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A Comprehensive Route for Safe and Sustainable Graphene Oxide Synthesis

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Abstract

For almost sixty years, the modified Hummers method has been used to oxidise graphite with the radicals of KMnO_4 (MnO^{3+}) to produce graphene oxide (GO) with the use of H_2O_2 as a terminating chemical in the reaction. NaNO_3 has traditionally been employed as a catalyst in the Hummers method, but its use is associated with the release of toxic byproducts such as NO_2 and N_2O_4 . Moreover, recent studies have shown that excessive H_2O_2 can reduce GO, rendering it hydrophobic and causing partial precipitation. In this study, we propose a variation to the conventional method by reducing the dosage of NaNO_3 and eliminating the use of H_2O_2 . This approach is experimentally evaluated and compared with conventional protocols that employ both NaNO_3 and H_2O_2 . The results highlight that minimising NaNO_3 avoids the high risk of releasing hazardous NO_x species, and H_2O_2 -free reaction helps to obtain more stable rGO (a high-quality colloidal dispersion with chemical modification). The colloidal solution retains its stability for up to three months for rGO suspension.

Keywords: Graphene Oxide, Modified Hummers method, Raman analysis, Tyndall effect, Thermal stability

1. Introduction

The derivative of graphite with the oxygen-containing functional groups covalently bonded to its layers is known as graphite oxide (GO). These functional groups are produced by intense oxidation during the synthesis of GO [1–3]. As a result of oxidation, GO exhibits a lamellar structure with randomly distributed unoxidized aromatic regions (sp^2 -carbon atoms), sp^3 -rich six-membered rings, and a high concentration of exposed oxygen-containing functional groups embedded in its layers, such as: hydroxyl, epoxy, and carboxyl [4]. GO is quite similar to montmorillonites, which have similar swelling, intercalation, and layered characteristics, and both of these materials contain such hydrophilic polar groups [5]. Because of this, GO is an ideal framework for the interlayer adaptation of long-chain aliphatic hydrocarbons, hydrophilic molecules, transition metal ions, and polymer chains [6]. It also holds potential for particle fabrication processes, particularly for the creation of thin films with advanced material properties. GO is a multifunctional material with wide applications in different areas of research, like sensors, energy storage, microwave absorption, solar cells, hydrogen storage, memory devices, and with its stimuli response behaviour, it is easy to control the functionality of GO in different environmental conditions [7]. While altering the properties like conductivity, hydrophilicity, oxidation states, and carbon to oxygen ratio in GO during synthesis leads to a highly efficient multifunctional 2-dimensional (2D) material [8,9].

Graphite is economical and widely accessible from both natural and artificial sources. It is made up of a stack of flat graphene sheets. For the creation of bulk graphene sheets, the common carbon substance is perhaps the most accessible source. One of the most effective techniques for producing 2D graphene is oxidative exfoliation of natural graphite by acid treatment, followed by chemical conversion [10]. Firstly, the GO was synthesised by Brodie in 1859 [11], using potassium chlorate in the fuming nitric acid to oxidise the graphite slurry. Then, in 1898, Staudenmaier [12] modified the Brodie method to oxidise the GO by using sulphuric acid with the fuming nitric acid and adding the amount of chlorate during the whole reaction, which increases the quality of the GO. After this, Hummers came up with a more practical method to synthesise the GO in 1958 [13], which is still being used on an industrial scale. With the use of $KMnO_4$ and $NaNO_3$ in the concentrated H_2SO_4 , the natural graphite powder is oxidised, while controlling the reaction time, temperature of the surroundings during the reaction, the amount of precursors, yield of the final amount and other variables that can be controlled during the reaction. Dimiev et al. (2014) [14], showed the mechanism for the formation of GO via Hummers' method. Firstly, the intercalation of H_2SO_4 (HSO_4^- and SO_4^{2-}) into the graphite flakes while stirring, provided a dark black colour of the solution. After adding a sufficient amount of $KMnO_4$, it starts reacting with H_2SO_4 , which results in the formation of (Mn_2O_7) and MnO^{3+} , and these reactants react with the graphite powder intercalated with H_2SO_4 ions to form pristine graphite oxide. After this, the Oxygen-containing functional groups commonly found in GO are formed when water molecules react with positively charged carbon atoms within the graphite layers. Further, H_2O_2 is used to change the Mn ions (Mn^{7+} to Mn^{2+}) and stop the oxidation process by reducing the residual oxidants by generating oxygen. In the past few years, researchers have been exploring a more effective method for removing $NaNO_3$ by adjusting the concentration of $KMnO_4$, thereby surpassing the role of $NaNO_3$ as an oxidant in the formation of GO [15]. Gunda et al. 2018 [16], state that sodium nitrate generates toxic gases during the synthesis, such as NO_2 , N_2O_2 . For numerous reasons, including the precise explanation of the GO structure, variation in the yield of GO due to various methods, the processes generating noxious gases as secondary reaction products, the different quality of oxidation of raw graphite material, and many others, more research is still required to comprehend the synthesis techniques.

Yoo et al. 2019 [17], show the effect of H_2O_2 in the synthesis of GO to reduce the oxygen-containing functional groups, as the H_2O_2 reacts with H_2SO_4 to produce highly reactive oxygen species with unpaired electrons. So, most of the elemental carbon bonds can be broken by the very reactive and potent oxidiser known as the free oxygen radical. Since the response is known to be extremely violent, most organic chemicals quickly break down into carbon dioxide in a matter of minutes, leaving no discernible traces behind. Meanwhile, H_2O_2 reacts with the remaining $KMnO_4$ to form the manganese sulphate (colourless), which renders the solution yellow in colour [18]. GO with a high degree of oxidation appears yellow due to the abundance of oxygen-containing groups that are produced after adding H_2O_2 . However, too much H_2O_2 can also reduce GO, making it hydrophobic and partially precipitate [19]. In order to avoid this, it is essential to establish an H_2O_2 -free process. In our study, we are proposing the precursor ratios where the need for H_2O_2 and $NaNO_3$ is being reduced to a minimum, while maintaining the quality of GO.

Aggregation is a major problem in the manufacture and handling of bulk-quantity graphene sheets, similar to many other 2D nanomaterials. Due to van der Waals interactions, graphene sheets with a high specific surface

area have a tendency to form irreversible agglomerates or even restack to create graphite if they are not adequately separated from one another. Attaching additional molecules or polymers to the sheets helps lessen aggregation [20]. For the majority of applications, however, the inclusion of foreign stabilisers is undesirable. It is necessary to develop new methods for producing relatively clean graphene sheets in large quantities while maintaining their individual separation. Most of the prior attempts to produce graphene on a large scale via chemical reactions or thermal growth/reduction have run into this issue [21].

Pristine graphene is typically nontoxic but insoluble, necessitating chemical functionalization or dispersing agents to prevent sheet agglomeration [22,23]. With characteristics including dispersion and solubility in water and organic solvents, suitably tailored graphene nanosheets may exhibit superior solution chemistry [24]. Thus, chemical functionalisation should be able to provide graphene nanosheets with hydrophilic and organophilic tendencies [25]. rGO, known for its hydrophobic and larger interlayer spacing compared to graphite, is a widely favoured derivative. The oxygen functional groups offer reactive sites for recognised carbon surface chemistry-based chemical modification [26,27]. In addition to causing the resulting rGO sheets to structurally separate, the chemical bonding of suitable organic groups enables the direct formation of stable GO dispersions. GO's excellent dispersion has made it possible to create a variety of potentially valuable compounds using relatively inexpensive solution processing methods [28]. For the next-generation multifunctional composites, it is crucial to develop materials that combine superior dispersibility.

In this work, we compared the routes to prepare GO with and without H_2O_2 with a variation in the ratio of $\text{NaNO}_3/\text{KMnO}_4$. This leads to the oxidation of graphite powder without H_2O_2 in GO1, 2, and 3, and the yellow colour of the solution is obtained just after the addition of deionised water. Further, the analysis of the synthesised GO is done to study the change in the functional groups and their effect on the defects on the surface. By modulating the amount of precursors, rGO can be stabilised into a highly soluble colloidal suspension that remains stable for up to three months, thereby demonstrating prolonged dispersibility and enhanced solution processability.

2. Experimental

2.1 Materials

Graphite powder (98%), potassium permanganate (KMnO_4) (99%-AR), sodium nitrate (NaNO_3) (99%-extra pure), sulphuric acid (H_2SO_4) (98%), hydrogen peroxide (H_2O_2), deionised water (DI), hydrazine hydrate (80%-AR), ethanol, hydrochloric acid (HCl) (35.4% AR), and ammonia (25%-AR) were purchased from Loba Chemie Pvt. Ltd. Every analytical-grade substance was utilised without further purification.

2.2 Synthesis and purification of GO

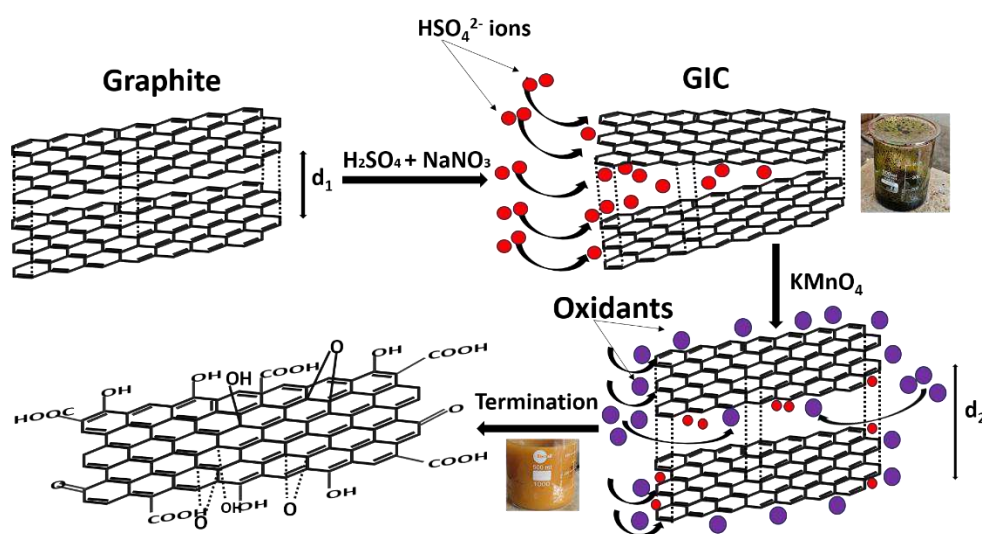
50 mL of concentrated H_2SO_4 was taken into a 500 mL beaker, and a certain amount of graphite powder was mixed into the acid by stirring with NaNO_3 . The entire reaction was conducted in an ice bath (0-5 °C) for 2 hours. After this, a specific amount of KMnO_4 was slowly added to the solution while maintaining the ice bath at the same temperature. Gradually, a dark green colour appeared in the solution as potassium permanganate was added. The solution was left for a few hours to form a thick, dark brown paste. Then, 300 mL of DI water was slowly added to the solution, causing the temperature to rise up to 98 °C, before allowing it to cool to room temperature. Next, H_2O_2 was added to terminate the reaction, resulting in a bright yellow colour. For washing, the solution was acid-washed with a 30 wt.% HCl solution with DI water. Afterwards, it was washed with DI water using centrifugation at 10000 rpm for 5 minutes until the pH was neutral. For drying, the sample was placed in an oven at 60 °C overnight (as shown in Scheme 1).

For the variation of KMnO_4 with NaNO_3 , see Table 1. Further part of the synthesis and washing process remains the same, except for the amount of the precursors; meanwhile, the amount of sulphuric acid and graphite powder remains the same. However, the yield of the synthesised GO varies with different amounts of precursor. For GO1 and 2, we observed that the yield is significantly the same as that of the conventional Hummers method [29], as shown in Table S1.

2.3. Preparation of GO colloid in DI water

We convert GO chemically to make it suitable for a stable colloidal solution. Firstly, we took a 0.5 mg/mL solution of GO in 10 mL of DI water and ultrasonicated it for 30 minutes. Then, hydrazine hydrate is added to the above solution of GO at a ratio of 7:10 ($\text{N}_2\text{H}_4/\text{GO}$). Further, to enhance the stability of the colloidal solution, we increase

the pH up to 10 with an appropriate amount of ammonia. Then we left the samples untouched for 3 months of observation. To check the stability of the solution after three months, we did the Tyndall effect test [24]. For clarity, the samples designated as GO1, GO2, etc. correspond to chemically enhanced reduced graphene oxide (rGO) solutions.



Scheme 1 Preparation of Graphene Oxide.

Table 1 Experimental compositions for KMnO_4 with NaNO_3 for each sample.

Sample name	NaNO_3 (gm)	KMnO_4 (gm)	H_2O_2 (mL)
GO 1	0.5	7	0
GO 2	0.5	9	0
GO 3	0.5	11	0
GO 4	1	7	10
GO 5	1	9	10
GO 6	1	11	10
GO 7	1.5	7	10
GO 8	1.5	9	10
GO 9	1.5	11	10

3. Characterization

The crystal structure is confirmed with the X-ray diffraction analysis (XRD, PANalytical Empyrean XRD Cu-K α radiation). The chemical compounds attached within GO are analysed with Fourier Transform Infrared Spectroscopy (FT-IR, SHIMADZU IRAffinity-1S). The molecular vibration pattern is observed with a Raman-AFM Confocal (Witec alpha300 RA Oxford Instruments). For the structural analysis, a scanning electron microscope equipped with EDX for elemental composition (SEM, JEOL JSM 6390LV) and high-resolution TEM (HRTEM, JEM-ARM200F NEOARM) is used. The thermal stability of the material is analysed with a thermal gravimetric analyser (METTLER TOLEDO TGA). A SHIMADZU UV-2600i UV-VIS spectrophotometer was used in recording the UV-VIS absorption spectra. For elemental and functional groups analysis, the XPS is done using a Thermo Scientific ESCALAB QXi instrument. The zeta potential of the sample is analysed by using the particle size analyser (Litesizer Series 500).

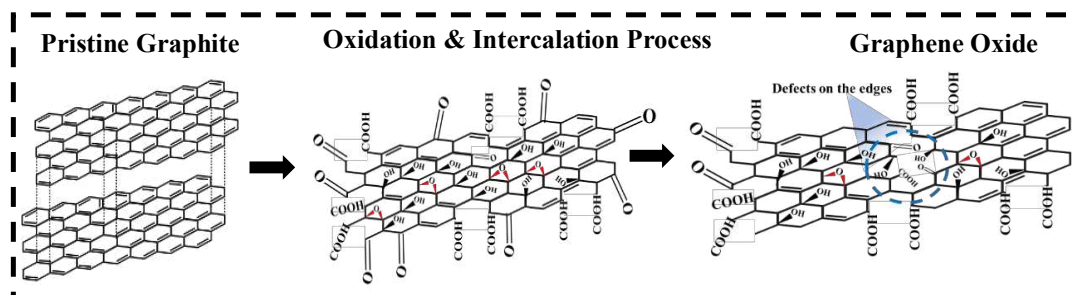
4. GO preparation

By oxidation of graphite with strong oxidisers, the GO is prepared, by inducing the intercalators that come from H_2SO_4 and the formation of oxygen-containing functional groups over the sheets of graphite. This results in an

increase in the interlayer distance of the GO sheets and the accumulation of charge carriers over the defects and the edges of the sheets. Furthermore, the sp^2 hybridisation of graphite will be partially converted to sp^3 ; a very low chance of full conversion of sp^2 hybridised carbon atoms to sp^3 has been observed so far [18]. Here, the modified Hummers method is used to synthesise the GO from graphitic powder. For the exfoliation and oxidation of graphite sheets, H_2SO_4 is used (HSO_4^- and SO_4^{2-} for intercalation in GO sheets); because of the absence of water in the reaction, the mixture is able to oxidise the graphite sheets. $NaNO_3$ acts as a catalytic promoter, while $KMnO_4$ serves as a strong oxidising agent under acidic conditions, thereby enhancing the oxidation process (Mn_2O_7 and MnO^{3+}) [30]. Marcano et al. 2010 [31] suggested that when GO is synthesised with reduced $NaNO_3$ content, the presence of Na^+ and NO_3^- ions is minimised. In contrast, oxidation carried out in the presence of sodium nitrate or sodium nitrite generates hazardous nitrogen oxides (NO_2 and N_2O_4), which pose significant risks to human health. In the absence of these ionic species, the reaction proceeds via a disproportionation pathway, following zero-order kinetics with respect to H^+ concentration and involving a coupled one-electron/ H^+ transfer mechanism [32].

In the presence of a small amount of $NaNO_3$, $KMnO_4$ reacts with H_2SO_4 to generate di-manganese heptoxide (Mn_2O_7), a dark green oily liquid, along with bi-sulfate ions (HSO_4^-) [33]. While adding water to the acidic mixture, there is an exothermic reaction, which is due to the reaction between water and the thick paste of sulfuric acid and Mn_2O_7 . In the synthesis of GO1, GO2, and GO3, the amount of $NaNO_3$ employed is minimal, thereby limiting the requirement for an acidic medium to stabilise residual $KMnO_4$. Chen et al. 2022 [34], stated that Mn_2O_7 undergoes vigorous hydrolysis, producing permanganic acid and finely dispersed manganese dioxide (MnO_2), where manganese is in the Mn^{+4} oxidation state, which reacts with the sulphuric acid to further produce $MnSO_4$. This hydrolysis is highly exothermic, often raising the solution temperature nearly $100\text{ }^\circ\text{C}$ due to rapid heat release. Concurrently, Mn_2O_7 can react with the acidic medium, forming soluble manganese (II) sulfate ($MnSO_4^{2-}$), which is colourless in solution [35]. Therefore, the Mn (VII) species is greatly diminished with these reactions.

During the termination process, DI water was first introduced into the reaction mixture, followed by the addition of H_2O_2 to terminate the oxidation. Zhou et al. 2023 [36], show, it is now thought that too much H_2O_2 can also reduce GO, making it hydrophobic and partially precipitating. Initially, H_2O_2 was applied after DI water addition, as outlined in Table 1. However, we sought to minimise the use of H_2O_2 ; and ultimately reducing its amount to zero by optimising the precursor $NaNO_3$ and $KMnO_4$ concentration. This intrinsic reduction of the Mn ions-driven pathway effectively diminishes the need for external H_2O_2 addition to terminate the reaction, thereby simplifying the process and reducing chemical consumption [37]. Under these modified conditions, the synthesis yielded yellowish GO solutions (GO1, GO2, and GO3), indicative of controlled oxidation and reduced incorporation of extraneous ionic species (as shown in Scheme 1).



Scheme 2 Illustrating the oxidation stage of GO from pristine graphite.

5. Results and Discussion

5.1 XRD Analysis

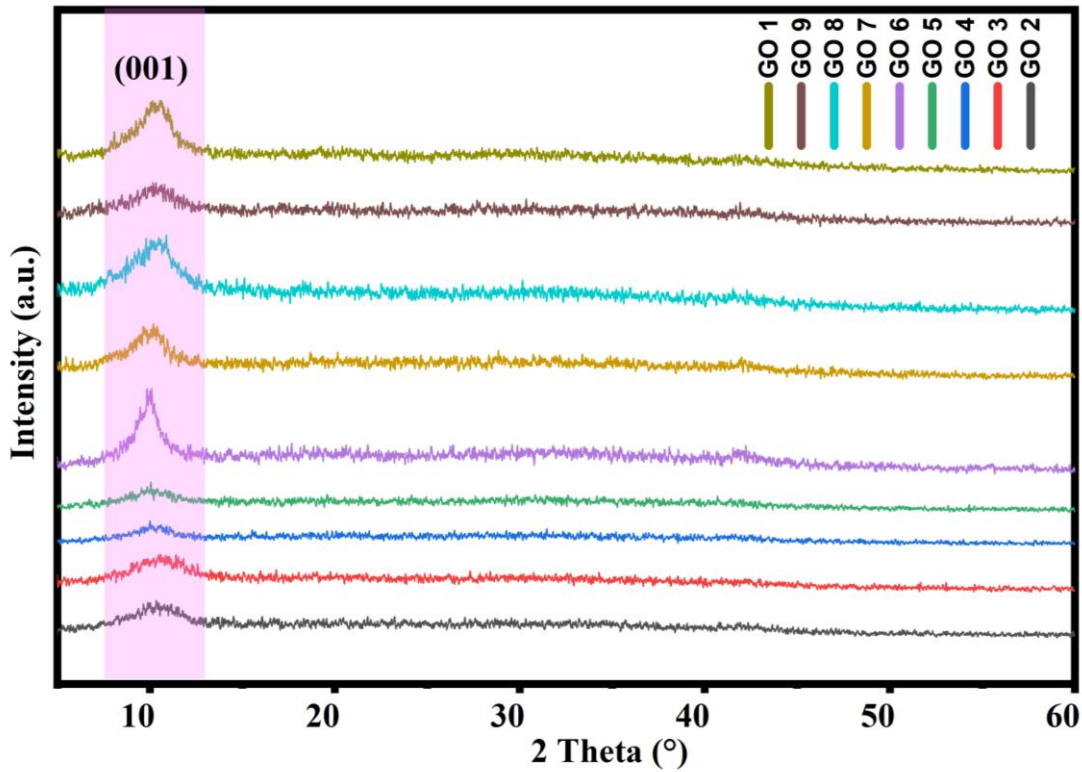


Figure 1 XRD pattern for all the GO samples.

Fig. 1 shows the XRD pattern for the GO samples with different ratios of $\text{NaNO}_3/\text{KMnO}_4$, where the observed 2 theta value is at 10.25° , 10.3° , 10.6° , 10.03° , 10.07° , 9.86° , 9.83° , 10.46° , and 10.11° , respectively, as shown in Table 2, which corresponds to the (001) plane. From the Bragg's formula, the d-spacing of the GO samples is calculated using the peak position from Fig. 1. This large d-spacing results from good intercalation of H_2SO_4 ions and oxidants to diffuse more easily on the sites, however almost same values for d-spacing shows that there is no significant effect on the intercalation of ions with the amount of NaNO_3 either we increase it or decrease it until the amount of sulfuric acid is sufficient. Meanwhile, the values of crystallite size change for GO6, which is the maximum, suggest a lower value of FWHM (full width at half maximum), indicating a sharp peak for GO6, which signifies good crystallinity of the sample. According to these findings, graphite exhibited noticeable intercalation growth only when sufficient NaNO_3 was applied [38]. Without the addition of H_2O_2 in the GO1, 2, and 3, we have lower values of crystallite size, almost the same value for d spacing, and the XRD peak at higher positions than other GO with H_2O_2 . The nearly identical d-spacing values observed across all GO samples indicate that the graphite lattice exhibited a consistent interlayer expansion characteristic of intercalation. This behaviour remained unaffected by the presence or absence of H_2O_2 and was almost independent of the NaNO_3 concentration (0.5, 1.0, and 1.5 g), suggesting that the intercalation process is primarily governed by the modified Hummers conditions rather than these specific additives. Moreover, the reduced crystallite size observed in GO1, 2, and 3 can be attributed to the presence of a small amount of NaNO_3 in the reaction medium, which facilitates the intercalation of NO_3^- and Na^+ ions between the graphene oxide layers, thereby disrupting their stacking and limiting crystal growth [39,40].

Table 2 Values of 2 theta ($^\circ$), d-spacing, and crystallite size (nm) for the prepared GO samples.

Sample name	2 theta ($^\circ$)	D spacing (nm)	Crystallite size (nm)
GO1	10.25	0.86	4.61
GO2	10.76	0.86	3.39
GO3	10.60	0.83	3.38
GO4	10.09	0.88	4.57
GO5	10.07	0.88	5.04
GO6	9.86	0.9	18.16
GO7	9.83	0.9	5.32

GO8	10.46	0.85	6.6
GO9	10.11	0.87	4.21

5.2 FTIR Study

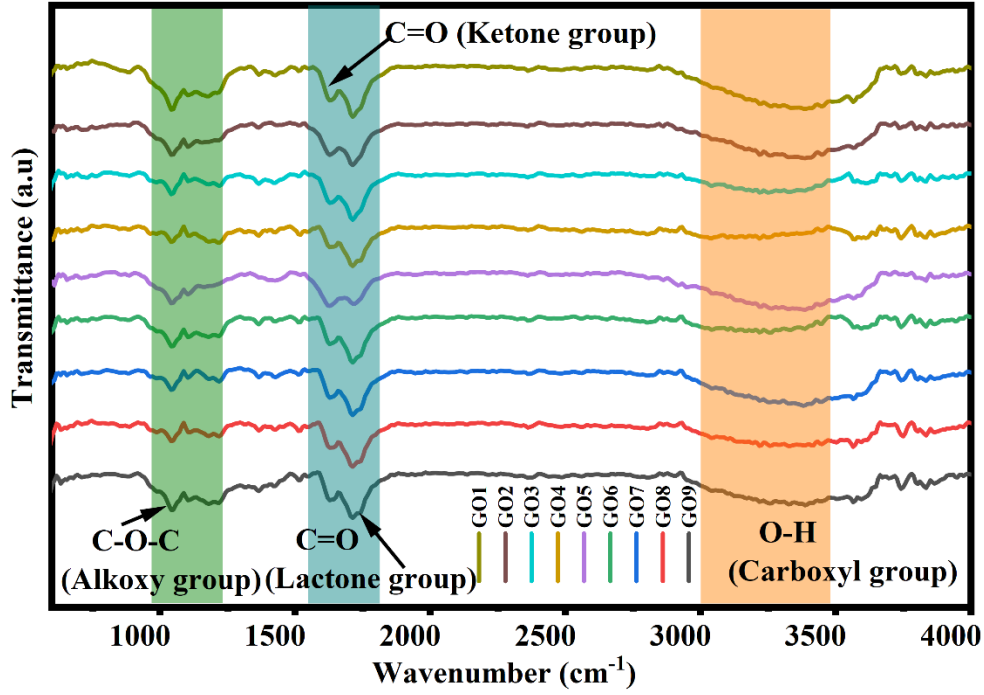


Figure 2 FTIR spectra for all the samples prepared in this work.

GO is a chemically exfoliated layered structure of graphite powder intercalated with different functional groups on the edges (carbonyl and carboxyl groups) and on the basal plane (hydroxyl and ether/epoxy) of the layers [41]. For the analysis of these functional groups (Fig. 2), FTIR spectroscopy is used. Fig. 2 shows the presence of CO bonds at various bands, like a band at $\sim 1036 \text{ cm}^{-1}$ (from stretching of alkoxy C-O-C group) for all GO samples, ~ 1220 and 1418 cm^{-1} , respectively, representing the symmetric and asymmetric stretching of the covalent sulphate bond (SO_4^{2-}) (as discussed in UV analysis) [42]. For the different types of C=O stretching band, in our analysis, the lactone groups at the sheet edges, with a combination of OH group, play a major role in the range $\sim 1720 \text{ cm}^{-1}$, and the peak at 1620 cm^{-1} represents the presence of C=O (ketone group), for all the samples [43]. The presence of the OH bending band associated with the edges of defects near 1420 cm^{-1} . Furthermore, the band at $3110\text{--}3360 \text{ cm}^{-1}$ indicates the presence of a carboxyl group (O-H), primarily due to the presence of water molecules. This is because FTIR spectra are a function of the change in bond dipole and are therefore more useful for examining asymmetric vibrations and vibrations involving atoms of different sizes, whereas raman spectra are dependent on changes in the polarizability of the bonds and thus applicable to symmetric vibrations and vibrations involving atoms of similar size [44]. The proposed lower concentration of NaNO_3 without H_2O_2 shows intensified peaks of GO as compared to other GO samples with H_2O_2 and NaNO_3 .

5.3 Microscopic study

Fig. S1, S2, and S3 (a, b, c, d, e, and f) show the SEM images of all GO samples, where the GO2 and GO3 represent the less damaged and larger in size GO as compared to other samples, because of a lower amount of NaNO_3 and H_2O_2 free environment. Whereas for GO1, we have damaged sheets with smaller-sized sheets, even though we have a lower dosage of NaNO_3 , for the other samples. Significantly fewer GO sheets were produced without NaNO_3 than with NaNO_3 when the intercalator or oxidant concentration is low. Due to the intense oxidation of H_2SO_4 , graphite was oxidised into fine pieces when the concentrations of intercalator and oxidant were high, and NaNO_3 was not utilised properly [39]. However, the increasing concentration of KMnO_4 and sodium nitrate leads to the more destroyed layers of GO in the presence of H_2O_2 . The elemental analysis of the

samples is shown in Fig. S1, S2, and S3 (g, h, and i), which represents the presence of carbon and oxygen in all the samples of GO. For higher resolution images, the HRTEM technique is used, which shows the layered structure of GO. GO nanosheets are seen to resemble crumpled silk veil waves. The GO sheets were intertwined and rippled. Under the electron beam, they show a very stable nature and are transparent. Monolayer graphene nanosheets are perhaps the most transparent and featureless areas shown by arrows in Fig. 3 (a and b).

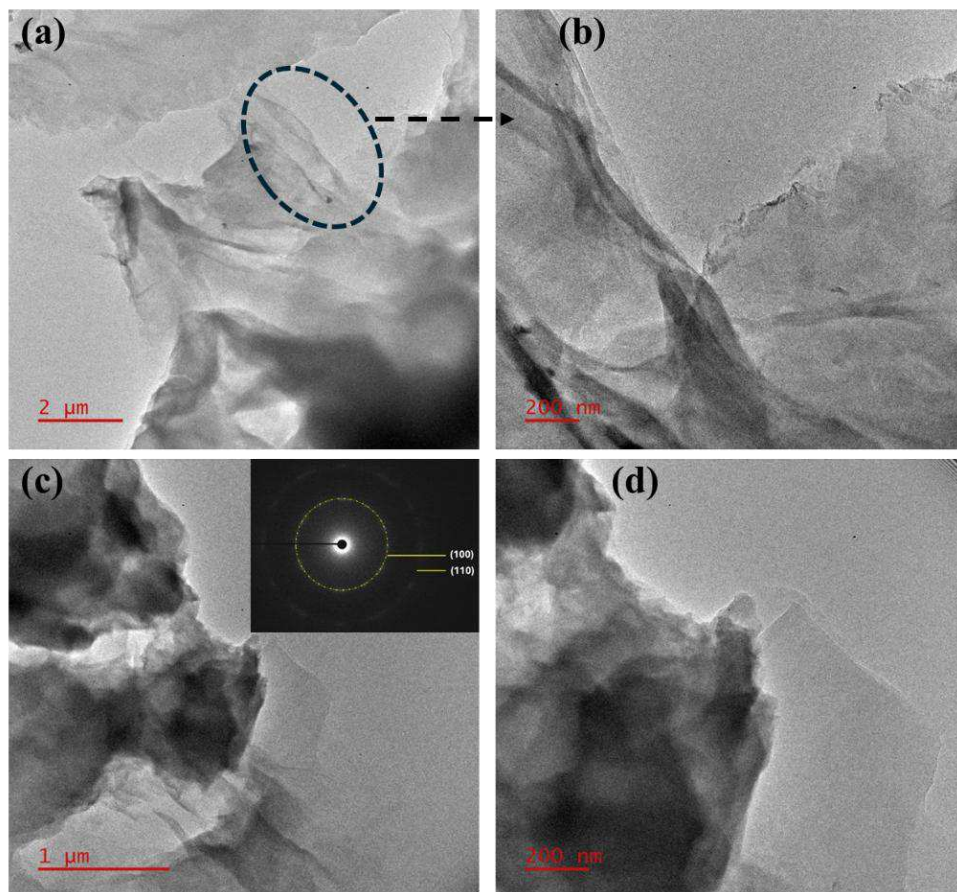


Figure 3 (a), (b), (c), and (d) HRTEM images of GO 6 with SAED pattern as an inset.

With a low atomic number, GO is highly desirable for transmission electron microscopy for better resolutions, as seen from Fig. 3. It is easy to see the organised graphite lattices in the HRTEM analysis in the inset of Fig. 3 (c). The GO were partially restored to an ordered crystal structure, albeit as evidenced by the presence of disordered patches [45]. In the ordered area, the graphitic laminar structure may be resolved. We used selected area electron diffraction (SAED) along the [110] zone axis [46]. The crystalline structure of the GO produced by chemically reducing graphite powder is confirmed by the distinct diffraction spots. The monolayers of GO are also witnessed in Fig. 3 (c and d). Further, the elemental analysis (EDS) of the GO samples is reported in Fig. S1, S2, and S3 (g, h, and i), respectively. The presence of carbon, oxygen and sulphur is clearly shown for all the GO samples.

5.4 Raman Analysis

Over the past fifty years, Raman spectroscopy has been used extensively to characterise graphitic materials, including glassy carbon, pyrolytic graphite, activated carbons, graphite ribbons, and CNTs [47]. The high dependency of carbon materials' physical properties on the ratio of sp^2 to sp^3 bonds accounts for their enormous adaptability. From low crystalline graphite to glassy carbon, there are numerous types of sp^2 -bonded carbons with different levels of graphitic structures. Further, any combination of different hybridisations - sp^3 , sp^2 , and even sp^1 sites can generally be found in an amorphous carbon [48].

With the interpretation of phonon dispersion in graphene to explain the Raman spectra, there are 6 phonon bands present in the hexagonal lattice of GO, which are bifurcated into acoustical (A) and optical (O) phonon branches (half for each). For these branches, the vibrations are perpendicular to the graphene oxide plane. And in all phonon modes, there are one acoustic and one optic branch, and also the second optic and second acoustic branches,

respectively [49]. According to the direction of vibrations with the next-door carbon atoms, the phonon modes are classified as longitudinal (L) and transverse (T) with respect to parallel or perpendicular vibrations of atoms with carbon-carbon directions. The degenerate zone-centre LO and iTO (in-plane) phonon modes are Raman active modes since they are part of the 2D E_{2g} (doubly-degenerate) representation, according to Group Theory [50], and the band arising near 1575-1596 cm^{-1} is associated with the G-band, which originates from the first-order Raman scattering. The peak positioning of the G band starts increasing as we move from GO1 towards a higher oxidation level. The highest wavenumber of 1596 cm^{-1} is recorded for GO2, GO3, and GO7, indicating a higher oxidation degree, comparatively [51]. As the amount of NaNO_3 is low, an appropriate amount of KMnO_4 leads towards a highly oxidised GO with increased sp^3 carbon atoms in the graphite lattice. The full spectra for Raman analysis are represented in Fig. S4 for all GO samples.

The G' band is observed in Raman spectra of GO, which originates from the second-order Raman scattering process by involving two iTO phonons near the Brillouin zone K point, which determines more information about the coupling between electron-phonon. The G' band is observed at 2700-2760 cm^{-1} (overtone of the D band); since it turns out that the G' band is susceptible to the c-axis stacking pattern, and after fitting, two or three Lorentzian peaks are observed in all the samples, which emphasises the presence of more than three layers of the synthesised GO [52]. The intensity of the G' band in the GO3 and GO4 samples is observed to be higher than that of the D and G bands, whereas in the other GO samples (Fig. 4 (c and d)) the G' band intensity is comparatively lower, which shows a lower oxidation of graphite [53]. This behaviour correlates with the I_D/I_G ratio, which is significantly elevated in the GO3 and GO4 relative to the other samples (as shown in Table 3). The variation can be attributed to the relative amounts of oxidising agents used during synthesis. In GO3, the concentration of NaNO_3 is low while KMnO_4 is comparatively high, whereas in GO4, the inverse condition is present. In both cases; imbalance leads to restricted diffusion of oxidants and intercalating species into the graphite layers, thereby affecting the oxidation dynamics. Consequently, the optimisation of NaNO_3 concentration is critical in achieving uniform oxidation. The observed enhancement in the G' band intensity for GO3 and GO4 reflects the altered defect density and structural disorder arising during these synthesis conditions. While considering the single-layer graphene, we have a single and wider G' peak in the Raman spectra, which also shows almost negligible interaction between the layers of graphene. Whereas, for the multilayered GO, the observed G' peak is not represented by a single Lorentzian peak, which suggests that the various planes in our GO may be dynamically oriented in a stacking order [52]. We observed the two-peak profile, suggesting the interaction between the GO planes, which strengthens the π -electron dispersion energy between the GO planes. The G' band in the GO Raman spectra, the variation of the G' peak is approximately 70 cm^{-1} in all the GO samples; showing the diffusing nature. However, the additional peak is observed along the G' peak with varying positions across the wavenumbers, representing the c-axis stacking order of the particular sample [54]. Such overtones represent D+G (combination band) and 2D' (overtone) bands at the positions of 2624-2840 cm^{-1} and 3092-3156 cm^{-1} , respectively. It varies with the oxidation states of the particular GO; showing the variation in the graphitic AB stacking. The observation of the 2D' band arises from a two-phonon Raman scattering process that intrinsically satisfies momentum conservation, and its occurrence is independent of defect-mediated activation in the GO sample [55]. However, these alterations were linked to a high oxidation-related defect concentration, followed by the emergence of a strong peak centred at the D band within a range of 1321-1358 cm^{-1} . By altering the basal plane due to oxidation of graphite flakes, the D band reflects the A_{1g} breathing mode. Overall, we can conclude that the peaks correlate well with the fundamentals of graphene oxide as present in the literature. However, there are shoulder peaks as deconvoluted in between or near the D and G bands, which are D* (1200-1290 cm^{-1}), D'' (1400-1480 cm^{-1}), and D' (1600-1650 cm^{-1}), presented in the Raman spectra of all the samples as shown in Fig. 4. Generally, these shoulder peaks are neglected in various research work as their intensity is very low [56]. The peak positioning of these shoulder peaks varies as per the ratio of $\text{NaNO}_3/\text{KMnO}_4$. Vollebregt et al. 2012 [57], show the dependence of the D'' on the amorphous nature, which is dependent on the crystallite size. The shift of the D'' peak in the case of GO1, 2, and 3 is higher in GO3, which shows a low oxidation of the material. Similar behaviour is observed for the case of GO4, 5, and 6, where 1 gm of NaNO_3 is used and for the GO4, the peak of D'' was shifted to a higher wavenumber as compared to GO5 and 6. For GO7, 8, and 9, the red-shifted peak is GO8, which shows a lower oxidation of graphite.

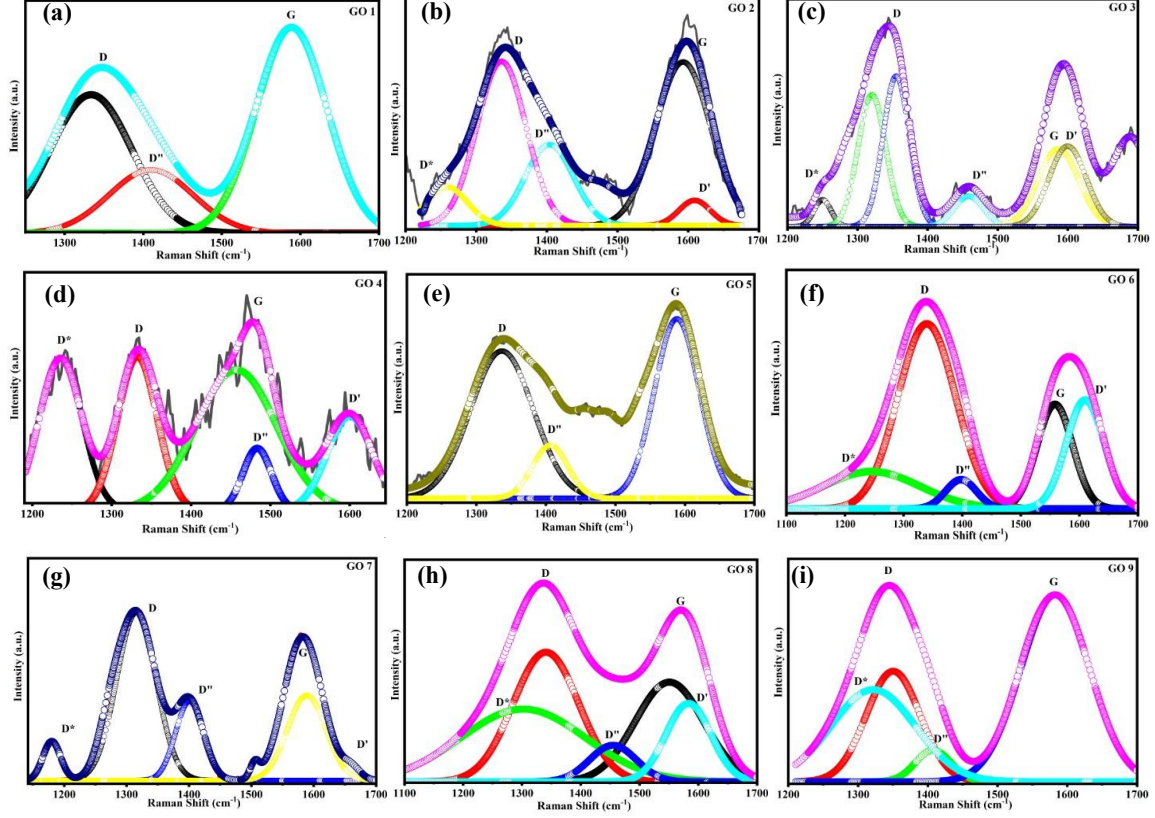


Figure 4 Deconvoluted spectra of Raman analysis for (a) GO1, (b) GO2, (c) GO3, (d) GO4, (e) GO5, (f) GO6, (g) GO7, (h) GO8, and (i) GO9.

Table 3 The characteristic peak of the D and G band, and the I_D/I_G ratio for all the GO samples using Raman Spectroscopy.

Sample name	D-Band (cm ⁻¹)	G-Band (cm ⁻¹)	I_D/I_G
GO1	1358	1585	0.99
GO2	1343	1596	0.94
GO3	1343	1597	1.27
GO4	1335	1596	1.62
GO5	1329	1587	0.99
GO6	1349	1582	1.00
GO7	1321	1595	1.00
GO8	1335	1571	1.13
GO9	1344	1580	1.04

The shoulder peak over the G band is also observed in the Raman spectra around ~ 1600 cm⁻¹, represented as the D' peak, responsible for the structural disorder due to the broken periodic lattice by the defects in the GO; it belongs to the E_{2g} symmetry. This peak usually comes from the impurities in the sample corresponding with the intra-valley resonance with the G peak. Curve fitting of the Raman spectra revealed a pronounced D' band across all samples, excluding GO1, GO5, and GO9. Further, the D* peak presented in the Raman spectra normally originates from sp³ orbitals, and the intensity of the peak is controlled by the oxygen functional groups [58]. However, the origin of the D* band is still not clear [59]. The observed range for the D* band is ~ 1190 -1290 cm⁻¹, for all the GO samples except GO1 and GO5.

The intensity ratio of the D and G bands (I_D/I_G) is widely recognised as a reliable metric for assessing the degree of graphitisation in carbon-based materials, since it serves as a conventional indicator of defect density [60]. Nevertheless, in the Raman spectra of GO, additional features such as the D', D'', and D* bands exert a significant influence, not only altering the I_D/I_G ratio but also modifying the spectral position and full width at half maximum of the associated peaks. In this framework, we analyse the I_D/I_G ratio in relation to the relative intensity of the

bands after fitting the Raman spectra [61,62]. The smaller GO sheets represent that higher edge density makes them more prone to oxidation, leading to the formation of additional oxygen-based functional groups, thus exhibiting larger I_D/I_G . It demonstrates that NaNO_3 and H_2SO_4 have a cooperative effect on the oxidation of graphite, which is beneficial for the oxidation and intercalation of ions in the graphite layers [63]. However, the samples show more structural damage to the graphite sheets for a large amount of NaNO_3 , and an inappropriate amount of KMnO_4 leads to lower oxidation of the graphite, which is emphasised by the I_D/I_G ratio. It is observed in GO3 and GO4 that the oxidation level is lower as the I_D/I_G ratio is increased because of a very unstable ratio of $\text{NaNO}_3/\text{KMnO}_4$ for the synthesis of GO [53]. A similar pattern is observed in GO8, where the I_D/I_G ratio is higher, representing a slightly lower oxidation of graphite. For other samples like GO1 and GO2, we got a low I_D/I_G ratio, which signifies good oxidised graphite sheets with a low concentration of NaNO_3 without H_2O_2 , as compared to the samples synthesised from the traditional modified Hummers method (GO6, 7, 8, and 9). The average crystallite size of the GO is thus decreased as the oxidation level of the graphite, which may be due to the breaking of crystallites, leads to the formation of higher defects in the sample [64]. The results of Raman spectroscopy might offer a way to investigate the disruption of stacking order with varying oxidation degrees, even if there is no direct relationship between the sp^3 and sp^2 states with regard to the oxidation level, as discussed above for the G' band. This work shows the highly oxidised GO using a low concentration of NaNO_3 without H_2O_2 and an optimised amount of KMnO_4 .

5.5 UV-Vis analysis

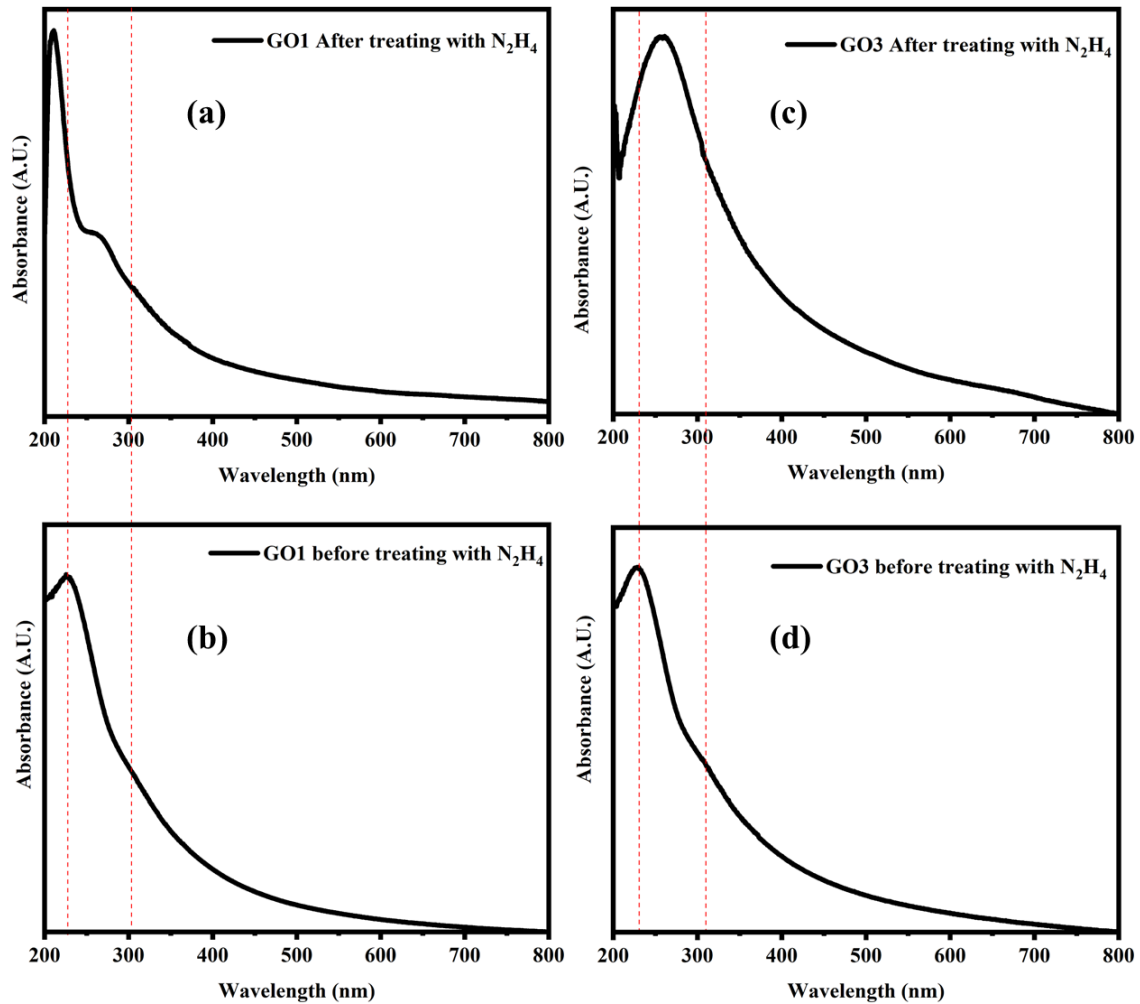


Figure 5 UV-Vis spectra (a and b), (c and d) for GO 1 and 3, respectively.

The UV-Vis absorption spectra of samples GO1 and GO3 were recorded in the wavelength range of 200 nm to 800 nm. In a typical graphene oxide, a primary absorption peak is observed near 230 nm, which is attributed to the $\pi \rightarrow \pi^*$ transitions of C=C bonds within the unoxidized aromatic rings. Additionally, a smaller shoulder peak

is usually present around 300 nm, corresponding to $n \rightarrow \pi^*$ transitions of C=O bonds from oxygen-containing functional groups[65].

For the highly exfoliated GO3 sample, the primary $\pi \rightarrow \pi^*$ absorption peak underwent a classic bathochromic (as supported by SEM and Raman analysis) shift to 261 nm. This shift, accompanied by the masking of the $n \rightarrow \pi^*$ shoulder and a broadband increase in visible light absorbance, confirms the successful deoxygenation and restoration of the conjugated sp^2 carbon network. The pre-exfoliated morphology of GO3 directly facilitated the success of this chemical reduction. The successfully separated nanosheets gave the hydrazine reducing agent free steric access to the basal planes, which made the reduction even. Despite the loss of hydrophilic oxygen groups, the aqueous rGO dispersion remained remarkably stable over extended periods. This long-term colloidal stability is attributed to electrostatic repulsion driven by a combination of unreduced edge-carboxyl groups and the highly electronegative residual sulphate groups (identified via EDS) covalently bound to the sheets, which effectively counteracted $\pi - \pi^*$ stacking interactions [24].

The GO1 sample exhibited an anomalous hypsochromic blue shift, with its primary absorption peak moving to 211 nm. The distinct retention of the $n \rightarrow \pi^*$ shoulder peak at 256 nm indicates that the bulk material is chemically stable. This divergent optical response is a direct consequence of GO1's initial aggregated morphology. The thick, tightly stacked chunks hindered the intercalation of hydrazine in the bulk galleries. Consequently, the chemical reaction was restricted primarily to the exposed outer surfaces under strongly alkaline conditions. This localised, aggressive surface etching induced the chemical cleavage of the outermost GO layers into nanoscale fragments. The physical restriction of these sp^2 domains induces quantum confinement effects, drastically widening the energy gap and resulting in the pronounced 211 nm absorption peak. Because the interior of the GO1 aggregates remained unreduced and heavily functionalised, the sample retained its exceptional hydrophilicity and bulk dispersion stability[66]. UV-Vis spectroscopic analysis revealed that GO1 exhibits favourable optoelectronic characteristics, indicating its strong potential for applications in electronic devices as well as serving as a precursor for the synthesis of graphene oxide quantum dots. In contrast, GO3 demonstrates physicochemical properties that make it particularly suitable for formulation into conductive inks, thereby expanding its utility in printing and coating technologies.

5.6 TGA Analysis

Thermogravimetric analysis (TGA) revealed the characteristic mass loss profile as a function of reference temperature (Fig. 5 (a)). The corresponding derivative thermogravimetric (DTG) (Fig. 5 (b)) curves provided quantitative insights into the rate of thermal decomposition. These combined techniques are extensively employed to elucidate the presence of adsorbed moisture, volatile constituents, combustible carbonaceous phases, and residual impurities in GO. Figure 5 (b) depicts the corresponding DTG curves, with the respective T_{max} values indicated at the bottom. The TGA profiles indicate that the GO samples undergo complete thermal decomposition in a nitrogen atmosphere upon heating to 800 °C. The thermal decomposition of GO samples can be categorised into three distinct regions [67]. The initial mass loss below 100 °C corresponds primarily to the evaporation of adsorbed and interlayer water molecules. The second stage, occurring between ~100–210 °C, is attributed to the decomposition and release of oxygen-containing functional groups. The subsequent mass loss observed in the range of ~210–290 °C, extending up to 800 °C, is associated with the degradation of the carbon framework and combustion of residual carbonaceous matter. The corresponding DTG peaks in these three regions are observed for all the samples. The T_{max} for Region 1 is observed at approximately 60 °C, while for Region 2 it lies between 200–205 °C across all samples; however, in the case of GO5, the T_{max} is shifted to 210 °C [68].

The pronounced DTG peaks can be correlated with the structural features of the carbon lattice, reflecting its response to external thermal energy during the oxidation of the carbon framework. The third region specifically denotes the combustion of carbon. Graphene, in this context, consists of sp^2 -hybridized carbon atoms organised into a 2D hexagonal lattice, interconnected through strong covalent bonding. In the case of GO, extensive oxidation converts a significant fraction of the sp^2 -hybridized carbon into sp^3 -hybridized carbon. This structural transformation weakens the interlayer interactions and facilitates the intercalation of oxygen-containing functional groups within the graphene sheets, thereby reducing the overall thermal stability of GO relative to pristine graphite [69,70]. For the GO5 sample, the elevated T_{max} value is indicative of a reduced defect density within the structure.

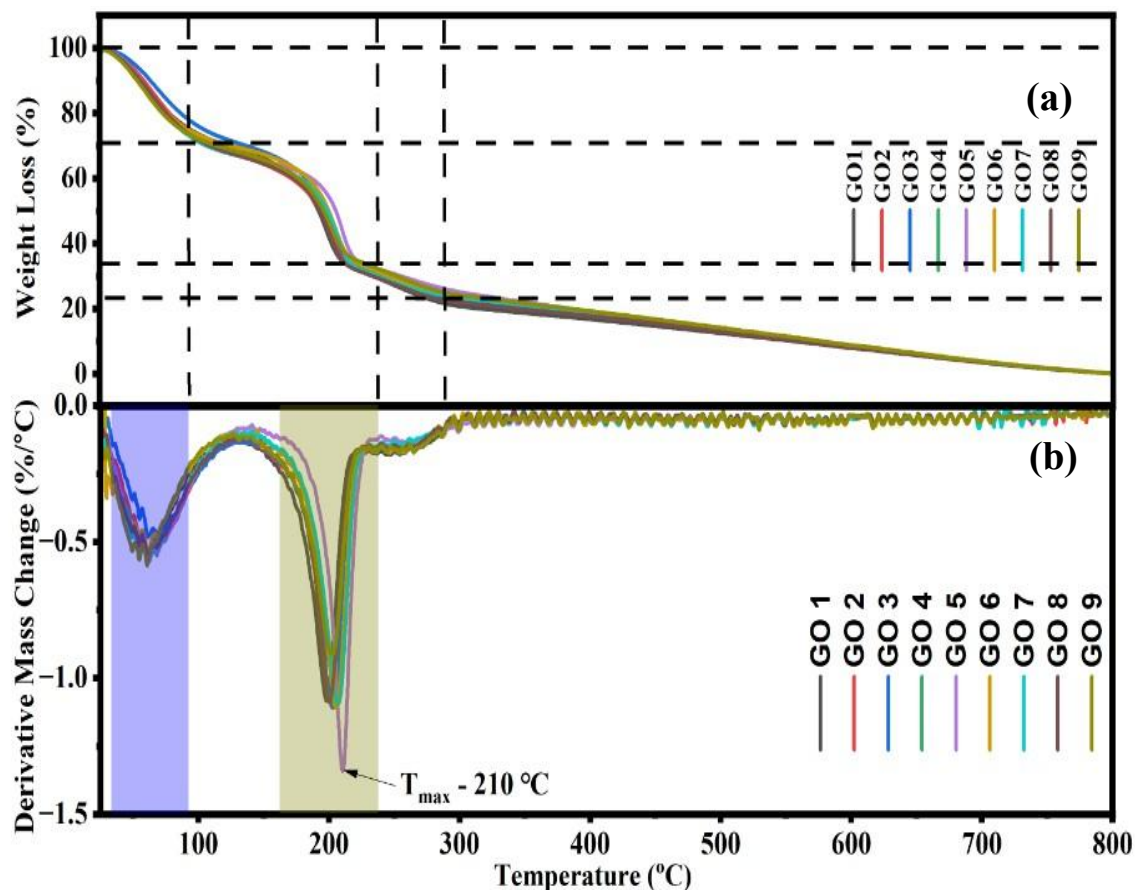


Figure 5 (a) combined TGA curves for all the samples, and (b) DTG graphs.

Conversely, lower $T_{\max}$ values reflect an increased degree of sp^3 hybridisation relative to sp^2 domains in the carbon framework. Fig. 5 (a), the GO3 and GO5 show a lower oxidation of the graphite sheets than the other samples. Samples GO1, GO2, GO6, GO8, and GO9 exhibit enhanced oxidation of the graphene oxide sheets, leading to the formation of relatively stable oxygenated functional groups. According to our analysis, GO1 and GO2 were synthesised with minimal amounts of $NaNO_3$ and oxidising agents, thereby yielding graphene oxide with high oxygen functionality and improved structural stability. In contrast, GO6, GO7, and GO8, prepared via a modified Hummers' method employing higher concentrations of $NaNO_3$ and intercalators, demonstrate appreciable thermal stability, though inferior to that observed in GO1 and GO2.

5.7 Colloidal Stability Analysis

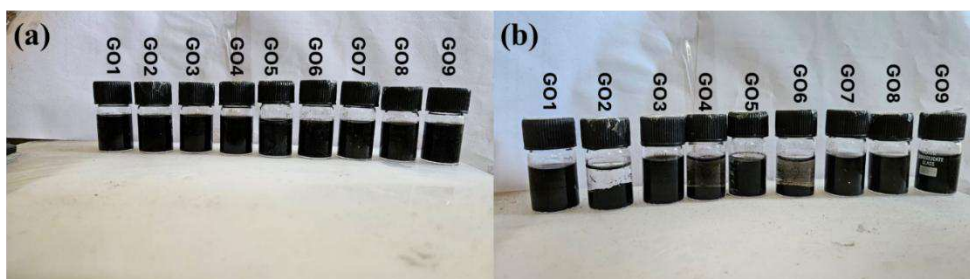


Figure 6 (a) just after sonication of rGO dispersion in DI water (b) after 3 months of dispersion.

Owing to the growing significance of graphene and its applications, the development of diverse dissolution and dispersion strategies is highly advantageous, as it enhances the accessibility and availability of graphene-based samples for experimental investigations [71,72]. Extensive investigations on the surface chemistry of graphene oxide have demonstrated that its sheets possess a pronounced negative charge, primarily attributed to the abundance of oxygen-containing functional groups such as carboxyl and hydroxyl moieties. These functionalities

impart electrostatic repulsion among the GO layers, thereby facilitating the formation of a highly stable colloidal dispersion in aqueous media, which is mainly attributed to the electrostatic repulsion [27,73]. Without chemical conversion of the material, a stable colloidal solution of reduced graphene oxide can be made using hydrazine hydrate and controlling the pH of the solution with ammonia, as described by LI et al. 2007 [24]. Following this route, stable colloidal solutions are obtained in this study. The colloidal behaviour of reduced graphene oxide suspensions was systematically monitored over a period of three months. As illustrated in Fig. 6, panel (a) depicts the homogeneous dispersion of rGO samples immediately following sonication, whereas panel (b) presents the state of the suspensions after three months of storage. This comparative analysis highlights the long-term stability of the dispersions. Notably, samples GO2, GO4, GO5, GO6, and GO8 exhibited sedimentation within the aqueous medium after the three-month interval, indicating limited colloidal stability relative to the other solutions.

To study the colloidal nature of the ensuing rGO dispersions commonly carried out in colloid science, examinations of the Tyndall effect further corroborate [74]. The Tyndall effect, in which a laser beam travelling through a colloidal solution leaves a noticeable trail due to light scattering, is caused by a diluted reduced GO dispersion (as shown in Fig. 7). In the case of GO1, GO4, and GO7, where the concentration of KMnO_4 (7 g) was maintained and the amount of NaNO_3 (0.5, 1, and 1.5 g), distinct differences in colloidal behaviour were observed. GO1 exhibited a highly stable and homogeneous colloidal dispersion, as evidenced by the pronounced visibility of the light path (Tyndall effect). In contrast, GO4 underwent sedimentation over time, indicating reduced colloidal stability, whereas GO7 behaved as a true solution, with the absence of a visible light path confirming the lack of scattering. For samples GO2, GO5, and GO8, where the amount of KMnO_4 is increased to 9 g, and the variation of NaNO_3 is the same, distinct colloidal behaviours were observed over the three months.

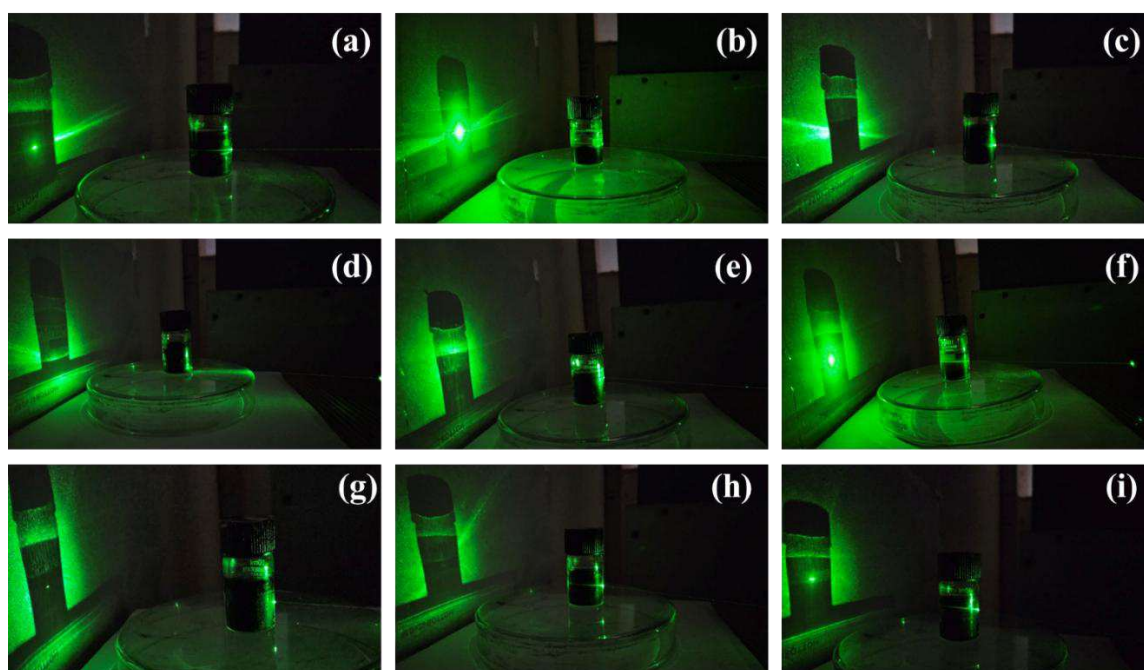


Figure 7 The Tyndall effect images for (a) GO1, (b) GO2, (c) GO3 (d) GO4, (e) GO5, (f) GO6, (g) GO7, (h) GO8, and (i) GO9.

GO2 exhibited sedimentation, indicating poor long-term stability in the aqueous medium. GO5 remained dispersed but did not display light scattering, suggesting the formation of a suspension that behaves more like a true solution. In contrast, GO8 maintained an unstable colloidal dispersion, as confirmed by the pronounced visibility of the laser path. Upon increasing the KMnO_4 concentration to 11 g for samples GO3, GO6, and GO9, distinct dispersion behaviours were observed. GO9 exhibited a stable colloidal solution, as evidenced by the clear manifestation of the Tyndall effect. In contrast, GO6 gradually underwent sedimentation over time, indicating reduced stability, while GO3 formed a suspension that did not display significant light scattering.

GO sheets are well known to form stable aqueous colloids, primarily due to electrostatic repulsion, as they carry a strong negative charge in water. This negative surface potential arises from the ionisation of hydroxyl and carboxyl functional groups [75,76]. Because these groups are not fully removed under conditions used in this

work; as pH optimisation and hydrazine reduction, the modified rGO sheets in our study are expected to retain residual negative charges [27,77]. Consequently, the stability and dispersion of rGO colloidal suspensions in samples GO1, GO8, and GO9 can be attributed to the persistence of electrostatic repulsion between rGO layers. For GO8 (Fig. 7 (h), S5), the laser beam generated a visible path within the dispersion but no transmitted spot beyond the solution, consistent with scattering by smaller, well-exfoliated flakes.

Phase Analysis Light Scattering (PALS) was used to systematically study the connection between aqueous dispersibility and electrokinetic properties of nine reduced graphene oxide (rGO) variants (GO1–GO9). The results showed a strong positive correlation (Pearson's $r = 0.975$, $p < 0.0001$) (Fig. S8) between bulk electrical conductivity and the measured zeta potential magnitude. Depending on electrolyte concentration, the samples naturally fell into distinct electrokinetic groups. In the low-conductivity group (GO2, GO4, and GO5; $\sigma \leq 0.69$ mS/cm), where ion screening is low, the instrument detected the true highly negative surface charges of the variants, with strong zeta potentials ranging from -30 mV to -35 mV[24]. In contrast, samples in the high-conductivity group (GO1, GO3, GO6, and GO8; $\sigma \geq 3.12$ mS/cm) showed much lower zeta potentials, ranging narrowly between -10 mV and -14 mV. This reduction is a typical effect of electrical double layer (EDL) compression. Higher ionic strength, mainly due to leftover buffering ions (NH_4^+ and OH^-) from the alkaline adjustment, greatly reduces the Debye screening length. Consequently, the hydrodynamic shear plane moves closer to the carbon surface, which masks the true surface charge from optical detection[78]. Importantly, the long-term macroscopic colloidal stability of these samples did not fully match typical electrokinetic predictions. Most formulations remained highly stable with no phase separation for over three months. However, samples GO2 and GO4, which had the strongest and most negative zeta potentials, began to show sedimentation after two months. In contrast, the high-conductivity samples with significantly reduced zeta potentials stayed completely stable throughout the three-month period. This contrast strongly suggests that the low zeta potential values measured at high conductivities are artifacts caused by electrical double layer (EDL) compression, rather than true signs of structural instability or aggregation [79].

When the laser was incident at different positions, the response varied—at times producing a spot and at other times not—indicating spatial heterogeneity and instability in the colloidal system. This irregular scattering behaviour suggests that GO8 forms a poorly stabilised colloidal suspension of low quality, with fluctuations in dispersion stability likely arising from uneven flake distribution and partial aggregation. In contrast, GO9 exhibited a pronounced transmitted spot following laser illumination, suggesting the presence of larger graphene oxide flakes that allow partial transmission of coherent light while still maintaining colloidal characteristics. For GO7, only a faint spot was observed without any discernible path inside the medium, signifying that the system behaves as a true solution rather than a colloid, with negligible scattering centres.

So, it is also confirmed here that without H_2O_2 , we got a better solution with segregation in the DI water for reduced GO. Our findings demonstrate that chemically modified rGO sheets are capable of forming stable colloidal dispersions through electrostatic stabilisation, achieved by tuning the relevant physicochemical parameters such as pH. Under controlled experimental conditions, hydrazine-mediated reduction effectively converts GO dispersions into stable reduced graphene oxide colloids. Notably, this stabilisation occurs without the need for external surfactants or polymeric additives.

6. Conclusions

In the current study, we demonstrate the safer synthesis of GO using variations in the modified Hummers method. In the conventional synthesis of GO, varying amounts of NaNO_3 and KMnO_4 are employed as precursors. Under the present modified conditions, we propose that the intrinsic formation of Mn_2O_7 undergoes vigorous hydrolysis, producing permanganic acid and MnO_2 , which reacts with the sulphuric acid to produce further MnSO_4^{2-} which is colourless. This intrinsic formation of these Mn oxidation states eliminates the need for external quenching agents and contributes to the characteristic yellow colouration of the final reaction mixture. Overall, the optimisation of NaNO_3 and KMnO_4 not only minimises hazardous emissions but also enables a safer and more sustainable route for GO synthesis. While this mechanistic interpretation provides a plausible explanation of the phenomenon, further experimental investigation is required to validate the proposed pathway and fully elucidate the underlying reaction dynamics. The synthesised GO1 and GO3 can be used in various applications, like electronic devices, printing and coating technologies.

Author contributions

Kartik Joshi: Writing - review & editing, Methodology, Investigation. Parveen Kumar: Writing - review & editing, Methodology, Investigation. Pawan Kumar: Characterisation. Rajinder Kumar: Characterisation. Ashavani Kumar: Writing - review & editing, Methodology, Supervision, Investigation.

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Conflicts of interest

The authors declare they have no financial interests.

Data availability

The data supporting this study are available in the Supplementary Information (SI). This contains SEM and EDS images, Raman analysis, Tyndall effect images for GO8, and a table containing the data for the yield of the GO samples. XPS characterisation of the GO1 sample. UV-Vis spectra of the remaining GO samples. Zeta potential and conductivity graph for all samples.

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