a powerful reducing agent widely employed for the deoxygenation of GO (Hidayah et al., 2017). Its effectiveness stems from its ability to efficiently remove various oxygen-containing functional groups, particularly epoxide and hydroxyl groups, thereby restoring the sp^2 conjugated carbon network (Gao et al., 2010).

The reaction mechanism is complex and can proceed via several pathways. Detailed computational studies, such as that presented in (Gao et al., 2010), suggest that the reduction of epoxide groups, a key deoxygenation step, can occur through nucleophilic attack by the hydrazine molecule on one of the carbon atoms of the epoxide ring. This leads to ring-opening and the formation of an intermediate. Subsequent intramolecular hydrogen transfer events and rearrangements can lead to the elimination of a water molecule (H_2O) and cis-diazene (cis-N2H2), which readily decomposes to nitrogen gas (N2), leaving behind a deoxygenated carbon site. Three distinct routes for epoxide removal by hydrazine have been proposed, differing in the initial point of attack and the sequence of intermediate steps. The reduction process is typically carried out by heating a dispersion of GO with hydrazine hydrate in an aqueous medium, with common temperatures ranging from 80°C to 100°C and reaction times varying from one hour to several hours.

2.3.2. Ascorbic Acid (AA/Vitamin C)

L-Ascorbic acid (L-AA, commonly known as Vitamin C) has gained considerable attention as a mild, non-toxic, and environmentally friendly reducing agent for GO(Chasanah et al., 2022). It offers a "green" alternative to hazardous chemical reductants like hydrazine.

The reduction mechanism involves L-ascorbic acid donating electrons to GO, thereby removing oxygen-containing functional groups. In this process, L-AA itself is oxidized, primarily to dehydroascorbic acid (DHA) (Meloni et al., 2025). The reaction is typically carried out in an aqueous dispersion of GO. The process can be influenced by factors such as temperature (commonly 60°C to 95°C), reaction time, the concentration of ascorbic acid, and the pH of the solution. For instance, (Fernández-Merino et al., 2010) mentions adjusting the pH to ~9-10 using NH_4OH to enhance the colloidal stability of the GO suspension prior to L-AA addition, which can facilitate a more effective reduction.

An important consideration when using ascorbic acid is the potential for rGO re-oxidation. Research indicates that using moderate to high concentrations of L-AA and/or extended reaction times can paradoxically lead to a degree of re-oxidation of the rGO product (El-Basha Hassan et al., 2025). This suggests that there is an optimal window for L-AA concentration and reaction duration to achieve maximum reduction without subsequent degradation. This phenomenon introduces a layer of complexity to the optimization of this "green" reduction process. Furthermore, some protocols describe an additional step of adding hydrogen peroxide (H_2O_2) after the reduction to oxidize any remaining ascorbic acid (X. Zhu et al., 2012). While H_2O_2 is relatively benign, its inclusion adds another reagent and processing step, slightly detracting from the ideal simplicity of a single-step green reduction.

2.4. Comparative Analysis

2.4.1. Characterization of rGO

The quality of the reduced graphene oxide (rGO) produced by both hydrazine and ascorbic acid is primarily assessed by characterizing the structural and chemical changes from the graphene oxide (GO) precursor via X-Ray Diffraction (XRD) that used to analyze the crystalline structure and interlayer spacing of the material. A successful reduction is confirmed by the disappearance of the characteristic GO peak for the (001) plane, which typically appears at 2θ value of 9-11°, and the emergence of a new, broad peak for the rGO (002) plane at a higher angle, around 23-26°. This shift signifies a decrease in the interlayer d-spacing, indicating the removal of oxygen functional groups and water molecules from between the graphene sheets.

Fourier-Transform Infrared (FTIR) Spectroscopy is employed to identify the chemical functional groups present on the surface of the material. The effectiveness of the reduction is determined by observing a significant decrease or complete disappearance of the absorption bands associated with oxygen-containing groups in the GO spectrum. These include the broad O-H stretching vibration (~3400 cm^{-1}), C=O stretching from carboxyl/carbonyl groups (~1720 cm^{-1}), C-O-C stretching from epoxy groups (~1220 cm^{-1}), and C-O stretching from alkoxy groups (~1050 cm^{-1}).

2.4.2. Assessment of Waste Profile

The assessment of waste generated focuses on the chemical composition and toxicity of the liquid effluent produced during the reduction and subsequent washing steps by Hydrazine Reduction that the primary waste concern is the presence of unreacted hydrazine in the washing solutions. Hydrazine is highly toxic and carcinogenic, making the effluent hazardous and requiring specialized, costly treatment. The main gaseous byproduct of the reaction is benign nitrogen (N2), but nitrogen atoms can also be incorporated into the rGO lattice, which can be considered a form of product contamination if not desired.

The Evaluation of Process Efficiency and Yield of Ascorbic Acid Reduction's byproducts are primarily dehydroascorbic acid and water, both of which are considered non-toxic and environmentally benign. The waste stream may also contain excess, unreacted ascorbic acid. The resulting effluent is significantly less hazardous than that from the hydrazine process, simplifying disposal.

2.4.3. Evaluation of Process Efficiency and Yield

Process efficiency is primarily evaluated by calculating the mass yield of the rGO product relative to the starting GO material. The yield is determined by the formula:

$$Yield\ (\%) = \left[\frac{Mass\ of\ dried\ rGO}{Mass\ of\ initial\ GO}\right] \times 100\%. \qquad (1)$$

This requires careful collection, washing, and thorough drying of the final rGO product to obtain an accurate mass measurement.

Factors Affecting Yield Measurement: The reported yield must be interpreted with caution. For the ascorbic acid method, yields have been reported to exceed 100%, which strongly suggests the final product was not fully purified and contained residual ascorbic acid, its byproducts, or trapped moisture, thus artificially inflating the measured mass. For the hydrazine method, while it is known for high conversion, using too high a concentration of GO can lead to incomplete reduction and a lower quality product, affecting the effective yield.

3. RESULTS AND DISCUSSION

3.1. Structure of rGO

The XRD pattern of GO typically exhibits a sharp diffraction peak for the (001) plane at a 2θ value around 8-11°, corresponding to an interlayer d-spacing of approximately 0.8-1.0 nm (Öztekin et al., 2025). Upon reduction with hydrazine, this peak diminishes or disappears, and a new, broader diffraction peak emerges at higher 2θ values, typically in the range of 23-26°. This peak is characteristic of the (002) plane of rGO and corresponds to a significantly reduced interlayer d-spacing of approximately 0.34-0.37 nm. For example, (Öztekin et al., 2025) reports that graphite shows a peak at 26.32° (d-spacing = 0.338 nm), GO at 8.5° (d-spacing = 1.036 nm), and H-rGO displays a broad peak around 23° (d-spacing = 0.368 nm). Similarly, (Hidayah et al., 2017) notes an rGO peak (hydrazine reduced) at 24.10°. This shift to higher 2θ values and smaller d-spacing clearly indicates the removal of bulky oxygen-containing functional groups and intercalated water molecules, allowing the graphene sheets to restack more closely, akin to the structure of graphite. The broadness of the rGO peak often suggests a degree of disorder, smaller crystallite size, or variations in interlayer spacing compared to highly crystalline graphite.

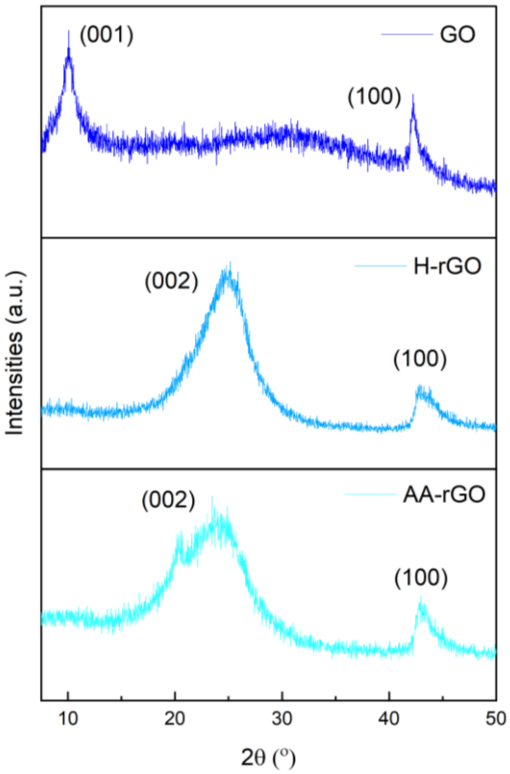

Figure 1. Plots of XRD spectra of GO, H-rGO, and AA-rGO.

Similar to reduction by hydrazine, the use of ascorbic acid effectively reduces GO, as evidenced by XRD. The characteristic (001) diffraction peak of GO diminishes, and a new, broader (002) peak corresponding to rGO appears at higher 2θ angles, typically in the range of 23−26°. For example, (Mulyani et al., 2023) reports a GO peak at 10.6° and AA-rGO peaks appearing between 23.2° and 23.9°, with the exact position depending on the amount of ascorbic acid used. It also visually demonstrates this shift from GO to rGO-AA. The decrease in d-spacing associated with this peak shift confirms the removal of oxygen functionalities and the partial restoration of the graphitic layered structure.

The broadness of the rGO peak in both cases suggests that the resulting material consists of relatively small crystallites or exhibits some structural disorder and variation in stacking, which is typical for chemically derived rGO. XPS studies, which provide complementary information on chemical composition, have indicated that both ascorbic acid and hydrazine can effectively remove C-OH and C-O-C groups, suggesting a comparable degree of deoxygenation at the chemical bond level under optimal conditions (Fernández-Merino et al., 2010).

Table 1. Summary of Typical XRD Characteristics for GO, H-rGO, and AA-rGO

Parameter	GO	H-rGO	AA-rGO
XRD GO (001) peak 2θ	8−11°	Disappears/Greatly Reduced	Disappears/Greatly Reduced
XRD GO d-spacing	0.8−1.0 nm	-	-
XRD H-rGO (002) peak 2θ	-	Broad peak at 23−26°	Broad peak at 23−26°
XRD RGO d-spacing	-	~0.34−0.37 nm	~0.35−0.38 nm

3.2. Functionals Group of rGO

FTIR spectroscopy provides direct chemical evidence of deoxygenation. The spectrum of GO shows prominent absorption bands corresponding to various oxygen functional groups. After reduction with hydrazine, the intensities of these bands are substantially reduced or may even disappear (Fernández-Merino et al., 2010).

Some key changes include a significant decrease in the broad O-H stretching vibration band (from hydroxyl, carboxyl groups, and adsorbed water) typically observed around 3200−3600 cm^{-1}. A marked reduction in the C=O stretching vibration band (from carbonyl and carboxyl groups) around 1700−1740 cm^{-1}. Diminished intensity of the C-O-C stretching vibration band (epoxy groups) around 1220−1280 cm^{-1}. Reduced intensity of C-O stretching bands (alkoxy/hydroxyl groups) around 1050−1100 cm^{-1}.

(P. Zhu et al., 2011) suggests a hierarchy in the ease of reduction of these groups by hydrazine, with hydroxyl groups (R-OH) being the easiest to remove, followed by carbonyl groups (R-C=O), and C-O-C (epoxy) groups being the most difficult. The extent of removal confirms the efficacy of hydrazine as a deoxygenating agent.

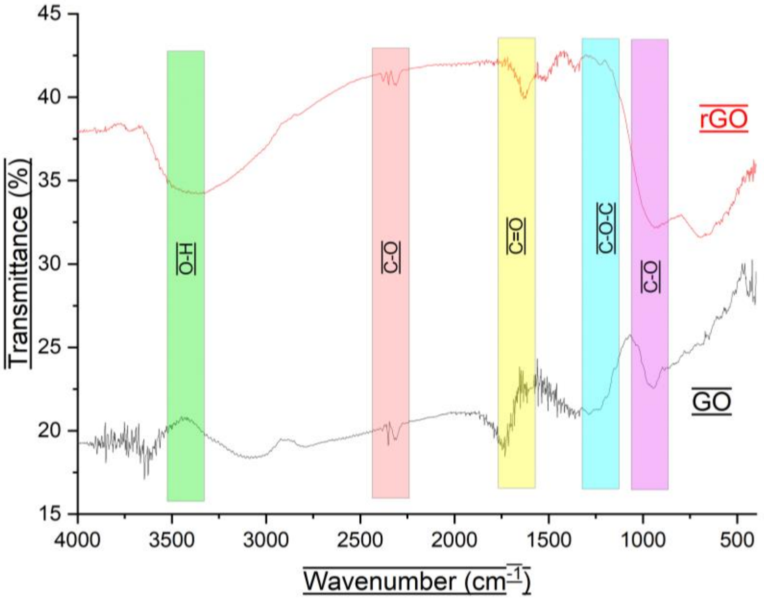

Figure 2. Plots of FTIR spectra of GO and rGO.

Table 2. Summary of Typical FTIR Characteristics for GO and rGO

Parameter	GO	rGO	Key Reference(s)
FTIR O-H stretch (cm^{-1})	Broad, strong peak ~3200−3600	Significantly reduced intensity / Disappeared	(Fernández-Merino et al., 2010)
FTIR C=O stretch (cm^{-1})	Peak ~1700−1740	Significantly reduced intensity	(Fernández-Merino et al., 2010)
FTIR C-O-C stretch (cm^{-1})	Peak(s) ~1220−1280 (epoxy)	Reduced intensity	(P. Zhu et al., 2011)
FTIR C-O stretch (cm^{-1})	Peak(s) ~1050−1100 (alkoxy/hydroxyl)	Reduced intensity	(Singh & Joshi, 2023)

The C/O atomic ratio is a common metric for assessing the degree of reduction. Hydrazine is known to produce rGO with high C/O ratios, for instance, values up to 10.2 have been reported.18 Ascorbic acid has also been shown to achieve comparable C/O ratios and, consequently, similar improvements in electrical conductivity to those obtained with hydrazine, positioning it as a strong green alternative (Chasanah et al., 2022).

3.3. Waste Profile and Environmental Considerations

Despite its effectiveness, the use of hydrazine is fraught with significant environmental and health concerns. Hydrazine is classified as a highly toxic and carcinogenic substance.[5] Its permissible exposure limit is extremely low (e.g., a threshold limit value of 0.01 ppm) (Destiarti et al., 2024). This necessitates stringent handling precautions, specialized equipment, and robust safety protocols, adding to the complexity and cost of its use.

The primary gaseous byproduct from the reduction mechanism is nitrogen (N2), which is environmentally benign (Gao et al., 2010). Water is also formed. A major concern is the potential presence of unreacted hydrazine in the rGO product and in the wastewater. Extensive washing is required to remove residual hydrazine (Faniyi et al., 2019), which in turn generates larger volumes of contaminated liquid waste that requires specialized and costly treatment before disposal. An important, often overlooked, aspect is nitrogen doping. Elemental analysis of H-rGO frequently reveals the incorporation of nitrogen atoms into the graphene lattice. For instance, (Park et al., 2011) reports C/N atomic ratios in H-rGO, confirming nitrogen presence. While N-doping can be intentionally sought to tailor the electronic properties of graphene for specific applications (e.g., catalysis, sensing), in the context of simple reduction, it represents a form of chemical modification or "contamination" by the reducing agent itself. This alters the intrinsic properties of the rGO and means hydrazine acts not just as a reductant but also as a doping agent. This duality complicates the assessment of H-rGO "purity" if the goal is solely deoxygenated graphene.

The high toxicity of hydrazine and the need for managing N-containing residues significantly increase the overall environmental burden and operational costs, detracting from its appeal despite its chemical efficiency.

Hence, using ascorbic acid as a reductant lies in its favorable environmental profile. Ascorbic acid is a naturally occurring compound, biodegradable, non-toxic, and readily available at low cost. The main byproduct of L-AA oxidation during the reduction of GO is dehydroascorbic acid (DHA) (Meloni et al., 2025). DHA is also a biologically relevant molecule (another form of Vitamin C) and is generally considered non-toxic. If ascorbic acid is used in excess, unreacted L-AA may be present in the solution. As mentioned, some procedures use H_2O_2 to remove this excess (X. Zhu et al., 2012). The waste stream generated from ascorbic acid reduction is significantly less hazardous compared to that from hydrazine reduction, simplifying waste treatment and disposal, and reducing environmental impact.

Regarding the "quantity of waste," while the volume of washing solutions might be comparable if similar purification protocols are followed for both methods, the critical difference lies in the hazard level of that waste. Hydrazine generates a highly toxic effluent, whereas ascorbic acid produces a largely benign one.

3.4. Process Efficiency and Yield

Hydrazine is generally recognized for its high reduction efficiency, leading to rGO with a significantly restored sp^2 carbon network, high carbon-to-oxygen (C/O) atomic ratios, and good electrical conductivity.618 reported a C/O ratio as high as 10.2 for H-rGO derived from exfoliated GO platelets, and (Mhlongo et al., 2025) mentioned an increase in C/O ratio from 2 (for GO) to 7.8 after a microwave-assisted hydrazine reduction.

While specific weight percentage yields of rGO from GO using hydrazine are not extensively detailed in the provided information, its strong reducing power implies a high degree of conversion. (De Silva et al., 2017) suggests that the amount of rGO obtained is proportional to the initial GO concentration, but also cautions that excessively high GO concentrations can lead to incomplete reduction and lower product quality. Typical reaction conditions involve temperatures of 80-100°C for durations ranging from 1 hour to 24 hours, depending on the desired degree of reduction and specific protocol.

Ascorbic acid has demonstrated the potential to achieve reduction efficiencies comparable to those of hydrazine, particularly in terms of restoring electrical conductivity and achieving favorable C/O ratios in the rGO product (Chasanah et al., 2022). reported an electrical conductivity of 755.70 S/m for rGO-AA, a value stated to be nearly similar to that achievable with hydrazine.

Reported yields for rGO synthesis using ascorbic acid vary. (Zulni et al., 2023) presented data showing yields of 92.42% when using a 10% ascorbic acid concentration, 101.98% with 20% AA, and 107.07% with 30% AA, relative to the initial GO mass. Yields exceeding 100% are anomalous for a process that involves mass loss (removal of oxygen). Such figures strongly suggest that the weighed rGO product may contain residual unreacted ascorbic acid, its oxidation product DHA, trapped solvent (water), or a combination thereof, if the purification and drying processes are not sufficiently rigorous. This highlights a critical point: reported yields must be interpreted with caution and alongside thorough characterization that confirms product purity. Incomplete removal of these species would not only inflate the measured yield but also affect the true quality and properties of the rGO.

Reaction conditions for ascorbic acid reduction typically involve temperatures between 60°C and 95°C, with reaction times ranging from 30 minutes to 24 hours. However, as noted in (El-Basha Hassan et al., 2025), prolonged reaction times, especially with higher AA concentrations, should be approached cautiously due to the risk of rGO re-oxidation.

Hydrazine is generally considered to provide efficient conversion of GO to rGO, reflected in the substantial restoration of graphitic properties. Specific weight percentage yields are not consistently reported but are implied to be high. For ascorbic acid, reported yields can be high, with (Zulni et al., 2023) even noting yields exceeding 100% (e.g., 107.07%). As discussed previously, such values likely indicate impurities (residual AA/DHA or moisture) in the final product rather than true conversion efficiency, underscoring the need for meticulous purification and drying. Nevertheless, under optimized conditions, ascorbic acid is considered an effective reductant.

Both reduction methods typically operate at moderately elevated temperatures, generally in the range of 60-100°C. Reaction times can vary widely for both: hydrazine reactions may last from 1 hour 19 up to 12-24 hours 15, while ascorbic acid reductions can range from 30 minutes 8 to 24 hours.8 However, for ascorbic acid, shorter reaction times might be preferable to avoid the potential re-oxidation of rGO that can occur with prolonged exposure or high.

When assessed holistically, ascorbic acid scores significantly higher in terms of "greenness". Its non-toxic nature, use of a renewable resource (if sourced naturally), and benign byproducts align well with the principles of green chemistry. Hydrazine, despite its chemical efficacy, is heavily penalized by its severe toxicity and the hazardous waste it generates.

Table 3. Comparative Summary of Hydrazine vs. Ascorbic Acid for rGO Reduction

Criteria	Hydrazine	Ascorbic Acid	Key Supporting Snippet(s)
Primary Chemical Action	Strong deoxygenation of GO	Mild, green deoxygenation of GO	(Gao et al., 2010)
Key Byproducts	N2, H2O, residual hydrazine, N-containing species in rGO	Dehydroascorbic acid, H2O, residual ascorbic acid	(Gao et al., 2010)
Toxicity of Reductant	Highly toxic, carcinogenic	Non-toxic, biodegradable	(De Silva et al., 2017)
Toxicity of Byproducts	Residual hydrazine is highly toxic; N2 is benign	Dehydroascorbic acid is generally non-toxic	(De Silva et al., 2017)
Nitrogen Doping of rGO	Common, inherent to the process	No (unless N-containing additives are used, e.g., NH4 OH for pH adjustment)	(Gao et al., 2010)
Reported Yield Range (Weight % from GO)	Generally high conversion, specific % not consistently reported	Variable, sometimes >100% (suggesting impurities if not well purified)	(Chasanah et al., 2022)
Typical Reaction Temperature (°C)	80−100	60−95	(Fernández-Merino et al., 2010)
Typical Reaction Time (hours)	1−24	0.5−24 (shorter times may be optimal)	(Fernández-Merino et al., 2010)
Relative Cost (Qualitative)	Higher (reagent + handling + waste disposal)	Lower (reagent + simpler waste management)	(Inferred from toxicity and nature of chemicals)
Waste Management Complexity	High, due to toxicity	Low, due to benign nature	(De Silva et al., 2017)

Criteria	Hydrazine	Ascorbic Acid	Key Supporting Snippet(s)
Overall "Green" Rating	Poor	Excellent	(De Silva et al., 2017)

The choice between hydrazine and ascorbic acid is not merely about achieving deoxygenation; it involves a complex balance of factors. The "better" reductant is highly dependent on the intended application of the rGO. For applications where trace nitrogen doping from hydrazine might be tolerated or even beneficial (e.g., in certain catalytic or sensing scenarios), and where stringent waste management infrastructure is available and economically viable, hydrazine might be considered for its historically proven robust reduction. However, such cases are likely limited, especially with increasing environmental regulations. For the vast majority of applications, particularly those in biomedical fields where biocompatibility is essential, or for large-scale industrial production where environmental impact, worker safety, and cost-effectiveness are paramount, ascorbic acid emerges as the clearly superior and more responsible choice. This is contingent on careful optimization of the ascorbic acid reduction process to achieve a degree of reduction and purity comparable to that of hydrazine, while avoiding issues like re-oxidation.

Furthermore, an often-overlooked factor in comparing these processes is the overall cost and scalability. While not explicitly detailed in a side-by-side manner in the available information, the cost of the reductants themselves (hydrazine being a specialized chemical versus ascorbic acid being a common commodity), the energy consumption (which may differ based on optimal reaction times and temperatures), and crucially, the cost associated with waste handling and disposal for hydrazine, will significantly influence the economic viability and scalability. The benign nature of ascorbic acid and its byproducts inherently leads to lower waste management costs, making it a more attractive pathway for sustainable and economically feasible large-scale rGO production.

4. CONCLUSION AND RECOMMENDATION

The comparative analysis of hydrazine and ascorbic acid for the reduction of graphene oxide reveals a clear dichotomy between traditional effectiveness and modern environmental imperatives.

Hydrazine stands out for its potent reducing capability, consistently yielding rGO with a high degree of deoxygenation, as evidenced by significant structural changes in XRD and FTIR spectra and the restoration of electrical conductivity. However, this chemical efficiency comes at a steep environmental and safety cost. Hydrazine is highly toxic and carcinogenic, and its use generates hazardous waste streams that require complex and expensive management. Furthermore, the inherent nitrogen doping of rGO by hydrazine, while potentially useful for specific niche applications, can be considered an impurity if pristine, undoped rGO is desired.

Ascorbic acid, in contrast, offers an excellent environmental profile. It is non-toxic, biodegradable, derived from renewable resources (in many cases), and its primary byproduct, dehydroascorbic acid, is also benign. Importantly, studies have shown that ascorbic acid can achieve a degree of GO reduction comparable to that of hydrazine, particularly when reaction conditions are optimized. However, the use of ascorbic acid is not without its own set of challenges. Careful control of parameters such as concentration, temperature, pH, and reaction time is crucial to maximize reduction efficiency and avoid potential issues like the re-oxidation of rGO at high AA concentrations or long reaction durations. Additionally, reports of yields exceeding 100% highlight the necessity for meticulous purification and drying protocols to ensure the removal of residual ascorbic acid or its byproducts, which could otherwise compromise the purity and accurately measured properties of the AA-rGO.

The central question revolves around whether the potentially more robust or historically more established reduction achieved by hydrazine justifies its significant environmental and safety liabilities. The evidence increasingly suggests that for most purposes, ascorbic acid provides a sufficiently effective reduction with vastly superior environmental credentials, making it a highly preferable alternative.

5. ACKNOWLEDGE

We gratefully acknowledge the supervision of our mentor Dr. Sri Cahyo Wahyono, discussions with the rGO research group, and technical support from Material Sciences Laboratory. Institutional support from the faculty, Lambung Mangkurat University, and funding from University Grant No. 1863/UN8/LT/2025 are also acknowledged.

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