Energy efficient functionalization of graphene for tunable fluorescence

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Abstract. Multifunctionality of Carbon-Based Nano Materials, Graphene in particular is gaining more relevance in their diversified applications. Today, the fabrication of luminescent graphene materials is significant for the field of bioimaging of healthy and malignant cells due to their biocompatible tunable fluorescence. In this aspect there is a need for a simple, energy efficient process for the introduction of hetero atoms of Oxygen and Sulphur into the graphene structure to explore the enhancement of fluorescence. The present study aims at the optimization of processing temperature and other experimental parameters for doping hetero atoms of Oxygen and Sulphur in the graphene structure for tuning their luminescence properties. The method involved hydrothermal carbonization of simple precursor of glucose at lower temperatures of 180°C and 220°C and alkaline pH followed by the analytical characterization of the product samples. The introduction of hetero atoms, the presence of sp² Carbon, band gap energy, microstructure along with layer structures were ascertained in the as-synthesized graphene samples. The influence of processing temperature, oxygen functionality and defect structures upon emission wavelength range of graphene in the visible region was well correlated. Ultimately, the study provided the fundamental aspects of fabricating graphene structures suitable for tunable fluorescence of graphene aimed at bio imaging technique.

Keywords: Graphene, Functionalized graphene, Hydrothermal Carbonization, Tunable fluorescence, bioimaging.

1. Introduction

Carbon-based nanomaterials (CBNs) have a great interest due to their low-cost, structural tunability, large surface area, and unique physicochemical properties. Carbon-based nanomaterials can be classified into different types due to its quantum confinements, Suchas 3D - Graphite and Diamond, 2D - Graphene, 1D - Carbon nanotubes, 0D - Fullerene, Carbon quantum dots, nanodiamonds. [1]

In recent years, among the CBNs, graphene has attracted considerable interest in various applications in electrical, electronic, catalytic, medicine, biotechnology and various interdisciplinary sciences. Graphene is a one-atom-thick layer of sp²-bonded 2D honeycomb lattice of carbon. The delocalized π electrons of sp² hybridized carbon atoms lead to an attractive electronic property for energy conversion and storage. Unfunctionalized graphene sheets are insoluble and infusible.
Functionalization of graphene with some nonmetal heteroatoms like oxygen, nitrogen, sulfur will enhance some properties like hydrophilicity, long term stability, changing the distribution of electron density and improving the electron spin density in their application of energy storage device, luminescence and catalytic activity. Functionalized Graphene-based nanomaterial (GBNs), such as Graphene Oxide (GO), reduced Graphene Oxide (rGO). Graphene oxide is a single unimolecular layer of graphite with various oxygen-containing functionalities such as epoxide, carbonyl, carboxyl and hydroxyl groups. GO and reduced rGO can be used in electronic devices, energy storage, biomedical applications and catalysis. [2]

Various methodologies have been reported to functionalize/introduce heteroatoms like oxygen, sulfur, and nitrogen into the carbon moiety of graphene viz: Chemical Vapor Deposition (CVD), Chemical exfoliation, Hummer’s method, Microwave method [3]. The nature of the precursor, experimental parameters, pH, temperature, play an important role in the nature of doping, amount of doping. Ultimately the physical, chemical and biological properties of the samples and their applications are modified.

In the present study, a simple, viable method of preparing oxygen doped graphene (GO) and Sulfur-doped Graphene Oxide (S-GO) structure from the simple precursor of glucose, a reducing monosaccharide. The study also aims at the setting up of optimum temperature and pH to realize a multifunctional graphene which is fluorescent and catalytic in particular. The results of the study will provide a good correlation between structural parameters of graphene and their fluorescence properties and the ideal experimental conditions to prepare such structures.

2. Materials and Method

2.1. Materials Required

Chemicals used for synthesis of Graphene based nanomaterials (GBNs) are Glucose (Nice Chemicals), Sulphuric acid (H₂SO₄), Sodium hydroxide (NaOH) (Nice chemicals), Glacial Acetic acid (Nice chemicals), 99.9% Ethanol (Analytical CS reagent).

2.2. Method of Preparation

2.2.1. Hydrothermal Method of Synthesis GBNs

A simple one-pot hydrothermal method was used to carbonize the glucose. The temperature and pH for the carbonization of glucose were fixed based on the emission color observed in visible region and the decomposition temperature of the precursor, glucose. A brown gel was obtained from the carbonization of glucose. Glucose was carbonized at different time periods, pH and different temperatures so as to optimize the condition to get GBNs that give fluorescence in the visible emission, green in particular for ultimate bio imaging application.

2.2.2. Preparation of Functionalized Graphene with Oxygen and Sulphur

Glucose solution (about M/2) was carbonized at 180°C in a Teflon lined autoclave for four hours at pH 9. The brown gel obtained was treated with ethanol and then it was refrigerated and stored for characterization. For the doping of Sulphur, the GO (brown gel) sample obtained from hydrothermal treatment was heated with Sulphuric acid in a water bath in the ratio of 1: 5. The brown solid residue obtained upon doping was dried under room temperature. The as synthesized Sulphur doped GO (S-GO) a black amorphous powder was characterized using analytical tools.
In order to analyze the effect of temperature (above the decomposition temperature of glucose), the glucose (M/2) was carbonized at 220°C in a Teflon lined autoclave for four hours in an alkaline pH. The brown crystalline sample as obtained was purified using ethanol to remove the organic moieties for characterization and analysis.

2.3. Material Characterization

The functional groups present in the GO and S-GO prepared at different temperatures and different time duration were identified by FT-IR spectra (IR Affinity, SHIMADZU) using potassium bromide (KBr) pellet. The bonding characteristics of the as synthesized GO and S-GO were analyzed using the FT-RAMAN spectrometer (BRUKER, RFS) in the scan range of 1200-1800cm⁻¹. The micro structural analysis of the as synthesized samples was carried out using Powder X-ray Diffraction patterns (PXRD). They were recorded using CuKα radiation with the diffraction angle between 20° and 80°. PXRD analysis was performed using a PANalytical model Xpert pro instrument. The crystallite size of the sample was calculated using the Scherer equation. The surface morphology of the as synthesized samples was studied from the Scanning Electron Microscopic (SEM) (FEI QUANTA) images and Transmission Electron microscopic (TEM) (JOEL) image. The relative percentage of elements at the surface was determined from the Energy Dispersive X-Ray analysis data (EDAX). Diffuse Reflectance Spectroscopy (DRS) (UV – 3600 Plus Shimadzu) was used to determine the bandgap energy of as synthesized samples. Absorption (UV -SHIMADZU 1601) and fluorescence (Agilent, Cary Eclipse) spectroscopy were used to identify the bond types and fluorescent behavior present in the GO and S-GO. Tunable fluorescence properties were analyzed from visible to near-infrared range. In this present study, Excitation dependent emission was analyzed for GO and S-GO.

3. Results And Discussions

After preliminary screening, three samples viz.: the precursor of glucose after carbonisation at 180°C (GO-180°C), doping with Sulphur at 180°C, carbonization at 220°C (GO-220°C) were considered for microstructural, morphological investigation for tuning towards selective emission.

![Figure 1](image1.png)

Figure 1. UV-Visible spectra of Carbonization of glucose at 180°C with respect to different time intervals (a) and different pH (b)

The UV-Visible spectra of carbonized glucose as given in Figure 1(a) include respective spectra taken at one hour intervals during the entire carbonization process for five hours. In these spectra, the peak
The UV visible spectra of glucose carbonized at different pH are shown in Figure 1(b). As the pH increases, there is a shift in $\lambda_{\text{max}}$ towards longer wavelength (Bathochromic shift) due to the introduction of number of chromophoric groups onto the structure and confirms the introduction of Oxygen as heteroatom, Graphene Oxide (GO). [6].

The FT-IR spectrum of the precursor (glucose) shown in the above Figure 2. As reference to substantiate the changes observed in the functionality or doping of the heteroatoms. The peak corresponding to O-H was identified at 3315 cm$^{-1}$ while the peaks corresponding to C-H were identified at 2941 cm$^{-1}$ and 2885 cm$^{-1}$ respectively. The peaks observed at 1111 cm$^{-1}$ and 1700 cm$^{-1}$ are due to the presence of C=C and C=O [8].

The FT-IR spectra of Carbonized Glucose at 180$^\circ$C (GO-180$^\circ$C), Glucose carbonized with Sulphuric acid to dope with Sulphur and Oxygen (S-GO) at 180$^\circ$C (S-GO-180$^\circ$C) and Glucose carbonized
at 220°C (GO-220°C) are given above Figure 3(a), Figure 3(b) and Figure (3c) respectively. The peaks corresponding to C-O, O-H, C-C, C-H stretching were obtained for GO-180°C, S-GO-180°C, GO-220°C. The peaks corresponding to C=C was also identified at 1653 cm⁻¹ indicates the retention of basic graphene structure. In the Sulphur doped graphene Oxide additional peaks at 651 cm⁻¹ and 605 cm⁻¹ due to C-S and 1491 cm⁻¹ were observed indicating the successful introduction of Sulfur onto the core structure of sp² domains of Carbon moiety. The intensity of the sp² Carbon, the peak corresponding to C=C increased with temperature.[9], [10], [11], [12], [13].

![FT-Raman spectra](image)

Figure 4. FT-RAMAN spectra of (a) GO-180°C, (b) Sulfur doped GO at 180°C and (c) GO-220°C.

The FT-RAMAN spectra of GO and S-GO as obtained at 180°C and GO obtained at 220°C shown in Figure. 4a, 4b and 4c. These spectra show that the G band was observed at 1558 cm⁻¹ and 1500 cm⁻¹ and 1525 cm⁻¹ for GO-180°C, S-GO-180°C and GO-220°C respectively. The D band was observed at 1358 cm⁻¹, 1389 cm⁻¹ and 1375 cm⁻¹ for GO-180°C, S-GO-180°C, and GO-220°C respectively. G band corresponds to E_{2g} symmetry of sp² carbon and D band corresponds to A_{1g} symmetry of sp³ carbon. The I_D/I_G ratio has found to be 0.4835, 0.4640 and 0.8285 for GO-180°C, S-GO-180°C and GO-220°C respectively. The I_D/I_G ratio of S-GO-180°C has slightly decreased in comparison with I_D/I_G ratio of GO-180°C. This proves that doping of more hetero atoms leads to a decrease in surface defects of GO. Also, the I_D/I_G ratio increases with increase in the degree of disorderliness in the structure creating defect structures and the trend increases with an increase in temperature. These results correlate well with FT-IR reports [14], [17]. The increased defect on the structure of sp² Carbon can be responsible for the enhanced luminescent property.
Figure 5. PXRD spectra of (a) Sulphur doped GO at 180°C and (b) GO-220°C

The Powder X ray Diffractograms (PXRD) of S-GO-180°C and PXRD spectrum of GO-220°C are shown in Figure 5(a) and Figure 5(b) respectively. The d values for GO-180°C were taken from the Transmission Microscopic images instead of X ray diffractograms as the sample was a gel. The values of d, 2θ and hkl of the samples along with the reported value for Graphene are given in the Table 1. The values indicate the successful doping of hetero atoms of Oxygen and Sulphur. The decrease in the d-spacing value with the introduction of Sulphur atom into the lattice of Graphene Oxide suggests that Sulphur takes the position of Oxygen due to size compatibility. [18].

Table 1. Comparing interplanar distance(d) and Crystallite size of oxygen and sulphur doped graphene at different temperature

| Name of the Sample | 2θ         | d-spacing        | Miller indices |
|--------------------|------------|------------------|----------------|
| Graphene[19]       | 26.4° and 54.2° | 0.3410nm         | 002,004        |
| GO at 180°C        | --         | 0.3960nm from TEM analysis | --             |
| GO-220°C           | 18.20°     | 0.4339nm         | 001            |
| S-GO-180°C         | 27.56°     | 0.2878nm         | 001            |

The HR-TEM image and Selected Area Electron Diffraction (SAED) pattern of the sample of Oxygen doped graphene (GO) are shown in Figure 6(a) and Figure 6(b) respectively. The irregular layer structure and flake morphology on the surface as indicated by the TEM images confirms the formation of graphene oxide. The C/O ratio of GO was found to be 15.5016 from EDAX analysis. The d- spacing value of Graphene oxide was found to be 0.396nm. The report was correlated well with PXRD reports. [15],[16],[19],[20].
Figure 6. (a) High Resolution – Transmission Electron microscopic (HR-TEM) image of Oxygen doped graphene at 180°C (b) SAED pattern of Oxygen doped graphene at 180°C

Figure 7. Field Emission Scanning Electron Microscopic (FE-SEM) image of Sulphur and oxygen doped graphene (S-GO) at 180°C

The FE-SEM image of sulfur and oxygen doped graphene (S-GO) are shown in Figure 7. The layer structure with spherical aggregates on the surface indicates that the formation of graphene oxide. Sulphur gets impregnated on the surface of graphene oxide which can be correlated well with the decrease in C/O ratio (1.1986) compared to Graphene oxide as taken from the EDX measurement. The report confirmed relative the replacement of Oxygen atoms by Sulphur atoms. [21].

Figure 8. Field Emission Scanning Electron Microscopic (FE-SEM) image of GO-220°C

The FE-SEM image of Oxygen doped graphene (GO) as shown in Figure 8. The layer structure indicates the formation of graphene and near-spherical dots were indicative of Oxygen on the surface. The Carbon to Oxygen (C/O) ratio was found to be 1.40 from EDAX analysis. The C/O ratio has decreased which indicates that the increased number of oxygen functionality on the surface from EDAX analysis and
the irregularity in layer structure has increased compared to graphene when the temperature increased to 220°C [22].

![Figure 9](image1)

**Figure 9.** UV-Diffused Reflectance Spectra (DRS) of a) Sulphur and oxygen doped graphene at 180°C and b) Oxygen doped graphene at 220°C

To correlate the above results with the direct band gap energy, the UV-DRS Spectra of S-GO-180°C 9(a) and GO-220°C 9(b) are considered which are shown in Figure 9. The direct bandgap value of S-GO-180°C was found to be 3.57eV. The bandgap value of S-GO-180°C has increased when compared with graphene oxide (3.5eV) which confirmed that the addition of Sulfur on graphene oxide moiety. The direct bandgap value of GO-220°C was found to be 1.717eV which also correlates with the report [23].

![Figure 10](image2)

**Figure 10.** Photoluminescence (PL) spectra for Carbonized glucose with respect to different pH (a) Excitation at 360nm (b) Excitation at 380nm

The safe and versatile imaging of healthy and cancer cells, (bio imaging) require wide emission wavelength range by tuning the excitation wavelength. All the above micro and morphological results of the as synthesised doped graphene samples suggested that they have the potential for exhibiting tunable fluorescence especially, green emission which can be explored further for wider applications. The tunability was screened at different pH and excitation wavelengths using their Photoluminescence spectra. The Photoluminescence spectra of Carbonized glucose at excitation wavelength of 360nm and 380nm as shown in Figure 10(a) and 10(b) respectively. In both cases as the pH has a significant role in the emission, PL spectra were recorded at different pH. By doing so, the role play of pH in influencing the defect states responsible for green fluorescence was studied.
The luminescence (PL) spectra show that there is a shift λmax towards shorter wavelength with decrease in emission intensity when pH is more alkaline and the study was carried out at different alkaline pH. It was found that Green emission was well stabilized in the pH range of 2 to 9.5. The chromporic groups enhanced the green emissions which were observed in UV visible spectra. [24], [25], [26].

![Image](image1.png)

**Figure 11.** Photoluminescence spectrum for carbonized glucose with respect to different temperature

Photoluminescence spectra for Carbonized glucose with respect to different temperature as shown in Figure 11. At low temperature the emission has a narrow band while at higher temperatures, the emission has very broadband due to the band edge of conducting material. The broadness of the peak has increased from 140°C-180°C and shift in λmax towards higher wavelength. At 220°C there is a shift in λmax towards shorter wavelength because of decomposition temperature of glucose was found at 160°C-180°C which correlates with well UV-Visible spectra [24], [25], [26].

![Image](image2.png)

**Figure 12.** Tunable fluorescence spectrum of oxygen doped graphene at 180°C with different excitation wavelength (350nm, 370nm, and 390nm)

Tunable fluorescence spectrum of oxygen doped graphene at 180°C with different excitation wavelengths as shown in Figure. 12(350nm, 370nm, 390nm). In this GO, tunable emissions were observed in green region due to band edge. When increasing the excitation wavelength. The emission wavelengths have increased from 498nm to 511nm, because of the introduction sp² Carbon and defects on the structure as indicated by FT-IR, FT-RAMAN and FE-SEM spectra given above. [26] [27]
The emission spectrum of GO-220°C with different excitation wavelengths as presented in Figure 13. (260nm, 280nm, 300nm). The tunable emission spectra of oxygen functionalized graphene as obtained at 220°C has enhanced when compared with GO-180°C due to enhanced interplanar distance and oxygen functionality between the layers. The tunable emission of oxygen doped graphene is present in the greenish yellow region (from 506nm to 606nm) due to the enhanced defect and irregular layer structure which were observed in FT-RAMAN and FE-SEM image. [27]. The report was well correlated with PXRD and FE-SEM reports.

Tunable fluorescence spectrum of Sulphur and Oxygen doped graphene at 180°C with different excitation wavelengths as shown in Figure 14. In S-GO, when doping sulfur on the surface of Graphene oxide, the tunable emission has enhanced which was observed in red region from 725nm to 800nm due to increased band gap energy of the material and introduction more defects observed in sp² Carbon on the structure with some of irregular layer morphology with spherical aggregates on the surface may be responsible for enhanced emission in red region which were correlates well with FT-IR, FT-RAMAN and FE-SEM analysis [3, 27].

4. Conclusion

The study optimized the experimental conditions for the synthesis of Oxygen and Sulphur doped Graphene. The use of simple precursor, energy efficient hydrothermal process and fine tuning of as synthesized samples towards variable fluorescence are the highlights of the study. The results of FT Raman spectra, PXRD, SEM and TEM images were well correlated to arrive at the micro structure and morphology of the graphene samples. It was observed that Sulphur and Oxygen functionalized graphene materials have enhanced luminescence. In Sulphur functionalized graphene material, the tunable
luminescence property increased due to enhanced defects as observed in layer structure. When the carbonization temperature increases, the tunable luminescence property of Oxygen functionalized graphene is enhanced due to increased inter planar distance between the graphene layers and increased oxygen functionality. The good tunable luminescence property were observed in as synthesised samples which can be used for further applications in bioimaging of normal cells and cancer cells (HeLa cells) for cell diagnosis. The study ultimately provided a fundamental approach towards the synthesis and application of functionalized graphene with hetero atoms of Oxygen and Sulphur.

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