Chapter 3

Synthesis of Graphene Oxide and Reduced Graphene Oxide
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This chapter describes the synthesis of graphene oxide by Hummer’s method and graphene through chemical reduction. The result shows that graphene oxide and reduced graphene oxide have successfully been synthesized. The thermal properties and morphology of graphene and graphene oxide have been investigated. The dispersibility of graphene oxide and reduced graphene oxide in various solvents has also been discussed.

3.1 Introduction

Graphene and its derivatives have attracted the attention of researchers due to their potential applications in various fields by virtue of excellent mechanical, electrical, thermal and optical properties. A number of methods are reported in the literature for the synthesis of graphene such as micro–mechanical exfoliation, chemical vapor deposition, chemical reduction of graphene oxide (GO) etc. The micro–mechanical exfoliation and chemical vapor deposition produce graphene of high quality with exigent properties but are not suitable for mass production because of poor yield and high cost. The chemical reduction of GO is being intensively researched due to its significant role for the cost effective mass production of graphene–based materials such as reduced graphene oxide (GR). A major advantage of GR is that it is easy to process and integrate it in electronic devices using thin film technique. This is the motivation behind the present work on synthesize of GO and GR using chemical method using graphite.

Selection of precursor

To synthesize GO different chemical used are listed below:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Chemical formula</th>
<th>Purity (%)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite powder</td>
<td>----</td>
<td>99.99</td>
<td>Source of GO</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>NaNO₃</td>
<td>99.0</td>
<td>Enhance oxidation rate</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>H₂SO₄</td>
<td>99.0</td>
<td>Solvent</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>KMnO₄</td>
<td>99</td>
<td>Oxidation agent</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>H₂O₂</td>
<td>30</td>
<td>Remove KMnO₄</td>
</tr>
<tr>
<td>Sodium borohydride</td>
<td>NaBH₄</td>
<td></td>
<td>Reducing agent</td>
</tr>
<tr>
<td>Hydrazine hydrate</td>
<td>N₂H₄</td>
<td>99.0</td>
<td>Reducing agent</td>
</tr>
</tbody>
</table>
Hydrochloric acid (HCl) and DI water was used as washing solvent.

3.2 Synthesis of GO

GO possess hydroxyl (–OH), carboxyl (–COOH) and epoxide functional groups. Hence, it can easily be dissolved into polar solvents. To synthesize GO, initially graphite oxide was prepared through Hummer’s method [1]. However, during synthesis of graphite oxide, it has been observed that operating temperature and stirring time duration affects the composition of oxygen containing functional groups.

To prepare GO, graphite (2 g), NaNO₃ (1 g) were mixed in cooled concentrated sulphuric acid (46 ml) under stirring in ice bath. KMnO₄ (6 g) was gradually added to the above placed mixture with stirring and cooling so that the temperature of mixture was maintained between 10–15°C [1]. The reaction mixture was then stirred at 40°C for 30 minutes to form a thick paste. Subsequently, 80 ml of de–ionized water added to the formed paste, followed by another 90 minutes stirring at 90°C. After that, additional 200 ml water was added to stop the oxidation reaction. Sequentially, 6 ml of 30% H₂O₂ was added in above mixture to remove the excess KMnO₄. The complete removal of KMnO₄ was indicated by change of color into yellow.

![Figure 3.1 Mechanism for the synthesis of GO and GR](image)

The solution was then washed with HCl (10%) to remove sulphate [2]. Subsequently, it was filtered and washed ten times with DI water to obtain graphite oxide. The filtered paste was dissolved in 100 ml of water. The solution was sonicated for 1 hour
to exfoliate the layers (Figure 3.1) and centrifuged for 20 minutes at 4000 rpm. GO powder thus obtained was dried at room temperature. The flow chart for synthesis of GO is given in Figure 3.2.

3.3 Synthesis of reduced graphene oxide

GR was prepared by the reduction of GO with sodium borohydride and hydrazine hydrate. To obtain good quality of GR, reduction process was performed in following two steps:

- Reduction of GO with hydrazine hydrate at 80°C for 1 hour to remove carbonyl and hydroxyl functionality
- Reduction of GO with sodium borohydride to remove the majority of other oxygen functionality.

To obtain GR, the GO (100 mg) was dissolved into 100 ml water followed by addition of hydrazine hydrate (10 µl, 0.2x10⁻³ mol). The reaction mixture was refluxed at 80°C for 1 hour. Hydrazine hydrate reduces oxygen functional groups except carboxyl groups. This selective removal is used to control the reduction of GO and hence their properties. Subsequently, sodium borohydride (1 mg) was added to reduce the carboxyl groups and remaining oxygen functional groups. Then, the mixture was refluxed for different time intervals (12 hours, 24 hours, 36 hours and 48 hours) at 100°C and it was
observed that optimized time for refluxing is 36 hours to get the best result. The flow chart for synthesis of GR is given below:

![Flow chart for synthesis of GR](image)

3.4 Results and discussion

3.4.1 X–Ray diffraction analysis

The crystalline structure was characterized by X-ray diffraction (XPERT-PRO diffractometer (45 kV, 40 mA) equipped with a Giono-meter PW3050/60 working with Cu Kα radiation of wavelength 1.5406 Å in the 2θ range from 5° to 80°). The samples were scanned in continuous mode at the rate of 0.040°/sec. The basic principle of XRD is based on Bragg’s law [3]:

\[ n\lambda = 2d_{hkl}\sin\theta \]  

(equation 3.1)

where \( \lambda \) is the wavelength of the X–ray, \( \theta \) is the scattering angle, \( n \) is an integer representing the order of the diffraction peak, \( d \) is the interplaner distance of the lattices and (hkl) are Miller indices.

Graphite consists of a number of graphene layers, so incident X–rays get scattered from each layer and scattered X–rays from adjacent graphene layer will constructively interfere. The path difference arise by scattering of X–rays from the GR layres that is equal
to integral multiple of the X–ray wavelength (nλ). The GR thickness can be estimated using Sherrer’s equation [3] which is expressed by:

\[ D_{002} = \frac{K \lambda}{\beta \cos \theta} \]  

(equation 3.2)

where \( D_{002} \) is the thickness of crystallite (graphene thickness), \( K \) is a constant dependent on the crystallite shape (0.9), \( \lambda \) is the X–ray wavelength, \( \beta \) is the full width at half maximum (FWHM) and \( \theta \) is the scattering angle.

![Figure 3.4 Bragg’s diffraction planes](image)

The number of GR layers (NGR) can be obtained from Sherrer’s equation (equation 3.2) by considering the parallel arrangement of layers. If parallel arrangement of layers have \( N \) layers, \( D_{002} \) for a parallel layers is defined by [4]:

\[ D_{002} = (N–1) d_{002} \]

Or

\[ N = \frac{D_{002} + d_{002}}{d_{002}} \]  

(equation 3.3)

where \( d_{002} \) is the interlayer distance between the layers.

XRD patterns of graphite, GO and GR are shown in Figure 3.5, diffraction peak of graphite observed at \( 2\theta=26.4^\circ \) could no longer be detected in GO, while the XRD pattern for GO exhibit a strong and sharp peak at \( 2\theta=10.56^\circ \) corresponding to the (002) plane. This indicates the formation of highly oxidized GO sample. Interlayer distance of GO (8.37Å) was greater than graphite (3.36Å). The larger interlayer distance of GO might be due to the formation of oxygen–containing functional groups such as hydroxyl, epoxy and carboxyl in graphite layers [5]. The peak corresponding to GO at \( 2\theta = 10.56^\circ \) is completely disappeared in XRD pattern of GR which is due to the removal of functional groups and indicate
complete deoxygenation of GO and exfoliation to GR. This confirms that the oxygen-containing functional groups of GO could completely be removed by reduction through hydrazine hydrate and sodium borohydrate [6]. The shift in the peak of graphite from 26.4° to 25.11° is due to less number of stacked layers. The number of layers in GO powder estimated using equation 3.3 is equal to two.

Figure 3.5 XRD of graphite, GO and GR

Interlayer distance obtained for graphite, GO and GR are as 3.36 Å, 8.37 Å, 3.54 Å respectively which matches the earlier reported interlayer distance range as 3.348–3.360 Å, ~5–9 Å and ~3.4 Å [8, 10, 11]. The GO has the largest interlayer distance (dGO) because of intercalated water molecules and various oxygen containing functional groups. The interlayer distance of GR (dGR) is slightly greater than the bulk graphite because GR has small number of oxygen functional groups that does not be removed in chemical reduction process. Moreover, due to its 2D structure it has intrinsic distortions [7-9]. Table 3.1 summarize the experimentally obtained peak position, interlayer spacing and FWHM for graphite, GO and GR.

Table 3.1 Peak position, interlayer spacing and FWHM of graphite, GO and GR

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position</th>
<th>d spacing (Å)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>26.4°</td>
<td>3.36</td>
<td>0.108</td>
</tr>
<tr>
<td>GO</td>
<td>10.56°</td>
<td>8.37</td>
<td>0.933</td>
</tr>
<tr>
<td>GR</td>
<td>25.11°</td>
<td>3.54</td>
<td>0.96</td>
</tr>
</tbody>
</table>
3.4.2 FTIR spectroscopy

The type of surface functional groups was studied by Perkin Elmer FTIR model SPETRUM 65 system. Dried solid samples were mixed with KBr powder and were pelletized before performing the scan from wave number 4000 to 400 cm\(^{-1}\). FTIR spectra of the GO and GR, shown in Figure 3.6, confirm the successful oxidation of the graphite. The presence of different types of oxygen functional groups in GO were confirmed by its FTIR spectrum. The peak at 3618 cm\(^{-1}\) (Figure 3.6 (a)) can be attributed to the O–H stretching vibrations of the C–OH groups and water [7] and peak at 1713 cm\(^{-1}\) assigned to C=O stretch and shows that carboxyl groups are situated at the edges of GO sheets. The peak located at 1643 cm\(^{-1}\) was associated with aromatic C=C bonds. Additionally, the peaks at 1273 cm\(^{-1}\) and 1041 cm\(^{-1}\) were ascribed to the stretching vibration of C–OH and C–O–C respectively [12].

\[\text{Figure 3.6 FTIR spectra of (a) GO, (b) GR obtained by reduction of GO}\]

In the spectrum of GR (Figure 3.6 (b)), peaks corresponding to different oxygen functionalities were either disappeared or weakened. Appearance of the peak at 1551 cm\(^{-1}\) corresponds to the C=C stretch verify high degree of reduction of GO. The weak peak at 955 cm\(^{-1}\) arises from C–O stretching vibrations implies the remaining carboxyl groups even
after reduction. The hydrophobic character is confirmed by the disappearance of peak at 1623 cm\(^{-1}\).

**3.4.3 Thermogravimetry analysis (TGA)**

TGA analysis was carried out using Perkin Elmer diamond TG/DTA analyzer. Dried alumina powder was used as a reference material for taking the thermograms. Thermal stability of the Graphite, GO and GR was studied by TGA as shown in Figure 3.7. Thermogravimetry traces of graphite exhibit almost no weight loss during the whole heating process (in the range from room temperature to 800°C).

GO shows low thermal stability as compared to graphite which might be due to larger interlayer spacing of GO (confirmed from XRD results) arises from the reduction of van der Waal interaction between the layers during oxidation reaction. Hence, GO starts to lose mass upon heating even below 100°C due to evaporation of water molecules absorbed by the material.

Significant weight loss of GO (approximately 40%) occurs around 200°C revealed from derivative thermogravimetry curve (DTG) of GO shown in Figure 3.8, presumably due to chemical decomposition of the labile oxygen–containing functional groups such as carboxyl, hydroxyl, carbonyl etc. to yield CO, CO\(_2\) and steam. Above 450°C, there was steady weight loss (about 15%) due to removal of more stable oxygen groups such as epoxy etc.

![Figure 3.7 TGA of graphite, GO and GR](image_url)
The thermal stability get enhanced in GR and major weight loss of about 72% occurs between 350°C to 500°C (Figure 3.7). The higher thermal stability of GR as compared to GO was due to fewer amount of oxygen functional groups but less stable than graphite because some of oxygen containing functional groups are still remaining on it during reduction process.

![Figure 3.8 TGA, DTG curve of GO](image)

### 3.4.4 Raman analysis

Raman spectra were recorded with a Raman microscope (Renishaw inVia), using a 514 nm wavelength laser having 50% power with 2400 l/mm grating focused through an inverted microscope (Leica), via a 20x objective. It is a powerful technique used for the characterization of carbon products, especially the conjugated and carbon–carbon double bonds gives high intensities Raman peaks. The Raman spectrum (Figure 3.9) of the pristine graphite displays a strong G peak at 1582 cm\(^{-1}\) corresponding to tangential G mode of first–order scattering of the \(E_{2g}\) mode (in–phase vibration of the graphite

![Figure 3.9 Raman spectra of graphite, GO and GR](image)
lattice) at the Brillion zone center. A weak D line at 1332 cm\textsuperscript{-1} and the overtone of the D line i.e. 2D line was located at 2695 cm\textsuperscript{-1} [16]. D band arise due to the out–of–plane breathing mode of A\textsubscript{1g} symmetry of the sp\textsuperscript{2} atoms near the K zone boundary. It reveals the presence of defects, whereas 2D band originates from a two phonon double resonance Raman process.

In the Raman spectrum of GO, the G band was broadened and shifted slightly to 1590 cm\textsuperscript{-1}. A possible explanation of this behavior is the presence of isolated double bonds which resonate at higher frequencies. The intensity of the D band at 1347 cm\textsuperscript{-1} increases considerably and the 2D line disappeared. The larger intensity and line width of D band as compared to G band indicates more disorder due to defects arising from strong treatment with chemicals.

In the Raman spectrum of GR, D and G peaks were observed at 1344 cm\textsuperscript{-1} and 1590 cm\textsuperscript{-1}. In addition to it, the 2D peak observed at 2945cm\textsuperscript{-1} shows significant change in the shape as compared to graphite.

It is difficult to measure absolute intensity in Raman spectroscopy, so normalized I\textsubscript{D}/I\textsubscript{G} ratio is used to measure the amount of disorder. Higher value of I\textsubscript{D}/I\textsubscript{G} means more disorder in sample i.e. there is more binding sites in the sample. The I\textsubscript{D}/I\textsubscript{G} ratio of GO is 1.04 whereas it is 0.94 for GR indicates GR has fewer defects and more ordered.

### 3.4.5 Energy dispersive X–ray spectroscopy (EDX) analysis

Element–specific quantification was performed by Energy dispersive X–ray spectroscopy (EDX). Oxford Instruments INCAx–act X–ray detector was used for this purpose. An accelerating voltage and current of 20 kV and 0.34 nA respectively were used. Chemical modifications in GO and GR are revealed by the carbon and oxygen content obtained by EDX measurements shown in Figure 3.10.

Table 3.2 shows that a maximum weight percentage of carbon in GO is 54.27% accompanied by 45.73% of oxygen related to hydroxyl and carbonyl groups. But in GR carbon content increased to 74.83% and that of oxygen reduced to 15.29% which suggests the successful reduction of GO using hydrazine hydrate and sodium borohydrate. It was calculated that in the reduction process oxygen content was decreased by 30.44%.
Table 3.2 Weight% and atomic% of carbon and oxygen in GO and GR

<table>
<thead>
<tr>
<th>Element</th>
<th>GO</th>
<th></th>
<th>GR</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight%</td>
<td>Atomic%</td>
<td>Weight%</td>
<td>Atomic%</td>
</tr>
<tr>
<td>C</td>
<td>54.27</td>
<td>61.25</td>
<td>74.83</td>
<td>84.71</td>
</tr>
<tr>
<td>O</td>
<td>45.73</td>
<td>38.75</td>
<td>25.11</td>
<td>15.29</td>
</tr>
</tbody>
</table>

3.4.6 Morphology of GO and GR

The morphology and structure of GO and GR were investigated through scanning electron microscope (SEM) and transmission electron microscope (TEM). SEM characterization was carried out using JSM-6510LV Series Scanning Electron Microscope having pre centered W hairpin filament (with continuous auto bias). TEM characterization was carried by Morgagni 268D (Fei Electron Optics) having tungsten filament. Figure 3.11 represents the SEM images of GO, revealing a crumpled and rippled structure which was the result of deformation upon the exfoliation and restacking processes. While using TEM observation as shown in Figure 3.12 (a), independent GO nanosheets were observed, which were due to breakage of van der Waal bond between layers in sonication process. These few layer GO nanosheets were flat and larger than 100 nm in width.

TEM image of GR as shown in Figure 3.12 (b) represent two or three layered, folded GR nanosheets with lots of wrinkles. Corrugation and scrolling suggests the intrinsic nature of graphene and prevent thermal fluctuations in it. This makes GR a thermodynamically stable structure [18].
3.4.7 Zeta potential measurement

Zeta potential is a crucial parameter for characterizing the stability of colloidal dispersions. It provides a measure of the magnitude and sign of the effective surface charge associated with the colloid particle [13]. Generally, high value of zeta potential (positive or negative) is considered to form stable dispersions due to inter particle electrostatic repulsion. Zeta potential of GO was measured from Microtrac Nanotrac Wave analyzer based on dynamic light scattering and operate in frequency range of 47-63 Hz with maximum power of 75 Watt.

According to the American Society for Testing and Materials (ASTM) colloidal suspensions having zeta potential below 30 mV (either positive or negative) shows poor
stability, between 30 and 40 mV (either positive or negative) shows moderate stability, higher than 40 mV (either positive or negative) resembles high stability [14].

For GO the observed value of zeta potential in aqueous medium was -69.29 mV which reveals the high dispersion stability of GO. This may be due to the dissociation of a greater number of acidic groups (COOH → COO⁻ + H⁺) at the surface [14]. The negative zeta potential values suggest the presence of electronegative functional groups on GO formed during the oxidation. It was observed that after placing the suspension of GO for 36 hours the zeta potential still have high value equal to -67.36 mV. The value of other parameters like mobility, charge and conductivity of GO is given in Table 3.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobility</td>
<td>5.41 μS/V/cm</td>
</tr>
<tr>
<td>Zeta Potential</td>
<td>-69.29</td>
</tr>
<tr>
<td>Charge</td>
<td>0.354 fC</td>
</tr>
<tr>
<td>Polarity</td>
<td>Negative</td>
</tr>
<tr>
<td>Conductivity</td>
<td>31 μS/cm</td>
</tr>
</tbody>
</table>

Figure 3.13 Particle size distribution of GO

The measured zeta potential of GR was equal to -19.5 mV. The smaller value of zeta potential of GR exhibits its low dispersion behavior in water. The negative zeta potential of GR reveals that some residue oxygen functional groups still remain on the surface of GR.

3.4.8 UV–Vis absorption spectroscopy

UV-Visible spectroscopy was carried out using a LAMBDA™ 650 UV/Vis/NIR spectrometer (Perkin Elmer, Inc., Shelton, CT USA). UV–Vis absorption spectroscopy was employed to confirm the dispersibility of the GO in water. As shown in Figure 3.14 the GO
dispersion exhibited a strong absorption band at 230 nm attributing to $\pi-\pi^*$ transitions of aromatic C–C bonds to $n \rightarrow \pi^*$ transitions of C=O bonds in sp³ hybrid regions [15].

![UV–Visible spectra of GO and GR](image1)

Figure 3.14 UV–Visible spectra of GO and GR

In GR, the aromatic C–C bonds are red shifted to ~265 nm indicating the restoration of a $\pi$–conjugation network. Stability of dispersion of GO in water was studied using time dependent UV–Visible spectroscopy [16]. GO was dispersed in water by sonication for one hour and absorbance spectra was recorded at different time interval up to 36 hours. Figure 3.15 shows the typical UV–Vis absorption spectrum of the GO dispersion as a function of time. The small difference in absorbance of GO with time showed its stability in water over a wide time period.

![Time–dependent UV–Visible curves of GO](image2)

Figure 3.15 Time–dependent UV–Visible curves of GO
3.5 Dispersion studies of GO and GR

The dispersion behavior of GO and GR has been further investigated in seven different organic solvents viz. water, acetone, ethanol, propan–2–ol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and tetrahydrofuran (THF) to a nominal concentration of 0.2 mg/mL. Subsequently, the solution was ultrasonicated for one hour and the dispersions were then allowed to stand for several weeks.

Figure 3.16 and Figure 3.17 show digital images of the dispersions of GO and GR immediately after sonication (top) and after 8 weeks of sonication (bottom) respectively. It was noticed from the just sonicated samples, that GO was dispersed uniformly in all solvents except THF. But many of these solvents display only short term stability and precipitated completely in a matter of hours to a few days. This was the case for acetone, DMF and THF. However, GO has long term stability for water, ethanol, propan–2–ol and DMSO.

GR was poorly dispersed in water, acetone, ethanol, DMSO and THF (Figure 3.17). It is soluble in DMF and slightly soluble in propan–2–ol. It is clear from Figure 3.16 that GO has best dispersing ability in water even after 8 weeks followed by ethanol and propan–2–ol. On the other hand GR has dispersing ability in DMF only.

Figure 3.16 Digital images of GO dispersions in different solvents immediately after sonication (top) and after 8 weeks (bottom)
Figure 3.16 Digital images of GR dispersions in different solvents immediately after sonication (top) and after 8 weeks (bottom)

3.6 Conclusion

GO was synthesized successfully by modified Hummer’s method and then it was reduced using hydrazine hydrate and sodium borohydride. The various characterizations confirm the success of chemical method in preparation of GO and GR. From XRD study it is logical to assume that the interlayer distance order is $d_{\text{GO}} > d_{\text{GR}} > d_{\text{graphite}}$. The presence of different oxygen containing functional groups was confirmed by FTIR. The prepared GR has lesser amount of oxygen content as compared to GO. Dispersion studies revealed that GO has long term stability in water, ethanol and propan–2–ol.
References