

Synthesis & Structural Study on Graphene Nano Particles

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Abstract: Graphene is one atom thick planar sheet of carbon atoms densely packed in a honey comb structure is the first stable two-dimensional crystal lattice in nature, has grabbed appreciable attention due to its exceptional electronic, mechanical, electrical, optical, thermal and opt-electronic properties. Advancement of research in graphene, in the area of synthesis, properties and applications due to its wide range of applications in gas sensor, touch screen, magnetic, catalyst and electronic devices. In this present paper, we report on the synthesis of Graphene Oxide, Graphene by a simple hydrothermal chemical co-precipitation (modified Hummers) method. Graphene oxide was effectively prepared by above process possesses different types of oxygen functionalities which allows GO to interact with organic and inorganic materials in covalent, non covalent or ionic manner. The GO was reduced by hydrazine hydrate as reducing agents to obtain graphene as end product. The prepared samples were characterized by X-ray diffraction (XRD), Raman, FT-IR, UV, Scanning Electron Microscopy (SEM) were reported.

Key Words: Graphene Oxide, Graphene, Raman, FTIR and SEM.

1. INTRODUCTION

Graphene consists of a single atomic layer of sp^2 hybridized carbon atoms that result in a hexagonal lattice. It is the basic building block for all sp^2 graphitic materials including fullerenes, carbon nano tubes, and graphite [1] has revolutionized the scientific frontiers in nano science, engineering technology and condensed matter physics due to its intrinsic and extrinsic physical and chemical properties [2]. Graphene and Graphene Oxide layers have been actively investigated and synthesized to build new novel materials. Around each carbon atom, three strong σ bonds are established with the other three surrounding carbon atoms, according to tight-binding, the valence and conduction bands touch at the Brillouin zone thus making graphene a zero band gap semiconductor [3]. Graphene, exhibits exceptional electronic, optical, magnetic, thermal and mechanical properties, including high values of its Young's modulus (1100GPa)[4], fracture strength (125GPa), [4] thermal conductivity ($5000Wm^{-1}K^{-1}$)[5], mobility of charge carriers ($200000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), [6] specific surface area (calculated value, $2630\text{ m}^2\text{g}^{-1}$), [7] high chemical stability and high optical transmittance, quantum Hall effect at room temperature[8-10] and a tunable band gap. These novel materials have great potential applications such as electrochemical, energy storage, cell imaging, drug delivers and biosensors.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of Graphene Oxide

Graphene Oxide was prepared from natural graphite powder by the modified Hummer's method [11]. 2g of Graphite powder and 1g of $NaNO_3$ were taken in a 1L flask kept at 0°C and 46ml of Conc. H_2SO_4 was poured slowly under continuous stirring. Then 6g of $KMnO_4$ was slowly added and temperature of the mixture was maintained at 25°C . Then the solution is stirred for 2h, after that 92 ml of water was slowly dripped into the

solution and stirred at 35°C for another 1hr. Adding 280 ml of water causes an increase in temperature to 100°C . Then, it was further treated with H_2O_2 (30%, 5 ml) after which the color of suspension changes to greenish yellow. The solution is washed 5 to 7 times with 5% warm solution of HCl and 250 ml of deionised water. The solution is filtered several times to get a fine black paste. Finally, the black paste is dried in oven for 24hrs at 80°C . Pure fine nano particles of black powder are obtained as Graphene Oxide.

2.2. Synthesis of Graphene

For the synthesis of Graphene, 1:5 ratios of hydrazine hydrate and deionised water solution is added slowly drop by drop to 1:1 ratio of Graphene Oxide and deionised water solution and the reaction is kept at 100°C for 3 hours under continuous magnetic stirrer and after that the solution is thoroughly washed with water and filtered. A dark black paste is collected and then the mixture is dried in oven for 24hrs at 80°C , a fine pure black soft and smooth powder particles are obtained as Graphene.

3. RESULT AND DISCUSSION

3.1. XRD analysis

The XRD studies were carried out for the Graphene Oxide which shows a major peak at 12.9° for corresponding (002) plane shown in fig.1 (b) with a "d" spacing of 6.87Å with the particle size of 13nm [12]. For Graphene, the predominant peaks are observed at 26.6° for (002) and 43° for (100) planes are shown in fig.1 (d) with an average particle size of 8.3 nm [4] for a "d" spacing of 3.34Å and 2.10Å . When Graphene Oxide is annealed at different temperatures, an intermediate stage of Graphene and Graphene Oxide known as reduced Graphene Oxide is also shown in fig.1(c) which has a peak value of 24.6° for (002) and 43.6° for (100) with a "d" spacing of 3.60Å and 2.07Å for an average particles size of 10.5 nm [13]. The pristine graphite crystal shows major peaks at 26.46° for (002) with "d" spacing of 3.36Å and other peaks are also illustrated in fig.1.(a)

having an average particles size of 18.9 nm. The particle size, dislocation density and strain constraints of the synthesized materials are calculated from XRD analysis for graphite, graphene oxide, reduced graphene oxide and graphene are given in table. 1

Table 1. Calculations of Particle size, Dislocation Density and Micro strain for graphite, graphene oxide, reduced graphene oxide and graphene

Materials	2θ	FWHM	Particle Size(nm)	Dislocation density 10^{15} lines m^{-2}	Micro strain 10^{-3} line m^{-4}
GO	12.9	0.6	13.0	5.62	2.60
RGO	24.6	0.6	13.0	0.14	4.24
	43.6	1	8.5	0.13	4.04
G	26.6	1	8.1	0.14	4.24
	43	1	8.5	0.13	4.05
GR	26.4	0.34	23.0	1.81	1.44

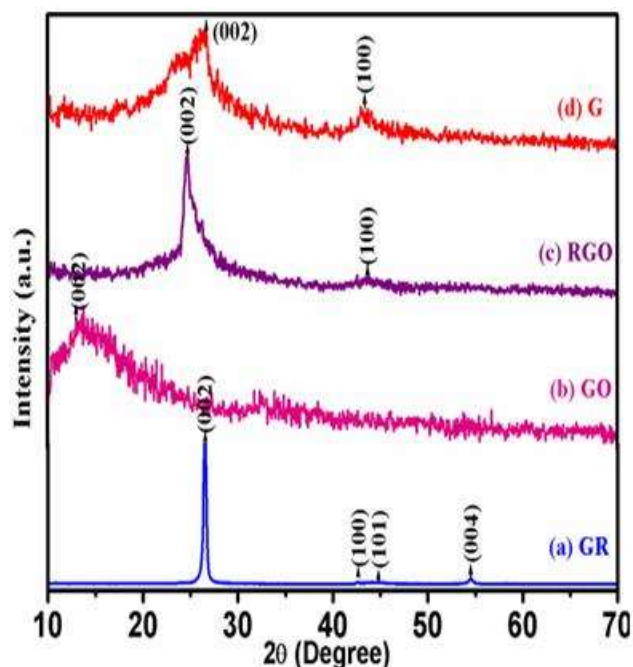


Figure. 1 The XRD patterns of (a) Graphite, (b) Graphene Oxide, (c) Reduced Graphene Oxide and (d) Graphene

3.2 RAMAN SPECTROSCOPY

The Raman spectrum of the pristine graphite, as expected, displays a prominent G peak at 1577 cm^{-1} corresponding to the first order scattering of the E_{2g} mode and D peak at 1351 cm^{-1} due to the presence of minimum number of sp^2 hybridization atoms stacking in basal plane of sub lattice crystalline in nature. In addition to the G and D bands, another peak appears at 2701 cm^{-1} is called 2D band. It arises due to the pure existing nature of sp^2 hybrid orbital stacked well in single layer structure of lattice arrangement depending upon the overlap of neighbouring atoms.

Graphene Oxide contains a G peak is the result of plane optical vibrations is due to first order resonance. It is also found that G band is broadened and shifted to 1572 cm^{-1} [60]. In addition, the D band is observed at 1336 cm^{-1} becomes prominent, is indicating the reduction in size of the plane sp^2 domains, possibly due to the extensive oxidation [14]. Similarly, we observe the major peaks of G and D bands for the graphene at 1336 cm^{-1} and 1572 cm^{-1} indicating the high purity of carbon compound existing in singular layers stacking. This change suggests a decrease in the average size of the sp^2 domains upon reduction of the exfoliated GO, and can be explained, if new graphitic domains were created that are smaller in size which are present in GO before reduction and also more numerous sp^2 domains are absorbed in number.

A small wide hump is also observed in the region of 2D in between 2600 to 2900 cm^{-1} which shows the presence of high crystalline single layers of graphene, but the extent of layers formed are less in quantity. The value of I_D/I_G ratio decreases from graphene oxide to graphene is shown in fig 2. (c). The G and D bands for pristine graphite is also given in (fig2. (a)).

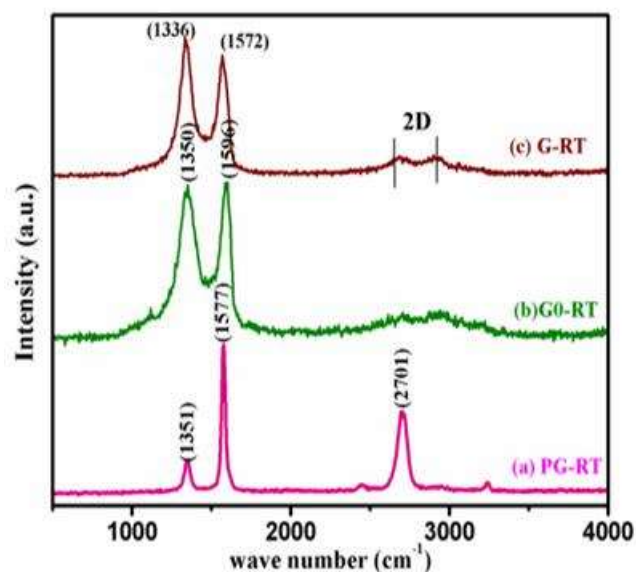


Figure 2. G and D bands of (a) graphite (b) GO and (c) G

3.3. FTIR analysis

FTIR analysis for Graphite gives a strong and broad absorption peaks at 1134 cm^{-1} (C-O (alkoxy)), 1207 cm^{-1} (C-O (epoxy)), 1398 cm^{-1} (C-O (tertiary)), 1535 cm^{-1} (C=C (aromatics)) skeletal vibrations; 1730 cm^{-1} (C=O (carbonyl/carboxyl)) stretching vibrations, 3147 cm^{-1} and 3431 cm^{-1} due to O-H stretching vibration. These absorptions indicate the presence of all carbon Π and σ bonding nature and structural stacking of K and K'¹[15].

For the Graphene Oxide, the functional groups are observed at 1076 cm^{-1} C-O (alkoxy/alkoids), 1135 cm^{-1} and 1555 cm^{-1} C=C (skeletal vibrations), 1633 cm^{-1} C-O bonding (skeletal vibration); 1731 cm^{-1} C=O (stretching vibration); and 3336 cm^{-1} at O-H (Stretching vibration), as the graphite converts to graphene oxide. Some of the major functional group remains as of graphite, but new vibration of stretching modes and bending are formed due to high hydrophilic in nature due to the removal of oxygen functional group [16]

The functional groups of graphene are observed a broad and high strength absorption at 1066 cm^{-1} (C-O(alkoxy)), 1205 cm^{-1} (C-O (epoxy)) ; 1399 cm^{-1} (C-O (carboxy)); 1715 cm^{-1} (C=O (carbonyl/carboxy) stretching vibrations) and 3132 cm^{-1} (attributes to O-H stretching vibration) are due to reduction of graphene oxide on thermal treatment makes the removal of some oxygen functional group and some loose bonding of Π and σ due to thermal effect and only the main carbon/carboxy functional group shows the existing of graphite in nature in singular plane sheet are shown in the fig 3.

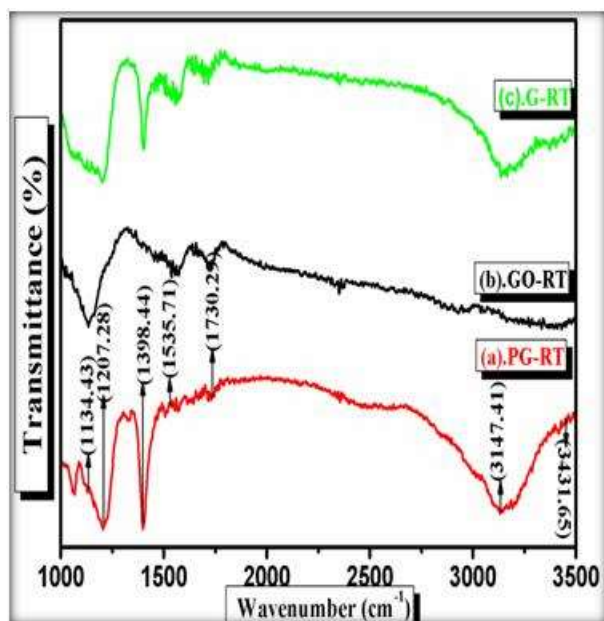


Figure 3: FTIR (a) Pure graphite (b) Graphene Oxide and (c) Graphene

3.4. UV analysis

The absorption spectra of GO dispersion exhibits a maximum absorption peak at about 216 nm corresponding to $\pi\text{-}\pi^*$ transition of aromatic C-C bonds and shoulder at about 230 nm ascribed to $n\text{-}\pi^*$ transitions of C-O bonds. The absorption peak for reduced GO is red shifted to 260 nm are also observed for higher annealed sample. The UV-Vis absorbance spectrum of the GO shows a higher transmittance of about 90 to 95%. Due to oxidation of graphite by chemical synthesis which makes the randomly arranged sp^2 hybrids planes into a regular periodic orientation of the respective indices create a shift in band level. Hence, it gives the change in absorbance and transmission of light from pristine graphite. This phenomenon of red shift has been used as a monitoring tool for the reduction of GO [16].

After reduction (blue shift), the aromatic C-O bonds red shift to 196 nm and 212 nm indicating the restoration of a π -conjugation network within Graphene sheets which indicates the uniformity of sp^2 hybridization is well defined mono layer crystalline in nature. The graphene absorption shows at lower level absorption of 2 to 5% and higher rate of transmission up to 98 to 95% are due to single crystalline nature of sp^2 atomic stacking in major planes with same orientation resulting in high uniformity. The corresponding peak values are observed at 196 nm and 212 nm. The optical transmission of graphene is found to 97% confirmed by theoretical and other experimental values which are matches with the result showing a high transmittance are shown in the fig 4.

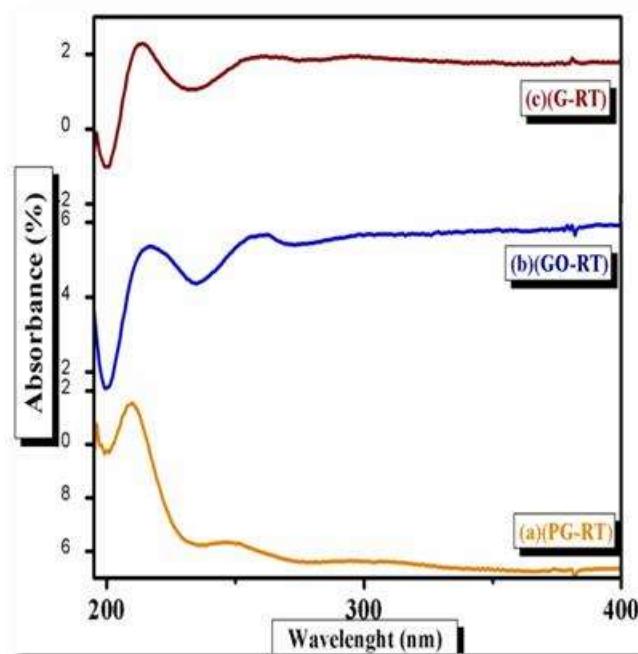


Figure 4: (a) Pure graphite (b) Graphene Oxide and (c) Graphene

3.5. SEM

Scanning Electron Microscopy images confirm morphological study of synthesized particles as a crumpled paper like structure which resembles in buds and flowers in nature for both Graphene Oxide Fig. 5(a)) and Graphene (Fig.5. (b)). It resembles like jasmine flower in nature [11].

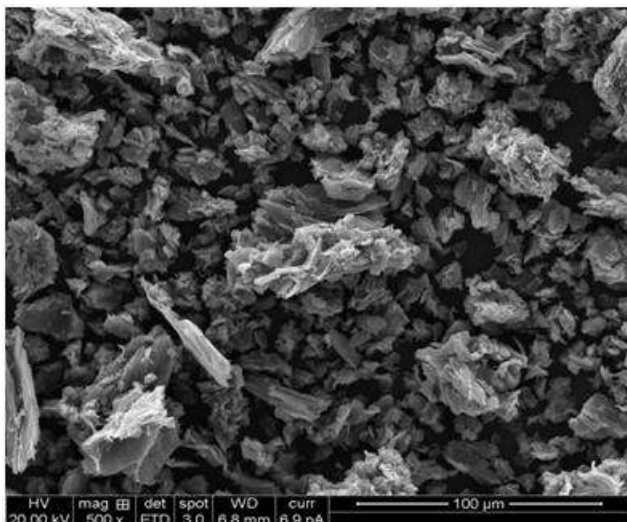


Fig 5(a) : SEM image of Graphene Oxide

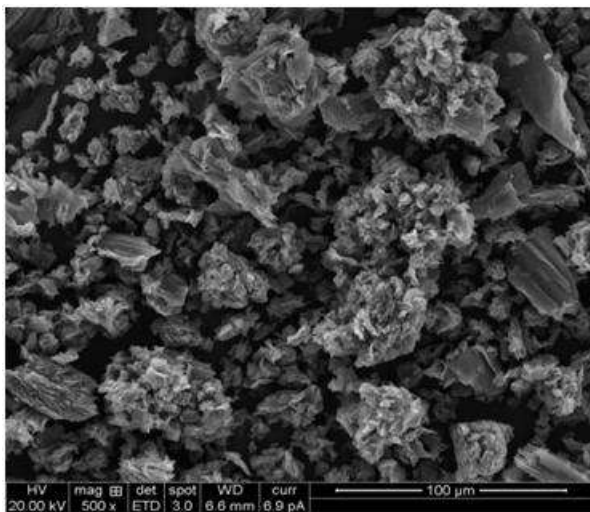


Fig 5(b): SEM image of Graphene nano particles.

4. CONCLUSION

The synthesized materials show the existence of very small particle with low crystalline for Graphene Oxide, Reduced Graphene Oxide and Graphene are confirmed from XRD data. The level of purity of carbon atoms and the absence of impurities are clearly stated by Raman. The functional analysis of the materials are characterized by the FTIR which shows the presence main compound of carbon, oxygen corresponding structural formation and bending of atomic orientations are obtained in well define high quality in manner. The optical and transmittance of the materials is characterized by the UV

spectrum which gives the indication of transmission of graphene at a good level. SEM images reveal the clear structural formation for the lower size nano particle. Finally, the graphene powder shows good properties for catalysts and ultra capacitors.

5. REFERENCES

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