

## Graphene Oxide Synthesized by using Modified Hummers Approach

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**Abstract:** The graphite oxide was prepared by oxidizing purified natural flake graphite via modified Hummers method. The graphene oxide was prepared by graphite oxide exfoliating in distilled water with ultrasonic waves. Structural and physiochemical properties of the products were investigated with the help of ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). UV-vis spectra of GO exhibit maximum absorption peak at ~237 nm attributable to  $\pi$ - $\pi^*$  transition of the atomic C-C bonds. The results of FT-IR and Raman showed that graphite oxidized by strong oxidants caused the oxygen atoms introduced into the graphite layer and formed C=O, C-H, COOH and C-O-C chemical bond with graphene. The XRD results showed  $2\theta$  of  $12.02^\circ$  with inter layer spacing equal to 0.77 nm. SEM images demonstrate ultrathin and homogeneous graphene films. Electrochemical behavior of GO modified glassy carbon electrode investigated with reference to  $K_3FeCN_6$  redox system and results reflect that electrochemical behavior is controlled by the electron transfer.

**Keywords:** Graphene oxide, Characterization, spectroscopy, Electrochemical

### 1. Introduction

Carbon nanostructures have been extensively studied due to their excellent properties and numerous applications [1-2]. Single-layer transferable graphene nano-sheets were first obtained by mechanical exfoliation ("Scotch-tape" method) of bulk graphite [3] and by epitaxial chemical vapor deposition [4]. These routes though preferred for precise device assembly, they are less effective for large-scale manufacturing. Chemical means are a practical approach for bulk-scale synthesis of graphene materials [5]. The most common approach to words graphite exfoliation is the use of strong oxidizing agents to obtained graphene oxide (GO), a nonconductive hydrophilic carbon material [6-7]. Although the exact structure of GO is difficult to determine, it is clear that for GO the previously contiguous aromatic lattice of graphene is interrupted by epoxides, alcohols, ketone carbonyls, and carboxylic groups [8-9]. The interruption of the lattice is reflected by an increase in interlayer spacing from 0.335 nm for graphite to more than 0.625 nm for GO [10]. Brodie first demonstrated the synthesis of GO in 1859 by adding a portion of potassium chlorate to a slurry of graphite in fuming nitric acid [11]. In 1898, Staudenmaier improved on this protocol by using mixture of concentrated sulfuric acid and fuming nitric acid followed by gradual addition of chlorate to the reaction mixture. This small change in the procedure provided a simple protocol for the production of highly oxidized GO [12]. In 1958, Hummers reported an alternative method for the synthesis of graphene oxide by using  $KMnO_4$  and  $NaNO_3$  in concentrated  $H_2SO_4$  [13]. GO prepared by this method could be used for preparing large graphitic film [14].

In the present paper, attempts have been made to synthesize graphene oxide with few layers by modifying the hummer's methods.

### 2. Experimental

#### 2.1. Chemicals and reagents

Graphite powder,  $H_2SO_4$ ,  $NaNO_3$ ,  $NaOH$ ,  $H_2O_2$  (30%),  $K_3Fe(CN)_6$  and  $KMnO_4$  were purchased from Sigma-Aldrich (USA). All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in Milli-Q water ( $18\text{ M}\Omega\text{ cm}^{-1}$ ).

#### 2.2. Instrumentation

Solutions were sonicated using an IMECO 34 KHz frequency, 500 W sonicator. The cyclic voltammetric (CV) measurements were performed on CHI 1100 Electrochemical Analyzer using a conventional three electrode system. All the electrochemical measurements were carried out in an air-tight borosilicate jacket glass cell with B-14 standard glass joints to fix the electrodes. The electrochemical cell consisted of a glassy carbon (GC) electrode (3 mm diameter) modified with GO and rGO as working electrode,  $Ag/AgCl$  /sat.  $KCl$  as a reference electrode and Pt as a counter electrode. For measurement of resistance, pellets of the samples ( $1\text{ cm}^2$  and  $500\text{ }\mu\text{m}$  in thickness) were prepared by placing 50 mg of each powder between two iron plates of a die and compressed at a pressure of 78 KN.

#### 2.3. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized from graphite powder using modified Hummer's method. In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid under constant stirring. After 1 h, 3 g

of  $\text{KMnO}_4$  was added gradually to the above solution while keeping the temperature less than  $20^\circ\text{C}$  to prevent overheating and explosion. The mixture was stirred at  $35^\circ\text{C}$  for 12 h and the resulting solution was diluted by adding 500 ml of water under vigorous stirring. To ensure the completion of reaction with  $\text{KMnO}_4$ , the suspension was further treated with 30%  $\text{H}_2\text{O}_2$  solution (5 ml). The resulting mixture was washed with HCl and  $\text{H}_2\text{O}$  respectively, followed by filtration and drying, graphene oxide sheets were thus obtained.

#### 2. 4. Preparation of electrodes

GC electrode (3.0 mm diameter) was polished with alumina nano-powder and rinsed with Milli-Q water. Fresh dispersion of sample (GO) were prepared for each experiment by dispersing 1.0 mg of each sample in 1.0 mL of Milli-Q water under sonication. From this, 10  $\mu\text{L}$  of solution was drop-casted on the pre-cleaned GC disk electrode and dried under vacuum at room temperature. Bare GC and GC modified with GO were used for the electrochemical measurements.

#### 2. 5. Characterization techniques

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Thermo Scientific NICOLET 6700 spectrophotometer using KBr as the mulling agent. Ultraviolet-Visible (UV-Vis) spectra of the samples were collected on a UV-Vis spectrophotometer (Perkin-Elmer LAMBDA 950). Photoluminescence (PL) spectra of the samples were recorded on a spectrofluorometer (JASCO, FP8300), and X-ray diffraction analysis (XRD) of powders were carried out on Bruker AXSD-8 Advance X-ray diffractometer with monochromatic  $\text{CuK}\alpha$ , radiation ( $\lambda=1.5406 \text{ \AA}$ ). Data were collected from  $10^\circ$  to  $60^\circ$  at a scan rate of  $0.1^\circ \text{ min}^{-1}$ . The morphologies of the samples were observed under scanning electron microscope (SEM, JEOL JSM-6360). Raman spectra of the samples were recorded by Horiba JobinYvon, France at  $\lambda=532 \text{ nm}$  laser power 1.7 mW, 100 x objective lens, 0.9 NA.

### 3. Results and discussion

Synthesis of graphene oxide was achieved by placing graphite in concentrated acid in the presence of an oxidizing agent. Hummer's method demonstrated a less hazardous and more efficient method for graphite oxidation. This and its modified versions are presently the most commonly used methods for the oxidation of graphite [15-17]. Individual sheets of GO can be viewed as graphene decorated with oxygen functional groups on both sides of the plane and around the edges as described by Lerf et al [18-19]. Due to ionization of carboxyl groups, which are

primarily present at the edges of sheet, GO can be electrostatically stabilized to form a colloidal suspension [20] in water, alcohols, and certain organic solvents [21-22] without surfactants. Exfoliation of graphite oxide into individual sheets can be facilitated by ultrasonic agitation or rapid heating [23-24] but excessive ultra-sonication can result in the decrease of lateral dimensions [25]. Oxidation of graphite results in a brown-colored viscous slurry, which include graphite oxide and exfoliated sheets along with non-oxidized graphitic particles and residue of the oxidizing agents in the reaction mixture. After repeated centrifugation, sedimentation, or dialysis, salts and ions from the oxidation process can be removed from GO suspensions [26]. To achieve a suspension of monolayer GO, non-oxidized graphitic particles and thick graphite oxide platelets are precipitated out by further centrifugation. Suspensions of GO flakes that are mono-dispersed according to their lateral size can also be obtained by density-gradient centrifugation [25].

From the Fig.1a, it is observed that graphene oxide (GO) shows maximum absorption peak at  $\sim 237 \text{ nm}$  attributable to  $\pi\text{-}\pi^*$  transition of the atomic C-C bonds and shoulder peak at  $\sim 300 \text{ nm}$  due to  $n\text{-}\pi^*$  transitions of aromatic C-C bonds [27].

The FTIR spectrum of GO (Fig.1.b) shows a broad peak between  $3000\text{--}3700 \text{ cm}^{-1}$  in the high frequency area together with a sharp peak at  $1635 \text{ cm}^{-1}$  corresponding to the stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide. Therefore, it can be concluded that the sample has strong hydrophilicity. The absorption peaks at  $2930 \text{ cm}^{-1}$  and  $2850 \text{ cm}^{-1}$  are represent the symmetric and anti-symmetric stretching vibrations of  $\text{CH}_2$ , while the presence of two absorption peaks observed in the medium frequency area, at  $1630 \text{ cm}^{-1}$  and  $740 \text{ cm}^{-1}$  can be attributed to the stretching vibration of C=C and C=O of carboxylic acid and carbonyl groups present at the edges of graphene oxide [28]. Finally, the absorption peaks at  $1385 \text{ cm}^{-1}$  and  $1110 \text{ cm}^{-1}$  are correspond to the stretching vibration of C-O of carboxylic acid and C-OH of alcohol, respectively. The presence of these oxygen-containing groups reveals that the graphite has been oxidized. The polar groups, especially the surface hydroxyl groups, result in the formation of hydrogen bonds between graphite and water molecules; this further explains the hydrophilic nature of graphene oxide.

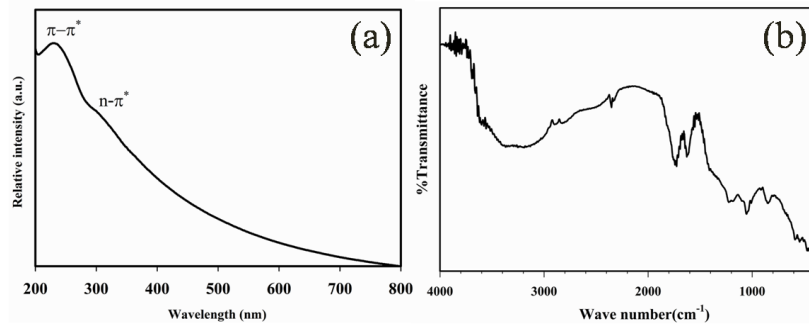


Fig.1. (a) UV-Vis spectrum and (b) FTIR spectrum of graphene oxide

Figure 2.a shows the X-ray diffraction pattern (XRD) of GO synthesized by modified Hummer's method, the sharp diffraction peak observed at  $2\theta = 12.02^\circ$  with an interlayer distance of 0.77 nm corresponds to

GO [29]. The stacking height and the number of layers is found to be 9.1 nm and ~12 respectively as calculated by scherrer equation and d-spacing for the synthesized graphene oxide.

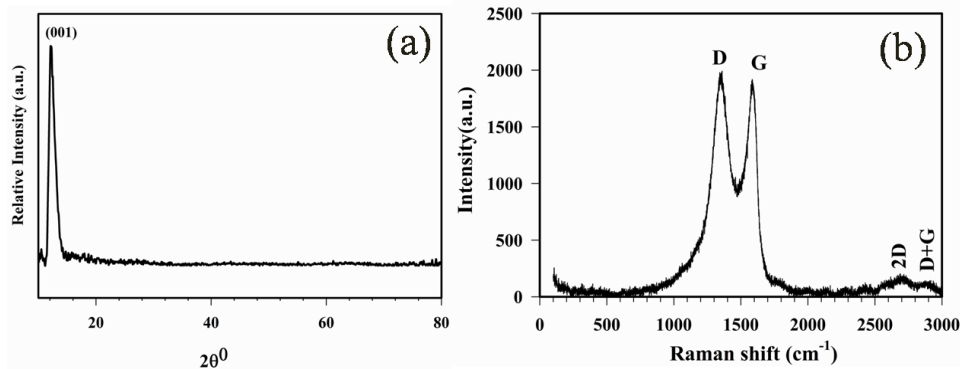


Fig.2. (a) X-ray pattern and (b) Raman spectrum of graphene oxide

Raman spectroscopy is a non-destructive technique that is widely used to obtain structural information about carbon-based materials [30]. The main features in the Raman spectra of graphitic carbon-based materials are the G and D peaks and their overtones. The first-order G and D peaks, both arising from the vibrations of  $sp^2$  carbon, appear at around  $1580\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$ , respectively. The G peak corresponds to the optical  $E_{2g}$  phonons at the Brillouin zone center resulting from the bond stretching of  $sp^2$  carbon pairs in both, rings and chains. The D peak represents the breathing mode of aromatic rings arising due to the defect in the sample [31]. The D-peak intensity is therefore often used as a measure for the degree of disorder [30]. The shift and shape of the overtone of the D peak, called as 2D peak around  $2680\text{ cm}^{-1}$ , can be correlated to the number of graphene layers (N) [32-33]. The 2D peak is attributed to double resonance transitions resulting in the production of two phonons with opposite momentum. Further, unlike the D peak, which is Raman active only in presence of defects, the 2D peak is active even in the absence of any defects. Typical Raman spectrum of GO obtained at an excitation wavelength of  $532\text{ nm}$  is shown in Fig .2b The prominent D peak at  $\sim 1348\text{ cm}^{-1}$  with an intensity

comparable to the G peak  $\sim 1592\text{ cm}^{-1}$  along with their large band width are indicative of significant structural disorder in GO. Weak and broad 2D peaks are another indication of disorder. A defect-activated peak called D+G is also readily visible near  $2950\text{ cm}^{-1}$  [34].

The SEM micrographs of synthesized GO with different scale bars are given in Fig.3. From the figure, it can be observed that graphene oxide has layered structure, which affords ultrathin and homogeneous graphene films. Such films are folded or continuous at times and it is possible to distinguish the edges of individual sheets, including kinked and wrinkled areas.

The PL spectrum of GO recorded by using an excitation wavelength of  $240\text{ nm}$  is shown in Fig. 4. The emission peak at  $307\text{ nm}$  is due to the oxidation of graphite and formation of crystalline graphitic  $sp^2$  in graphene oxide. Additionally, a strong peak at  $\sim 470\text{ nm}$  is attributable to the  $\pi-\pi^*$  transitions of GO. The remarkable sharp emission peak at  $\sim 567\text{ nm}$  (visible range) in GO arise due to the CO, C=O and O=C-OH functionalized groups present on the GO.

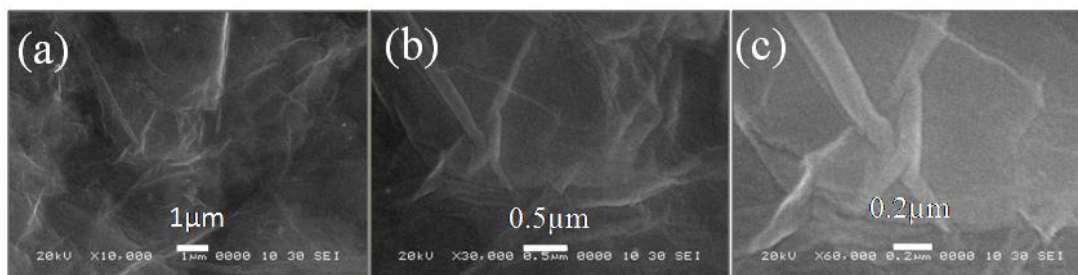


Fig.3. SEM micrograph of graphene oxide (a) 1  $\mu\text{m}$ , (b) 0.5  $\mu\text{m}$ , and (c) 0.2  $\mu\text{m}$

The conductivity of GO was determined by measuring the electrical resistance of the sample which was found to be  $\sim 600 \text{ k}\Omega$ .

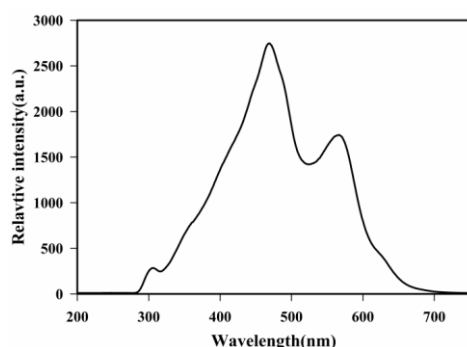


Fig. 1. PL spectra of GO was recorded using an excitation wavelength of 240 nm.

### 3. 2. Electrochemical studies

Carbon-based materials such as glassy carbon, graphite, fullerene and doped-diamond, with different electronic and structural properties, have been shown to have different electrochemical properties [35]. A relation between structure, morphology and electrochemical reactivity has been established and therefore it can be predicted that different structural forms of carbon nanomaterials will exhibit different electrochemical behavior. The electrochemical behavior of the synthesized GO was determined by recording the cyclic voltammograms of GO modified GC electrode, in presence of  $\text{K}_3\text{Fe}(\text{CN})_6$ . This redox couple was chosen due to its sensitivity to the surface chemistry and microstructure as well as the density of electronic states near the Fermi potential [36].

Two main features to analyses in a cyclic voltammograms are the peak current and the peak separation. The first can give insight on the macroscopic electroactive surface and the second one provides a measure of heterogeneous reaction rate constant.

The electrochemical response of GO modified GC electrode as a function of scan rate illustrate in the Fig.5. In the investigated scan range, The  $I_p$  varies linearly with the square root of the scan rate (Fig.5.inset), and the peak separation becomes larger with increasing scan rate. These results reflect and

electrochemical behavior is controlled by the electron transfer.

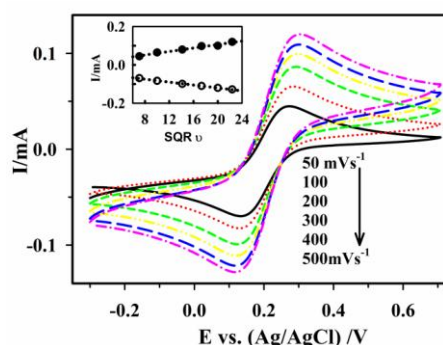


Fig.5. The cyclic voltammograms of samples recorded on GO modified GC electrode in 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  +1.0 M KCl solution vs. Ag/AgCl reference electrode at different scan rate ranging from 50 to 500  $\text{mVs}^{-1}$ . Fig inset is plot of  $I_p$  (oxidation and reduction peak) vs. square root of scan rate.

### 4. Conclusion

The graphene oxide was prepared by oxidizing purified natural flake graphite via modified Hummer's method. UV-vis spectrum of GO exhibits maximum absorption peak at  $\sim 237 \text{ nm}$  attributed to  $\pi$ - $\pi^*$  transitions of the C-C bonds. The results of FT-IR and Raman spectroscopy show that the graphite is oxidized by strong oxidants and the oxygen atoms are introduced into the graphite layers forming C=O, C-H, COOH and C-O-C bonds with graphene. The XRD results show  $2\theta$  of  $12.2^\circ$  with inter layer spacing equal to 7.26 nm. SEM images demonstrate ultrathin and homogeneous graphene films. Electrochemical behavior of GO modified glassy carbon electrode investigated with reference to  $\text{K}_3\text{Fe}(\text{CN})_6$  redox system reflect that the electrochemical behavior is controlled by the electron transfer.

### Acknowledgements

The authors acknowledge financial supports provided by Department of Chemistry, University of Pune. CNQS, Department of Physics University of Pune for XRD, SEM, FTIR facilities, Prof. Pavankumar, IISER, Pune for Raman spectra.

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