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Research Article

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An Improved Method of Synthesis of Graphene Oxide(GO) and Reduced Graphene Oxide(rGO) Nanocomposites

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ABSTRACT

The oxidation and exfoliation of graphitized carbon was successfully achieved using modified Hummer's method. Graphene is a remarkable material, electrical, thermal and barrier properties, graphene–based nanocomposites have been area of research in the past decade. Graphene possesses a large number of materials parameters such as superior mechanical stiffness, strength and elasticity, very high electrical and thermal conductivity. The synthesis and physical properties of graphene oxide and reduced graphene oxide (GO-rGO) Nanocomposite. The GO-rGO Nanocomposite was prepared by a modified Hummer's method and then reduced using hydrazine hydrate (reducing agent) to produce rGO.XRD spectrum reveal that crystalline structure for both GO and rGO. The d-spacing is observed to be reduced for rGO as compared to that for GO because of removal of oxygen containing functional groups. The optical property was analysed using UV-vis Visible and photoluminences(PL) spectroscopy.

Key Words: Graphene Oxide, Exfoliation, Hummer's method, Reduced Graphene Oxide, XRD, FT-IR and Raman Spectroscopy.

INTRODUCTION

Graphene, the mother of all carbon atoms, is a single atomic thick, no sized, two- dimensional structure and provides high surface area with adjustable surface chemistry hybrids. It was synthesized from graphite. In this study, the current state of science and identified the knowledge gap for the future research development.[1,2,3,4,5,6] Graphene oxide(GO) has garner significant attention due to its unique properties. It has honeycomb carbon geometry, Two- dimensional (2D) crystal combined with one-atom thickness, large surface area, along with amazing electrical, optical, thermal and mechanical properties. This amazing characteristic are originating from its chemical structures composed sp^2 carbon domains adjoining sp^2 carbon domain and various functional groups such as hydroxyl, epoxy and carboxyl groups.[7,8] Their prepared hybrid of magnetic graphene oxide showed a good electrical property.[9] Graphene oxide (GO) is of great interest due to its low cost, easy access, and widespread ability to convert to graphene. Graphene oxide is graphite that has been oxidized to intersperse the carbon layers with oxygen molecules, and then reduced, to separate the carbon layers completely into individual or few layer graphene. Graphene oxide is effectively a by-product of this oxidation as when the oxidizing agents react with graphite, the interplanner spacing between the layers of graphite is increased. The completely oxidizer compound can then be dispersed in a solution such as water, and graphene oxide is then produced.[10-20] A large number of oxygen–containing functional groups have been introduced onto both sides of a single graphite sheet. The implantation of functional groups overcome the intersheet van der Waals force and enlarges the interlayer spacing. GO acquire multiple defects and the degree of the defects is subject to the additive amount of oxidant and oxidizing time.[20] Moreover, due to the presence of large number of exposed edges as electro active sites, higher surface area, and absence of metallic catalysts impurities, the reduced graphene oxide (rGO) exhibits improved electrochemical performance as compared to carbon nanotubes (CNTs).[21] The concept of graphene and studied the electronic properties of graphene using tight-binding model. It is concluded that graphite is a semiconductor without activation energy, because of small portion of valance band of graphite extended to the conduction band, in which data established a foundation for the use of physical properties of graphite.[22-26] In this case, the chemical reduction of GO was using Hydrazine hydrate is reduced graphene oxide.[27] The aim of this study is synthesis of reduced graphene

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oxide by using modified Hummer's method using the cheapest material that is graphite, as a starting material using different parameters such that effect of concentration, temperature, and reduction time in the oxidation level of graphene oxide in a cost effective way. This was mainly carried out using sulfuric acid and potassium permanganate and excluding sodium nitrate that emits toxic gases to the environment. Graphene has a potential of replacing the costly and brittle silicon-based electronic devices, but it is in its infant stage.[28]

MATERIALS AND METHODS

Chemicals and materials

Graphite flakes (Natural), Sodium Nitrate($NaNO_3$), Potassium Permanganate $KMnO_4$,DI water, and Hydrogen Peroxide (H_2O_2) with purity of 99.8% was purchased from sigma Aldrich. All Chemicals were of analytical grade and used as received.

Synthesis of Graphene Oxide (GO)

Graphene oxide (GO) was prepared according to the modified Hummers method[29-34]. In present details, 6g of graphite flakes and 3 g of $NaNO_3$ were mixed with 50 ml H_2SO_4 and stirred in an ice bath for 2hrs. Next 6g of $KMnO_4$ were slowly added so that the temperature of the mixture lower than below 5°C. The suspension was then reacted for 2 hrs. in nan ice bath and stirred for 1hr. The ice bath was then removed and mixture was stirred at 35°C until become the pasty brownish color and kept under stirring for 3 days. It is then diluted with drop by drop addition of 100 ml water. The reaction temperature was rapidly increased to 98°C with effervescence, and the color changed to brown color. Further the Deionized water was further added so that the volume of the suspension was 200ml. The final solution treated with 15ml 0f H_2O_2 was added after 5 minutes to terminate the reaction by appeared the yellow color solution. The reaction product was washed by rinsing and centrifuged and washed with deionized water and 5% Hcl solution repeatedly. After filtration and drying under vacuum at room temperature. The final product was dried at 60°C at using muffle furnace. The graphene oxide (GO) was obtained as a powder.

Synthesis of Reduced Graphene Oxide

For the reduction of Graphene oxide using Hummer's method, One of the Most commonly used reducing agent is hydrazine Hydrate.[35] One major reason for its popularity is its inertness to water, which is present in GO as a dispersing solvent. Nevertheless, after careful studies of the products of the reduction process coupled with the knowledge of the reaction mechanisms of hydrazine with other organic species, it is suggested that the reduction of GO is similar to that reaction with hydrazine.[36] The technique conists of the initial oxidation of graphite to graphite oxide, followed by the subsequent chemical exfoliation of graphite oxide to graphene oxide.[37-40]

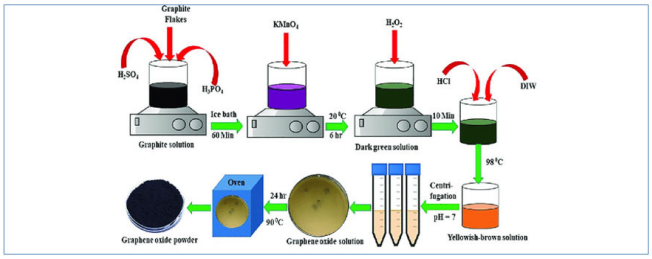

Figure 1: Schematic diagram of synthesis of GO.

RESULTS AND DISCUSSION

X-Ray diffraction:

X-ray diffraction is one of the resolvable characterization to observe the crystallinity of the GO. The XRD was performed using XPERT-PRO diffractometer with CuKα radiation at wavelength 1.5406A°. The Scanning angle was done in the range from 2θ= 10° to 80°. The X-ray Diffraction patterns for graphite powder, graphene oxide powder and reduced graphene oxide powder were recorded. The average of crystallite size (D) of the GO-RGO was calculated from Scherrer's equation for the (002) plane.[39]

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

Where, λ is the X-ray wavelength, βis the full-width at half-maximum of the peak and θ is the reflection angle. Dislocation density(δ) and strain(δ) for (002) plane was evaluated using relations[40].

$$\delta = 1/D^2 \quad (2)$$

The number of crystallites per unit area is calculated from the following relation:

$$N_c = t/D^3 \quad (3)$$

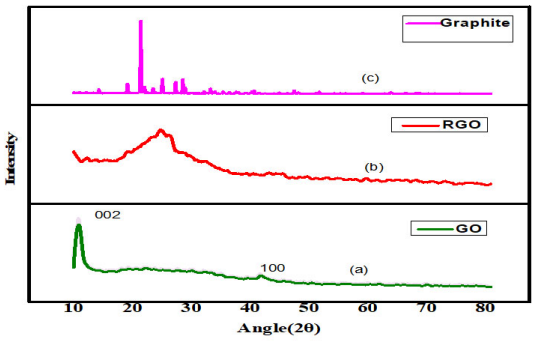

Figure 2: X-ray diffraction patterns of (a) Graphene Oxide powder (b) rGO powder (c) graphite powder.

Table 1: Structural parameters, band gap of prepared GO and RGO nanocomposites

Sample	Crystallite size(nm)	Dislocation Density ($X\ 10^{15}$) m^{-2}	Strain($X10^{-3}$)	Direct bandgap $(\alpha\hbar V)^2$	Indirect bandgap$(\alpha\hbar V)^{1/2}$
GO	12.9	0.076380477	0.000357586	1.2 ev	1.6 ev
RGO	14.9	0.069316062	0.00675116	1.3 ev	1.6 ev

Fourier Transform Infrared Spectroscopy

FTIR spectra of GO and rGO presented in figure 2 were collected from Perkin Elmer under transmission mode. The spectra show the presence of oxygen containing functional groups in GO. The peak at 3450 cm^{-1} GO and 3445cm^{-1} shows the stretching of hydroxyl group [C=O carbonyl stretching at 1630 cm^{-1} and the C-O epoxide group stretching at 1096 cm^{-1} . High intensity of major peak in Go reveal that large amount of oxygen containing groups are present after oxidation process. The peak at 1623 cm^{-1} is related to the skeletal stretching of C=C alkene group. After reduction of GO peak intensities due to alkoxy and hydroxyl groups were decrease significantly and C=C phenol ring stretching at 1623 cm^{-1} was present. All corresponding peaks in rGO have smaller intensities as compared to GO.

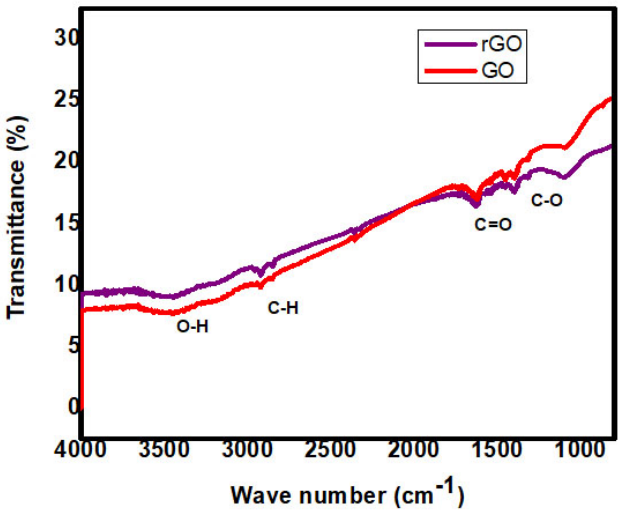

Figure 3: FTIR spectra of GO and rGO.

Raman Spectroscopy Analysis

Figure show the Raman spectrum of GO and rGO. Raman spectroscopy was used to be observe structural changes in the samples through the oxidation and reduction process. Raman spectroscopy is a widely used for the characterization of carbon products, especially considering the fact that conjugated & double carbon-carbon bonds lead to high Raman intensities. Figure the Raman spectra of GO and rGO, where the in-phase vibration (G band) of GO and rGO is at 1580 nm and 1588nm . and disorder band (D band) of GO and rGO is at 1342nm and 1354nm.

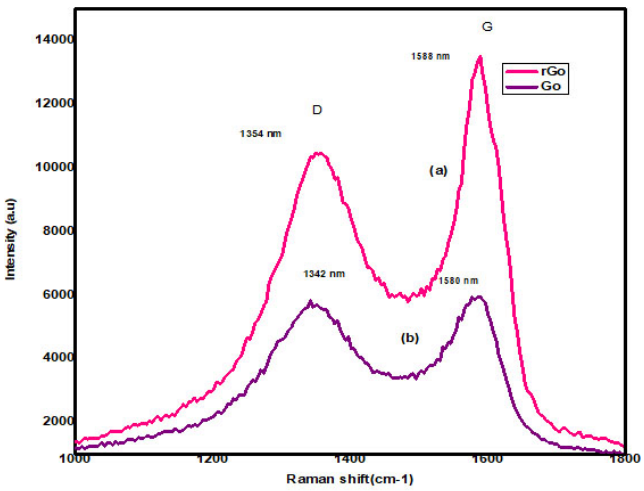

Figure 4: Raman spectra of (a) GO and (b) rGO nanocomposite.

UV –Vis Visible Analysics:

UV-Vis spectrometry was commonly used in the detection and estimation of organic and inorganic compounds. The synthesis of Graphene Oxide and Reduced graphene oxide composite were characterized by UV-Visible spectroscopy as display in support in figure. According to UV-visible spectra, the samples haven Wavelength absorption ranging from 200 to 800 nm in support figure(5). The absorbance value is observed for GO and RGO nanocomposites. The band gap of the nanocomposite materials calculated by using Tauc's equation.

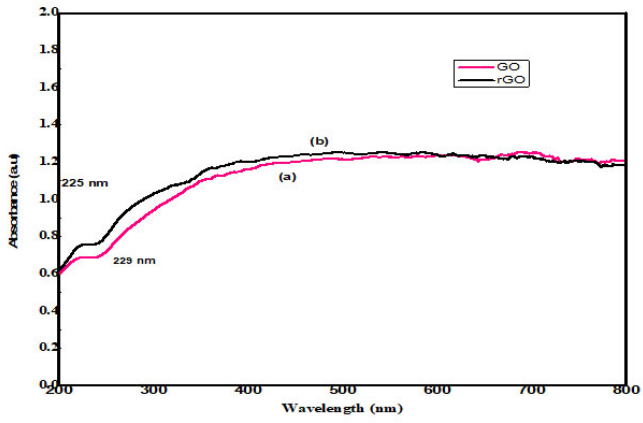

Figure 5: UV-Vis Absorbance Spectra GO and RGO Nanocomposites.

The optical band gap (E_g) of the sample was estimated from the absorbance data where the photon energy (hv) and absorption coefficient (α) are related by the equation.

$$\alpha hv = B(hv - E_g)^n \quad (5)$$

where E_g represents the band gap, hv is the photon energy, E_g is the optical band gap energy and " B' is constant ,n is the number that depends on the nature of the absorbtion.For allowed direct transition , the value of n=1/2 and B is constant. Tauc graph is plotted between $(\alpha hv)^2$ against hv to calculate the band gap of prepared GO and rGO samples. The bandgap of the GO and RGO is found to direct bandgap energy is 1.2 and 1.6 ev and indirect bandgap is found to 1.3 and 1.6 ev for the optical bandgap of GO and RGO nanocomposites.

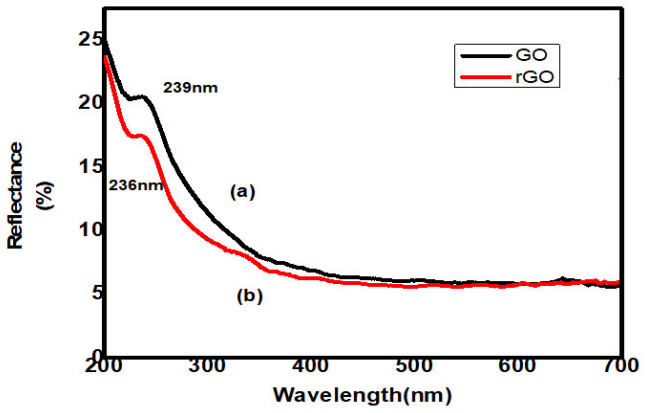

Figure 6: UV-Vis Reflectance spectra of GO and RGO Nanocomposites.

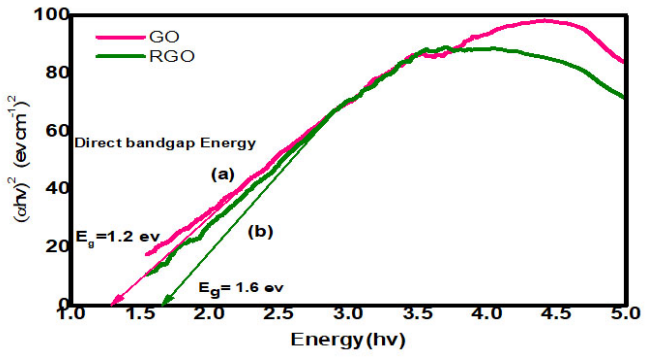

Figure 7: Tauc plot direct of GO and RGO Nanocomposites.

Photoluminescence Spectroscopic analysis:

PL spectroscopy is used to determine the optical quality of GO- RGO semiconductor material and common radioactive transition in the semiconductor occurs between states at the bottom of the conduction band and top of the valance band in prepared sample. Room temperature luminescence spectrum was recorded using (CaryEclipse) spectrofluorometer. The peak (Ultraviolet light emission) about 360nm was caused by free exciton recombination. The blue emission due to the passage from electron from oxygen vacancies to the valance band is attributed to the peak centred at 458nm. The blue emission peak at 495nm is generally attributed to the radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy. The peak is attributed to the excitonic transition which are size-dependent and excitation wavelength independent of certain wavelength range. The peak at 505nm arise from the combination of the holes from the valance band and electrons from the conduction band.

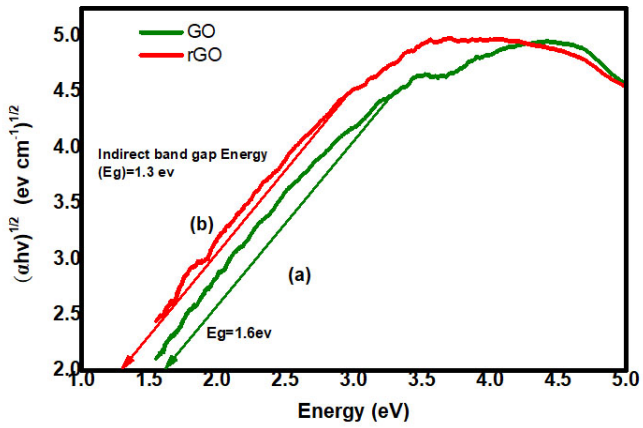

Figure 8: Tauc plot indirect bandgap of GO and RGO Nanocomposites.

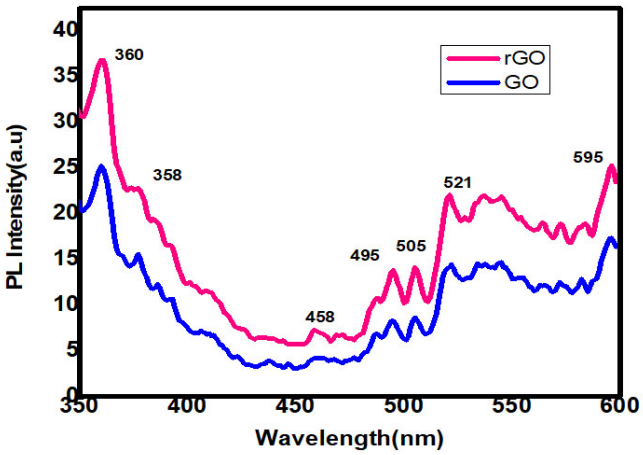

Figure 9: Photoluminescence Spectroscopic analysis of GO and RGO Nanocomposite.

CONCLUSION

GO and RGO Nanocomposites were successfully synthesized using the modified Hummer's method. The sample

were crystallized and textured along (002) plane .The crystallite size of GO and RGO at 12.9nm and 14.9nm respectively. FTIR analysis were carried out the identify functional groups and to confirm the formation of nanomaterials. An average of optical absorption in the wavelength range 200-800nm the Tauc's graph plotted and revealed that the optical bandgap measured from the absorption spectrum GO and RGO 12 ev and 1.6ev respectively. In PL emission spectrum peaks were observed at different wavelength at 360,356,458,495,505 nm are detected.

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Conflict of Interest:

The authors declare no conflict of interest in the current work.

The authors declare that: The manuscript has not been previously published is not currently submitted for review to any other journal and will not be submitted elsewhere before a decision is made by this journal.

Authors' contribution:

N. Thangaraj: First author, conceptualization, methodology, Investigation, Writing-Original Draft, Formal analysis.

Dr. N. Joseph John : Validation, Visualization, Supervision, Writing-review & Editing.

C. Gnana Sambandam: Validation, Visualization, Co-Supervision, Formal analysis.

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