A Comprehensive Review over Green Synthesis of Graphene

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Abstract: Energy security has become a serious global issue and a lot of research is being carried out to look for economically viable environment friendly alternatives. Recent years Graphene has acquired immense recognition among various researchers. Synthesis of graphene through green route has now become a paramount area. The prospects of producing Reduced Graphene Oxide (RGO) from different types of green material appear bright because of its sustainability, low cost and environment friendly in nature. Conventional chemical reducing agents are highly toxic, hazardous and harmful to both environment and human life. The object of this article is to provide a comprehensive review on various methods of Reduced Graphene Oxide (RGO) from green synthesis to date, as well as to discuss their advantages, disadvantages and beneficially characterization. In this article we covered all areas of the green methods which employed in natural reduction of Graphene Oxide (GO) including use of plant extracts, microorganisms, endogenous agents, metal-mediated procedure, bacterial respiration procedure, bio-antioxidant (Melatonin), baker’s yeast, non-harmful acids (hydriodic acids, trifluoroacetic acid), glucose and glucosamine apart from some of the latest green technologies. The synthesized Graphene Oxide (GO) and green Reduced Graphene Oxide (RGO) samples were characterized using several methods. The formation of Reduced Graphene Oxide (RGO) was evident from Ultraviolet visible spectroscopy (UV-Vis) and Fourier Transform Infrared (FTIR) spectroscopic analysis which implied a clear indication of the removal of oxygen containing groups from the Graphene Oxide (GO). Additionally the thermal stability of the Reduced Graphene Oxide (RGO) nanomaterial was scrutinized using thermo gravimetric analysis or thermal gravimetric analysis (TGA). Dynamic Light Scattering (DLS) was also utilized for zeta potential measurements to monitor the stability and size of the obtained Reduced Graphene Oxide (RGO) sheets. Other spectroscopic techniques are SEM (Scanned Electron Microscopy), TEM(Transmission Electron Microscopy) etc. Further research is required in this area for successful implementation of this technology at production scale.

Keywords: RGO, GO, Plant extracts, microorganisms, endogenous agents, bacterial respiration, Graphene, green technology.

I. INTRODUCTION

Graphene as two – dimensional sheet of carbon atoms bonded through sp² hybridization is one of the most attractive nanomaterial, due to its unique and promising characteristics in condensed – matter and high energy physics[1,2,3], material science [4,5,6,7], and a broad range of technical applications[8,9,10]. During the past years, diverse procedures have been established for producing graphene, such as ultrasonic exfoliation [11, 12], chemical vapor deposition [13], epitaxial growth [14], chemical via reduction of graphene oxide (GO). The most widely used reducing agents, such as hydrazine, dimethyl hydrazine and NaBH₄ are highly toxic; trace amount of the poisonous agents could have detrimental effect, especially for bio related applications. Moreover, the handle of the hazardous waste generated by the reduction reaction may significantly increase the cost of on industrial scale [15, 16]. Another obstacle in practical applications of chemical reduced graphene oxide (RGO) is the poor process ability because the RGO tends to form irreversible aggregation which results from strong Van der Waals attractive forces between the graphene planes[17,18,19]. From last few years efforts have been made towards addressing the above mentioned problems by using natural product instead of toxic reducing agents under mild condition. For example aqueous leaf extracts of Colocasia esculenta, Mesua ferralinna, aqueous peel extract of orange (Citrus sinensis), tea polyphenol, different types of microorganisms, bacteria, plant extracts etc. are used as green reducing agents. Graphene oxide (GO) can be reduced to graphene in a normal aerobic set up under ambient conditions as mediated by microbial respiration of shewanalla cells [20]. Although the degree of reduction of RGO prepared by these strategies is usually lower than that of the hydrazine – based method, the excellent biocompatibility of these RGO sheets may enhance their feasibilities for use in biological and biomedical fields this reduction increases the atomic carbon to oxygen (C:O) ratio[21] which is about 2 in GO. With increasing C: O ratio, the band gap of GO become smaller [22, 23] reaching zero in perfect graphene. These changes in
the C: Oratio will affect the properties of the nanocomposites, as the sheets electronic properties, as well as their mechanical interaction with the polymer are altered.

II. SOURCES AND COMPOSITIONS

For reducing graphene oxide to reduced graphene oxide (RGO) scientists had used different types of aqueous phytoextracts such as Mangifera indica L. (mango) leaves extract, Solanum tuberosum L. (potato) extract, Cocos nusifera L. (coconut) extract, carrot extract, tea polyphenols, Salvadora persica L. (Miswak) extract, Annona squamosa L. leaf extract, orange extract (Citrus sinensis) and various types of bacterial microorganisms like Escherichia coli., Shewanalla etc. as reducing agents which are commonly available, eco-friendly, non-hazardous and have low environmental impacts. These phytoextracts contain many phenolic compounds such as caffeic acid, chlorogenic acid, gallic acid, protocatechuic acid, salicylic acid, vanillic acid etc. and have a large number of hydroxyl groups, which endow them in having mild reducing properties. This helps in the partial removal of the oxygen containing functionalities from GO during reduction in order to restore electronic conjugation in RGO. The presence of these phytoextracts will also help to prevent the extensive agglomeration in an aqueous dispersion of the resulting RGO through electrostatic repulsion interactions of the negative charge densities of many carboxylic groups. The green synthesized RGO is highly dispersible in water.

III. MATERIALS AND METHODS

The graphite oxide was synthesized from natural graphite powder by the modified Hummer’s method [24]. Graphite powder and nano3 were added into 50 ml 80% concentrated H2SO4 under vigorous stirring in a conical flask in an ice bath. After some time converting the whole mass to the black slurry, the kmno4 was slowly added into the slurry maintaining the reaction temperature below 20°C. After 4 h the whole system was taken out from the ice bath and diluted with water and the stirred for 2 h at 70°C – 80°C. To control the pH of the reaction medium and also to terminate the reaction, some amount of water followed by H2O2 were added to the above reaction mixture which resulted in a color change from brownish black to bright yellow. After washing the resultant mixture with distilled water, the pure graphite oxide powder the GO slurry was then collected.

After producing GO, various scientists were prepared Reduced graphene oxide via green route in solution reaction method followed by heating. Like, Tapas Kuila et al.,[24] gave a biological approach using wild carrot root for the first time as a reducing material as well as surface stabilizing agent for the synthesis of GO. In order to ensure the reduction of GO by wild carrot root, the experiment was carried out in DI water, the sliced carrot was added to GO dispersion at room temperature followed by heating for 48 h. It was found that the color of GO dispersion remained unchanged, this indicated that the wild carrot played an important role in the reduction of GO to graphene. Another control experiment was carried
out to confirm the reduction of GO by Gongming Wang et al., Using the entrophic microorganisms of Shewanalla bacteria. For this microbial synthesis *Shewanalla oneidensis* was cultured in trypticase soy broth at room temperature for 12 h in an incubator shaker with shaking at 200 r/min. Cultures were incubated in a normal aerobic or strictly anaerobic setup where appropriate, the solution was sampled at different time intervals [25]. Whereas, Omid Akhavan et al., [26] Obtained GO suspension reduced by glucose in the presence of Fe catalyst. Here glucose solution was added to the prepared GO suspension. Then by using magneto – stirrer heater, the glucose – GO suspension was stirred at temperature of 95º C. By this process the glucose-GO suspension was obtained.

Synthesis of reduced graphene was carried out according to the method described with slight modification by Sang Iliyandi et al.,[27,28] Bacteria were grown in an Erlenmeyer flask that contained LB broth, Escherichia coli biomass was added to GO dispersion and the mixture was stirred at 37ºC for 72h. After reduction the stable black dispersion was sonicated for 5 min to disperse the cells from graphene materials. The obtained black dispersion was designated as Escherichia coli reduced graphene oxide. Various process for the synthesis of go which have contributed to the development of relatively new and unexpected area of research based of the biosynthesis of phytoextracts and microorganisms.

![Figure 2: Schematic diagram of the total synthesis process(Picture Courtesy: Tapas Kumar Ghosh et.al (47)).](image)

**IV. MECHANISMS OF THE FORMATION OF GO AND RGO**

The detailed study of chemistry involved in Hummer’s method for the production of GO reveals so many things. This method actually uses a combination of H₂SO₄ and KMnO₄ which is the most widely used oxidant. Also few other oxidants are used in this method like H₂SO₄, NaNO₂ but it’s very tough to predict actual mechanism of the oxidation process. Some researchers suggested that the oxidizing agent in the reaction is Manganese Heptaoxide (Mn₂O₇) which is formed after addition of KMnO₄ in a mixture of sulphuric acid and graphite. The formation of Heptaoxide is shown below:

\[
\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}^+ + \text{MnO}_3^+ + \text{H}_2\text{O}^+ + 3\text{HSO}_4^- \\
\text{MnO}_3^+ + \text{MnO}_4^- \rightarrow \text{Mn}_2\text{O}_7
\]

So we can say that in H₂SO₄, Mn (VII) exists in the form of planner permanganate cation MnO₃⁺ which is closely associated with hydrogen sulphate (HSO₄⁻) and sulphate (SO₄²⁻) ions. The reason of change in solution color is due to the formation of graphite by sulphate (light green) which then converts into GO (Brown Color) after oxidation. According to our assumptions formation of graphite bisulphate to GO is a slow process so the conc. of H₂SO₄ and KMnO₄ can play an important role during oxidation. At last stage of oxidation process excess Mn₂O₇ can give yellow coloration after the addition of few drops of H₂O₂. During the oxidation process of graphite flakes it can be said that as graphite contain numerous localized defects in its π structure which may acts as seed point for oxidation process. Formation of RGO is also not cleared mechanistically by researchers. Although some previous reports show that exfoliated graphite oxide can be
deoxygenated under alkaline condition. Fan et al.,[29] reports a green route to prepare graphene using NaOH or KOH as a reducing agent but the mechanism remains unclear, they think the deoxygenation of exfoliated GO under alkaline conditions appears to the reverse of the oxidation reaction of graphite in strong acids. This mechanism is supported by the pH dependency of this deoxygenation reaction – the higher pH of the exfoliated GO suspension, the faster the reaction. Yuhong Jin et al., [30] reported that using Na₂CO₃ as a new chemical reducing agent for the reduction of GO dispersion. Na₂CO₃ can produce sodium ions and carbonate ions in the aqueous solution, then carbonate ions hydrolysis and yield hydroxide ions and bicarbonate ions, and bicarbonate ions can further hydrolysis and produce hydroxide ions. The hydroxide ions can create alkaline conditions. The yellow brown color of GO rapidly darkens within 4 h in the presence of hydroxide ions at 80°C. This experimental phenomenon can prove that GO dispersion is reduced under alkaline conditions.

![Fig-3 Reduction of GO by sodium carbonate (Pic courtesy Yuhong Jin et al., [30])](image)

V. CHARACTERIZATIONS ANALYSIS

For analysis of interlayer spacing and diffraction peak of any material is studied by XRD analysis. In this article we tried to demonstrate XRD patterns of graphite, graphite oxide (GO) and reduced graphite oxide (RGO) from various published article. pristine graphite exhibits a basal reflection peak at 26.6° (d spacing = 0.335nm) [31]. Compared with pristine graphite, the diffraction peak of exfoliated GO appears at the lower angle from almost 10.54. A typical broad peak near 10.27° (d spacing ~ 0.86 nm) was observed for the GO powder [32]. After microbial reduction the 10.54° peak disappears and a broad peak appears starting from 24° to 30° and interlayer spacing decreases to 0.37 nm which suggests that removal oxygen from the GO surface. The disappearance of reflection peak of GO and appearance of a broad-band from at 24° in the RGO indicated the great reduction of GO and formation of few-layer graphene [33].

![Figure 4: XRD patterns of GO and RGO (Picture Courtesy: Tapas Kumar Ghosh et.al (47)).](image)
Ultraviolet Visible spectroscopy (UV-Vis) is used to obtain the optical measurements of material. Mujeeb Khan et al.,[34] stated that Graphene oxide (GO) is reduced by plant extracts and microorganism exhibited absorption peak at 230 nm which was attributed to the π-π* transitions of the aromatic C-C bonds and a weak shoulder at 301 nm due to n – π* transitions of C=O bonds present in Graphene oxide on reduction of Graphene oxide to Reduced Graphene oxide, the characteristics absorption band at 230 nm in Graphene oxide spectrum is red shifted to 280 nm in Reduced Graphene Oxide, which confirms the reduction of Graphene oxide and the partial restoration of π network of Reduced Graphene[35].Vorrada Loryuenyong et.al [36] stated that the peak of Reduce graphene oxide is shifted to 255 nm due to a decrease in oxygen functional groups and an increase in aromatic rings, causing electrons to be easily excited at lower energy[37]. So that ultraviolet spectra analysis confirms the restoration of electronic conjugation after the reduction.

Fourier Transform Infrared Spectroscopy (FTIR) is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas and it collect high spectral resolution data over a wide spectral range. Suman Thakur et al.,[38,24] stated that the presence of intense bands at 1720 cm\(^{-1}\), 1204 cm\(^{-1}\), 1049 cm\(^{-1}\) and a broad band at around 3400 cm\(^{-1}\) for hydroxyl group indicate the presence of oxygen containing moieties such as carboxyl, carbonyl, carboxylic, epoxy and hydroxyl in GO. The removal of such oxygen containing groups of GO in all the RGO are clearly indicate by disappearance of the bands of C=O stretching, C-O-C stretching, C-O stretching and relative decrease in the intensity of broad band at 3400 cm\(^{-1}\) for the hydroxyl group. Chuanbao Li et al., [39] stated that FTIR was employed to analyze the functional groups on GO and their changes after the reduction with glucosamine(GL). The graphite sample has two strong peaks at 3450 cm\(^{-1}\) and 1610 cm\(^{-1}\) as a result of absorbed water and aromatic C=C respectively. In contrast, to the graphite, there are two new peaks at 1250 cm\(^{-1}\) and 1120 cm\(^{-1}\) which testifies to the presence of oxygen containing functional groups. For the spectrum of RGO-P0-7h, the peaks at 1250 cm\(^{-1}\) and 1120 cm\(^{-1}\) almost disappear due to the removal of the C-O group during the reduction of glucosamine (GL). Some scientists also stated that the some oxide groups are partially reduced in plant extracts. FTIR helps to measure intensity over a narrow range of wavelengths at a time.
By using Raman Spectroscopy the different reduction condition can be known. O.Akhavan et al., [40, 41] stated that due to well known properties of carbon materials in Raman Spectra are the G-band (~1580 cm\(^{-1}\)) relating to the first order scattering of the E\(_{2g}\) phonons of the graphite structure of carbon atoms and the D-band (1350 cm\(^{-1}\)) relating to a breathing mode of K-point phonons of A\(_{1g}\) symmetry which can be assigned to structural defects induced by hydroxyl and epoxide bonds on the carbon surface. The D-band can present decrease in the in-plane sp\(^2\) domain sizes and so formation of sp\(^3\) bonds caused by oxidation [42]. Usually Raman Spectroscopy (HR-800Jobin-Yvon) was carried out at room temperature using an Nd-YAG laser source operating at wavelength of 532 nm. Each and every sample for Raman Spectra was prepared by drop-casting a graphene containing suspension onto the Si substrate followed by heating at 100\(^\circ\)C in air for 30 minutes. In Raman Spectroscopy it is cleared that after reduction of GO, the 2D band is shifted toward higher value which means stacking of graphene layers. Suman Thakur et al.,[38] stated that GO has different types of functional groups which may prevent stacking of graphene layers but after reduction due to decrease of such functional groups a few graphene layers are stacking and formed multilayer RGO.

<table>
<thead>
<tr>
<th>Samples</th>
<th>GO</th>
<th>Hydrazine reduced GO</th>
<th>Green reduced GO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time of reduction(min)</td>
<td>N/A</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Raman(I(_D)/I(_G))</td>
<td>1.22</td>
<td>1.37</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 1: Raman Spectroscopic peaks (Courtesy: O.Akhavan et al. (40))
Thermal stability of material can expose good potential towards high temperature and structural compactness. In thermal analysis of Graphene oxide (GO) and Reduced Graphene Oxide (RGO) it is continued that the half degradation of both of these materials is very important for stability concern. Suman et al., [38] had reported that GO exhibit two stage degradation at different temperature. First degradation occurs at almost 175°C-190°C due to loss of some functional group like hydroxyl, epoxy, and remaining water molecules. Yan Wang et.al.[43] had also reported that at this stage only 12-15% weight loss of GO is observed where as a mass loss of almost 45% observed at a temperature of almost 450°C and this due to the loss of remaining oxygen containing functionalities present in GO. In comparison RGO shows only 8-9% degradation at a temperature of 250°C which is lower than of GO [44]. B.Rartwik et al., had stated that the major weight loss of GO observed due to loss of CO, CO₂ and water vapor and oxidation of residual matter[45]. Higher thermal stability of RGO is due to the smaller amount of oxygen functionalities present in the structure [46].
Zeta potential of Graphene Oxide (GO) and Reduced Graphene Oxide (RGO) has been carried out in a dynamic light scattering instrument to a certain stability of the solution. Tapas Kumar Ghosh et al. [47] stated that GO shows an average zeta potential value of -19.9 ±0.53 mV, indicating the existence of a sufficient amount of negative charge density arising from the carboxylic groups present in GO [48]. The trend of zeta potential data proved that RGO possessed more surface negative change density compared to GO. The chemicals present in the leaf extracts during reduction are absorbed on the surface of RGO as they act as a stabilizing moiety also, leading to more stable dispersions and subsequently higher zeta potential values. Sangiliyandi et al., showed that the size of GO and RGO are almost 1.489 and 0.702 µm respectively. This size reduction proves the removal of oxygen functional groups from the surface of GO successively.

Figure 9: DLS study of GO and RGO at different time intervals (Picture Courtesy: Tapas Kumar Ghosh et al. (47)).

The morphology was studied using Scanned Electron microscopy (SEM) and Transmission Electron microscopy (TEM). Vorrada Loryuenyong et al. [49] were suggested that graphite particles are in the platelet like crystalline form of carbon. After acid oxidation and ultrasonic, graphene oxide sheet is so thin that electron beam can be passed through samples. These samples were shown as SEM and TEM images of RGO. Vorrada Loryuenyong et al., was confirmed the reduced GO exhibits typical wrinkled structure by both SEM and TEM analysis [50,51]. Whereas, Basavaiah Chandu et al. [52] had shown the performance of understanding the morphology of the obtained RGO nanosheets by transmission electron microscopy analysis. The RGO Nanosheets confirm the crystal nature [53]. Another illustration of Mujeeb khan et al., [54] determined the morphology and layer thickness of the RGO by TEM. The TEM images revealed the transparent and sheet like structure of RGO. An enormous number of scrolls and wrinkles were observed the surface of the RGO sheet which remained stable under the high energy electron beam. It has been noticed that the edges of the suspended graphene layers were folded back, and few layer thickness of RGO was observed in the resolution TEM [55]. In further research Tapas Kuila et al., [24] used TEM to access the number of layers at multiple locations where the edges of the suspended graphene films tend to fold back, allowing cross-sectional view of the films. Apart from those researchers many of the scientists like C.A. Amarnath et al., [56] was shown the RGO sheets by TEM analysis. B.Kartick et al., [57] stated that EDX confirmed the presence of about 14.2 atomic % of oxygen in graphene. This could be attributed to the presence of atmospheric oxygen and unreduced functional groups on the surface of graphene platelets. Sangili andi Gurunathan et al., [58] further examined the size of GO and RGO by another morphological analysis Scanned Electron Microscopy. The dispersion were further dropped on aluminum foil and SEM images were taken randomly for each sample. Exfoliation of GO results in flakes which are smaller in size SEM images of GO flakes are hexagonal shape and SEM images revealed that the reduced GO material consists of individual sheets closely associated with each other. For the morphological analysis,
the RGO thin film samples were examined under the SEM. The SEM produces better resolution because of the intensive and monochromatic electronic beam employed. Sadhukhan et al.[59] reported that SEM images of RGO revealed a well separated platelets which are closely associated with each other. B.Kartick et al.,(57) stated that Atomic Force Microscopy(AFM) is regarded as an important tool to characterize graphitic oxide and graphene. According to this, the individual graphitic oxide layers non thickness are well separated from one another [60]. Also, the height profiles of graphene indicate the thickness to be ~2 non suggesting [24].Such stacking tendency in graphene is in all probability due to the absence of any stabilizing agent. In case of binding energy calculation of GO, RGO and graphitic material some researchers enlightened over X-ray photo electron spectroscopy study. Tapas Kuila et al.,[24] stated that XPS of GO shows typical C1s peaks at 284.2, 286.4, 288.3 and 289.4 eV from sp² C, C-O, -C=O and –COOH groups respectively. The XPS of pure graphitic shows very low intense band at 286.3eV corresponding to C-O functionally. This is due to the aerial oxidation of graphite in air. Tapas Kuila et al., [24] suggested that XPS indicates the presences of 69.2% carbon and 30.1% oxygen by atomic concentration in GO [61]. Elemental analysis of RGO shows significant increase of the atomic ratio of C/O in comparison to GO. This is due to the reduction of oxygen functionalities in RGO.

Graphene holds great promise for potential use in next generation electronic and photonic devices due to its unprecedented high carrier mobility, good optical transparency and large surface area [62]. Suman Thakur et al. [38] stated that the graphene opens up the window of novel applications for electronic devices such as touch panels, p-n junction materials flexible thin film transistors and solar cells [63]. Graphene has been used as a reinforcing agent to improve the mechanical properties of bio degradable polymeric nano composites for engineering bone tissue applications [64]. Another possible application is in diseases detection if graphene is found to change shape at the presence of certain diseases markers such as toxins [65]. Graphene’s high electrical conductivity and high optical transparency make it a candidate for transparent conducting electrodes, required for such applications as touch screens, liquid crystal displays, photovoltaic cells and light emitting diodes [66]. Graphene conducts heat better than diamond. As it's two dimensional, it could be used to detect single molecules of gas. In 2009, researchers built experimental graphene frequency multipliers that take an incoming signal of a certain frequency and output at a multiple of that frequency [67]. Graphene strongly interacts with photons, with the potential for direct band-gap creation. This is promising for optoelectronic and nano-photonic devices [68]. Due to extremely high electron mobility, graphene may be used for production of highly sensitive Hall effect-sensors [69]. Scientists discovered using graphene as a lubricant works better than traditionally used graphite [70].
VI. CONCLUSION

In summary, graphene has been prepared by green route involving the reduction of graphite oxide by leaf extract, microorganisms etc which are environmental and eco–friendly reagents. The reaction is carried out in an aqueous medium at room temperature. The reduction of GO is confirmed by XRD, FTIR, UV-Vis, Raman Spectroscopy, TGA, DLS, SEM, AFM, TEM, EDX and XPS. SEM and TEM analysis indicate that the RGO materials are layered and are formed into individual sheets, which are closely aligned with each other. FTIR analysis shows the deoxidization of oxygen functionalities from the surface of GO. Thermo gravimetric analysis confirmed that graphene is thermally more stable compared to graphite oxide. Zeta potential analysis also confirmed lower charge density on the surface of graphene. Graphene obtained through such green routes could be of great importance in a myriad of application, especially in biologically sensitive areas. The main advantages of this technique over traditional chemical reaction are its cost effectiveness, environmentally friendly approach and easy product isolation procedure. These studies may open new possibilities in the sector of the bulk production of graphene in nontoxic way as well as a cost effective one.

REFERENCES


