Review of Research

STRUCTURAL, FUNCTIONAL AND OPTICAL INVESTIGATION OF CHEMICALLY PREPARED GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE FROM NATURAL GRAPHITE

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ABSTRACT:
In the present article successfully prepared the Graphene oxide from natural graphite powder via Hummers-Offman's methodand further it reduced through chemical reduction method for forming the reduced graphene oxide. Afterthat, their structural, functional, and optical properties has been investigated through XRD, FT-IR and UV-Visible spectroscopy measurements. XRD confirms the broadening of the sharp peak of GO after reduction. FT-IR spectra confirms the reduction of the excess functional moieties present in the GO. UV-Visible spectroscopy measurements successfully confirms the shifting of the absorption band after the reduction process.

Keywords : *natural graphite powder , structural, functional.*

1.0 INTRODUCTION
Graphene is the few layers of two dimensional sheet of sp^2-bonded carbon atoms arranged in a honeycomb crystal lattice [1]. Also, the intrinsic graphene is zero band gap semiconducting material it has high electron mobility, huge specific surface area to volume ratio, high mechanical strength, good chemical stability, high conductivity and optical transparency, high sensitivity to electrical perturbations etc.[2-5]. Due to these unique physiochemical and electrical properties make it an ideal choice for various potential applications viz. energy conversion and storage devices, used as a photoactive material for environmental remediation, acts as a supportive material for organic transportation, and used in various photo-electronic devices such as touch panels, p–n junction, flexible thin-film transistors. Also, the other applications of graphene and graphene-based materials are field emitters,hydrogen storage, supercapacitors, gas sensors, and bio-sensors have also been reported[6-9].To meet the demand, large-scale production of graphene is required. Hence, in literature it is seen that, several methods has been deployed for the synthesis of graphene and graphene based materials such as chemical vapour deposition, plasma-enhanced chemical vapour deposition, epitaxial growth on electrically insulating surfaces, electric arc discharge, and solution-based chemical oxidation–reduction have been developed to produce graphene [10,11]. Among these reported techniques, the most promising method for the large-scale production of graphene is the chemical oxidation of graphite for the conversion of the resulting graphite to graphene oxide [12]. However, the surface of GO bears different oxygen-containing functional groups such as carboxyl, hydroxyl, epoxy, and keto groups, which make graphene oxide hydrophilic and insulating in nature. Hence to enhance its conductivity the subsequent reduction of graphene oxide for forming the reduced graphene oxide through suitable reducing agents [13].

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Hence in the present investigation our intent for the ease fabrication of graphene oxide through simple, ease chemical method and thereafter it reduced through chemical reduction method for forming the highly conducting reduced graphene oxide. Thereafter, the structural, functional, and optical properties of the graphene oxide and reduced graphene oxide has been successfully demonstrated through few spectral studies.

EXPERIMENTAL:
Materials:

Natural Graphite powder (<20 um, synthetic), were purchased from Sigma-Aldrich. Other all the necessary chemicals are of analytical grade (AR) and used directly without any purification.

Synthesis of Graphene Oxide (GO):

GO was prepared by using modified Hummers-Offeman method with slight modifications. Particularly, calculated amount of the natural graphite and sodium nitrate were added into the beaker containing cooled conc. H_2SO_4 with constant stirring. Then appropriate amount of $KMnO_4$ is grinded and slowly adding to the above solution with stirringand cooling. Afterthat, whole mixture was stirred for half hour in room temperature, adding more distilled water (DW), temperature was raised above 100º C due to the exothermic reaction with acid and DW. Then above mixture was terminated by adding excess amount of DW and followed by the addition of 20 mL 30% H_2O_2. Then brown colored precipitate was observed, it indicates the oxygen containing functional groups were directly attached to the carbon sheet, collect the precipitate, washed few times using DW until P^H of the solution was neutral and finally dried in electric oven at 353 K for 8 hours then brown coloured GO was obtained.

Synthesis of Reduced Graphene Oxide (rGO).

Chemical reduction method has been deployed for the reduction of GO into rGO. Particularly, calculated amount of prepared GO was dispersed in DW using ultrasonic treatment for half hour. Then calculated amount of hydrazine hydrate was slowly added to the dispersed GO suspension and refluxed at 368 K for 2 h, and then black colored precipitate was formed. It was washedwith DW until P^H of the solution was neutral and finally dried in electric oven at 343 K, then black colored sheets of rGO were obtained.

MEASUREMENTS

The powder X-ray diffraction (XRD) analysis was performed by using X-ray powder diffractometer (Bruker D2-Phaser) with Cu Kα radiation (λ=1.5406 Å). UV-Visible diffused reflectance spectra (UV-Visible DRS) of absorption spectra of all the samples were recorded through UV-VIS spectrophotometer (LABINDIA, UV 3092). Fourier transform infrared (FT-IR) spectra were measured with an infrared instrument (Bruker, Tensor 27).

RESULTS AND DISCUSSION
XRD analysis

X-ray diffraction analysis has been deployed for knowing the structural properties of the prepared GO and rGO prepared from chemical method.Figure 1 shows the XRD patterns of GO and rGO. The natural graphite powder was oxidized with $KMnO_4$ then it oxidizes the layers of the graphitic sheets and incorporated the oxygen containing functional groups directly in to the surface

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of the graphitic carbon layer and hence the peak appeared at 11.2º and expands the interlayer graphitic carbon layers from 0.337 to 0.786 nm indicates that it completely exfoliated in to the individual layers of carbon.
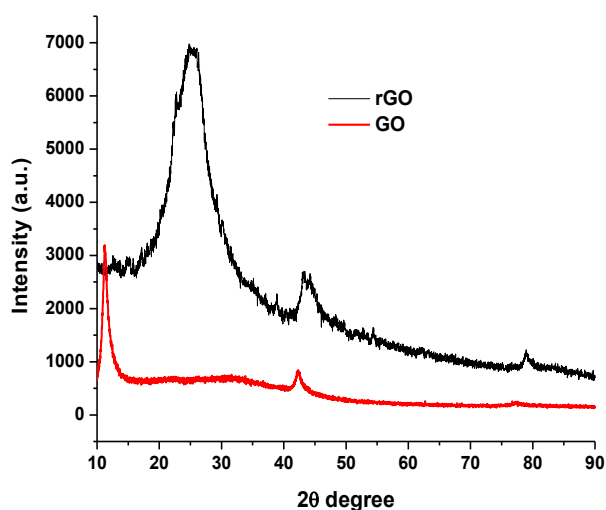

Figure 1. XRD patterns of GO (red) and rGO (black).

Again excess functional moieties on the exfoliated graphitic carbon layer were reduced to minimize the defects in the graphitic carbon hence chemically reduced GO disappears the sharp peak of GO and broad peak is appeared at 25.2º having d-spacing value at 0.378 nm indicates the reduction of chemically oxidized GO and disorder loading of rGO. XRD analysis gives clear evidences of the different structural properties of these three forms of graphitic carbon structures.

FT-IR ANALYSIS:
Fourier transforms infrared (FT-IR) spectroscopy gives the information regarding the various functional moieties present in the desired materials. Figure2 shows the FT-IR spectra of GO and rGO respectively.
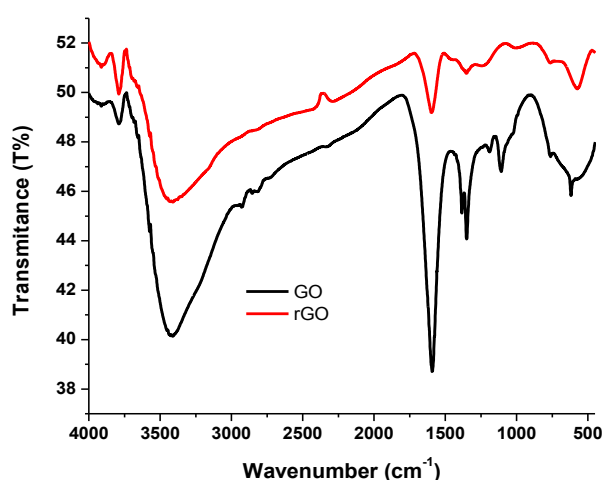

Figure 2. FT-IR spectra of GO (black line) and rGO (red line)

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The spectrum of GO shows the broad peak at 3430 cm^{-1} corresponding to the -OH stretching frequency vibration and other peak positions mainly 1594,1190, and 1110 cm^{-1} corresponding to the different oxygen containing functional moieties such as aromatic C=C and O-H bending vibration, epoxy C-O stretching vibration and alkoxy C-O stretching vibrations respectively [14, 15]. The spectrum of rGO showing all the peak positions of GO with shorting of the peak intensity to that of GO indicates the reduction of GO for forming rGO [16].

UV-VISIBLE ANALYSIS:

UV-visible absorption spectroscopy was employed to study the electronic states of different forms of graphene through defects from the acidic functional moieties. The UV-visible absorption spectra of GO and rGO are as shown in the Figure3. The absorption spectra of GO shows the main peak at 241 nm and shoulder peak at 302 nm corresponding to the π-π* and n-π* transitions of C=C and C=O functional moieties respectively [17]. Upon chemical reduction, the main peak of GO gradually shifted to longer wavelength at 269 nm demonstrating the successful reduction of GO in to rGO through increased π electron density [18]. While the shoulder peak 301 nm evidently disappeared during the reduction process [19].
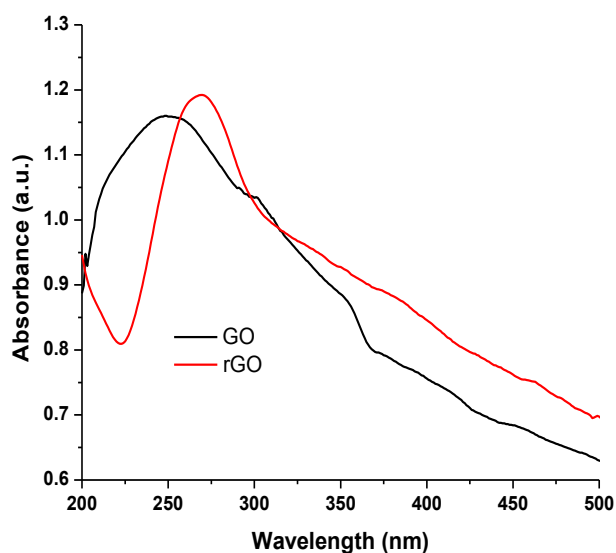

Figure3. UV-visible absorption spectra of GO (red) and rGO (blue) in ethanol

The absorption spectra of GO shows the main peak at 241 nm and shoulder peak at 302 nm corresponding to the π-π* and n-π* transitions of C=C and C=O functional moieties respectively [17]. Upon chemical reduction, the main peak of GO gradually shifted to longer wavelength at 269 nm demonstrating the successful reduction of GO in to rGO through increased π electron density [18]. While the shoulder peak 301 nm evidently disappeared during the reduction process [19].

CONCLUSION

In the present investigation successfully demonstrated the structural, functional and optical properties of the oxidized and reduced form of graphite through various spectroscopic techniques. The different oxygen containing functional moieties in the GO and the reduction of the excess functional moieties after reduction process was confirmed through FT-IR spectroscopy technique.

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XRD study reveals that, the structural changes of the graphitic carbon after the oxidation and reduction treatment on natural graphite powder. The optical properties of the GO and rGO shows the shifting of the absorption edge after chemical treatment on GO to forming rGO.

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