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Tailoring of Energy Band Gap in Graphene-like System by Fluorination

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Abstract

Fluorinated graphene has a two-dimensional layer structure with a wide band gap. In the present study, Fluoro Graphene (FG) is obtained from Graphene Oxide (GO) through a deoxyfluorination reaction with the aid of Diethylaminosulphurtrifluoride (DAST). The FT-IR exhibited a peak at 1216 cm^{-1} and the shoulder at 1312 cm^{-1} were ascribed to the stretching vibration of covalent C-F bonds and C-F₂ bonds, respectively. Surface morphology revealed a leafy structure in GO and a rocky structure in FG. The EDS analysis confirmed the fluorination of the graphitic structure. The TEM analysis confirmed the formation of a mixed structure of graphene and carbon dots. The results of structural, morphological and electrical properties of both graphene oxide and fluorographene show the possibility of using these samples as electronic/electrochemical devices in future.

Keywords: Band Gap, Fluorographene, Graphene Oxide, Nanocarbon

1. Introduction

Graphene is an sp^2 hybridised one atom thick 2D layer arranged in a hexagonal honeycomb lattice similar to benzene rings ripped off

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their hydrogen atoms covalently bonded to three other atoms. The nanocarbon family includes fullerene analogues (C_{60}), carbon nanotubes (CNTs) and graphene which have sp^2 hybridisation. All properties of these materials depend on factors such as the number of layers, nanocarbon size, synthesis method, concentration and type of defects and so on [1-2]. The basic nature of graphite is highly compromised by oxidation which leads to a decrease in conductivity. Also, further derivatisation of graphene oxide renders the initial hydrophilic sheets hydrophobic [3-6]. The ability of graphene to alter its property (particularly the introduction of the band gap) suggests potential optoelectronic applications. Graphene is considered a semi-metal since its valence band meets its conduction band. This property hinders it from different electronic applications. Hence, the band gap is introduced to graphene matrix usually by oxidation, halogenation, attachment of various non-covalent molecules and so forth. In halogenated graphene, certain C-atoms are connected with halogens which have sp^3 hybridisation while others have sp^2 hybridisation itself. In patterned halogenation, the metal grids are kept above the graphene. Therefore, parts of graphene covered with the metal act as conductive pathways, used mainly for the fabrication of devices.

The fluorinated graphene is a neonate member in the graphene family. They have a two-dimensional structure, stable, wide band gap, nanomaterial with good thermal and chemical stability, high electromotive force, high negative value for magnetic resistance and high resistance at room temperature. These enchanting properties make it a solid lubricant, a thin insulator, a self-cleaner for superhydrophobic coating, a tunnel-barrier based on heterostructure, and an excellent material acting as a cathode for lithium-ion batteries. Fluorographene (FG) exhibits several unique properties because, Fluorine (F) atoms have high electronegativity (4.0) compared to Oxygen (O), Carbon(C), and Hydrogen (H). Because of the difference in electro-negativity, FG shows different C-F bonding characters (ionic, semi-ionic, covalent). However, the C-F bonding character and the various properties associated with it have not been reported yet [7-8].

In the present study, functionalisation has been done for graphene. Initially, Graphene Oxide(GO) is synthesised from graphite

powder by the Modified Hummer's Method. Graphene Oxide contains a range of reactive oxygen functional groups which renders it a good candidate for aforementioned applications through chemical functionalisation. From the above-obtained GO, FG is prepared by deoxyfluorination reaction.

2. Materials and Methods

Graphite powder (3 g) is added to 70 ml H_2SO_4 (98%), with continuous stirring in an ice bath for 1 hour. $KMnO_4$ (9g) is added to the above mixture slowly (within half an hour) while maintaining the temperature at $20^\circ C$ for 2 hours. The sample is kept at $40^\circ C$ in an oil bath with vigorous stirring for 30 minutes. De-ionised water (150 ml) is added within 10 minutes with further stirring for 15 minutes at $95^\circ C$. 500 ml of de-ionised water is added further and 15 ml H_2O_2 (30%) is mixed slowly. Further, filtration and washing with 1:10 aqueous solution of HCl (250ml) is carried out with an addition of 600ml de-ionised water. The sample is kept for dialysis for 1 week. 1.2 l de-ionised water is added and kept for overnight stirring followed by sonication for 30 minutes. Finally, the sample is separated by centrifugation at 10000rpm for 45 minutes and dried in vacuum. Then, 0.15 g of GO is added to 150 ml of de-ionised water in a 250ml flask and stirred vigorously for 12 hours. 5ml DAST is added dropwise at $0^\circ C$ in 10 minutes. The mixture is kept for ultra-sonication for 6hours and stirred for three days. 100ml methanol is added for quenching. The FG is obtained after drying in a vacuum.

2.1 Characterisation

The electrical parameters obtained are:

$$\text{Ac conductivity } (\sigma_{ac}) = \frac{d}{Rp * A} \quad 1$$

$$\text{Dielectric Constant } (\epsilon^1) = \frac{Cp * d}{\epsilon 0 * A} \quad 2$$

$$\text{Imaginary Dielectric Constant } (\epsilon^{11}) = \frac{\epsilon''}{w * Cp * Rp} \quad 3$$

$$\text{Dielectric loss } (\tan \delta) = \frac{\epsilon''}{\epsilon'} \quad 4$$

Where,

- d - thickness of the pellet

- A - area of the pellet
- ω - angular frequency ($2\pi \nu$ (where ν is the applied frequency))
- R_p -parallel resistance
- C_p -parallel Capacitance
- ϵ_0 - absolute permittivity.

3. Structural Elucidation of Graphene NanoSystems

The X-ray diffraction profile of the graphite and its fundamental derivatives are presented in Figure 1.

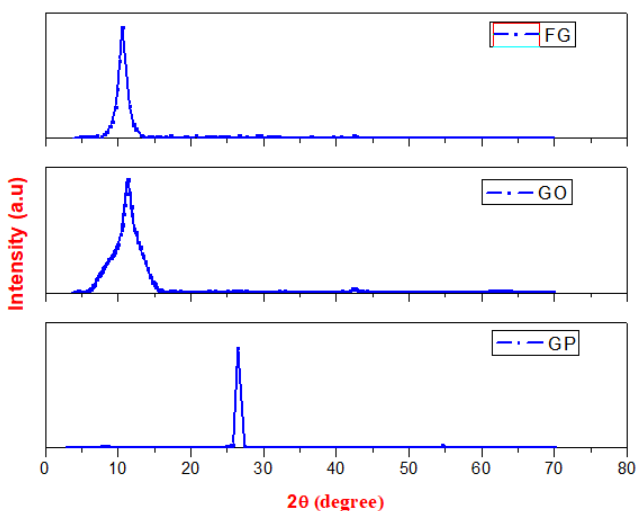


Figure1: X-ray profile of Graphite Powder (GP), Graphene oxide (GO), Fluorographene (FG).

There is a clear shift of (002) peak to 11.314° with a corresponding increase in interlayer spacing to 0.78nm. This shift is an indicator of the formation of a few layers of Graphene Oxide. Also, the peak becomes broader, showing the nano-crystalline nature of Graphene oxide [9-14]. The peak at $\sim 42^\circ$ is also the indicator of the formation of Graphene Oxide. Upon fluorination, a new sharp peak is formed at 10.49° . This is the characteristic peak of Fluorographene. The interlayer spacing is further increased to 0.84nm. This is attributed to the incorporation of the fluorine atom to the graphene plane. The

X-ray profile analysis confirms the formation of Graphene Oxide and Fluorographene. The change in interlayer spacing is attributed to the incorporation of oxygen and fluorine atoms to the graphitic plane respectively.

The change in the functionality of the graphitic structure is further investigated by Fourier Transform Infrared Spectroscopy (FTIR) is depicted in Figure 2.

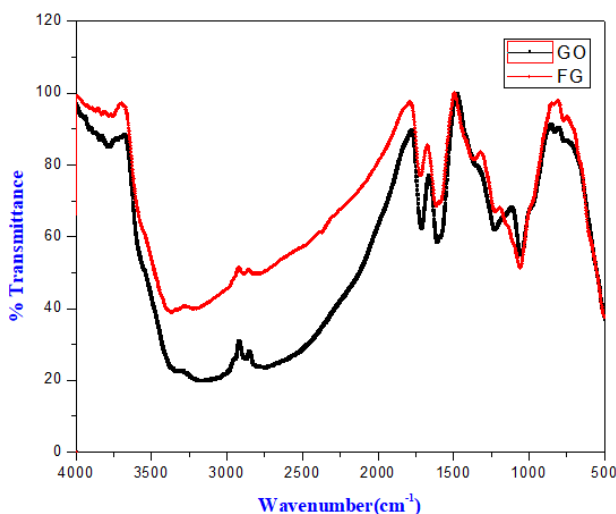


Figure 2: FTIR Spectra of Graphene Oxide (GO) and Fluorographene (FG)

The FTIR spectra of the samples show broad similar characteristics (Figure 2). The band at 870 cm^{-1} is attributed to the aromatic C-H deformation while the absorption of 1052 cm^{-1} arises owing to the C-O stretching. In GO Spectra, the peaks at 2854 cm^{-1} and 2921 cm^{-1} indicates sp^3 C-H bonding. The 1220 cm^{-1} is mainly due to the phenolic C-OH stretching present in GO while 1216 and 1312 cm^{-1} is attributed to the stretching vibration of C-F bonds and C-F₂ bonds present in the Fluorographene. The presence of this band is an indication of incorporation of fluorine to the carbon matrix. Both the samples show the dominant C=O stretching, C=C aromatic stretching vibration and O-H stretching vibration of hydroxyl group [15-22]. The IR analysis confirms the presence of oxygenated and fluorinated graphene. These results support the findings of X-ray analysis.

The Energy gap, estimated by Tauc plot is found to be 2.47 eV and 2.77eV for Graphene Oxide and Fluorographene respectively. The optical energy gap is within the range of compound semiconductor[3-4]. This is mainly due to the incorporation of oxygen and fluorine functionalised groups. This also may be due to the lowering of particle size which needs to be investigated. The introduction of a band gap into the graphene layers alter the electrical properties of GO and FG.

4. Morphological Analysis:

From the SEM images of GO, flaky structures are observed, attributed to the formation of layers (Figure 3&4). The SEM image of GO shows a dense skin layer and a flaky sub-layer. After being blended with fluorine, the layers show structural changes as in the XRD.FG shows the formation of layers with micro-sized ($\sim 5\mu\text{m}$) particles embedded in layers resulting in rocky structure. The EDS analysis shows the presence of carbon and oxygen as the major elements while sodium, aluminium and sulphur as minor elements. Presence of fluorine is also confirmed with the EDS analysis. The analysis reveals the presence of carbon and oxygen as major elements in GO with traces of aluminium, silicates and sulphur. The TEM image of the graphene derivatives(Figure 5 &6), the formation of dots are noticed in the fluorinated graphene. The SAED pattern shows the formation of the polycrystalline phase in the composite.

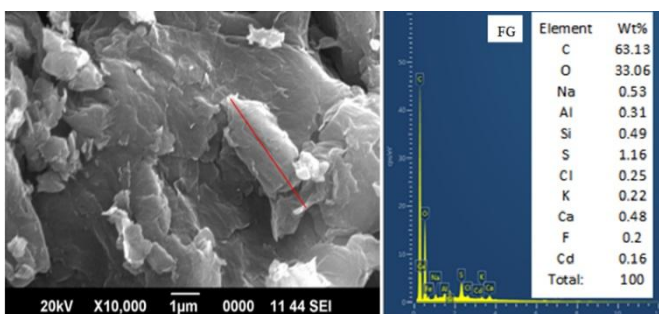


Figure 3: SEM Micrograph of Fluorographene (FG)

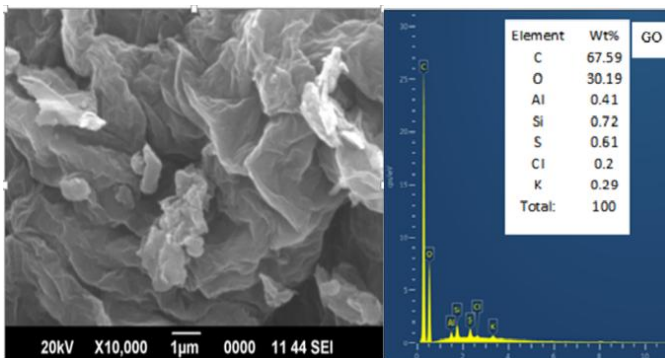


Figure 4: SEM Micrograph of Fluorographene (FG)

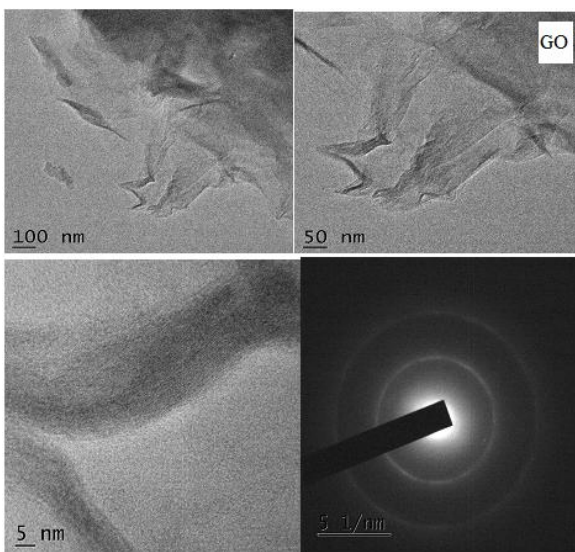


Figure 5: TEM Micrograph of Graphene Oxide (GO)

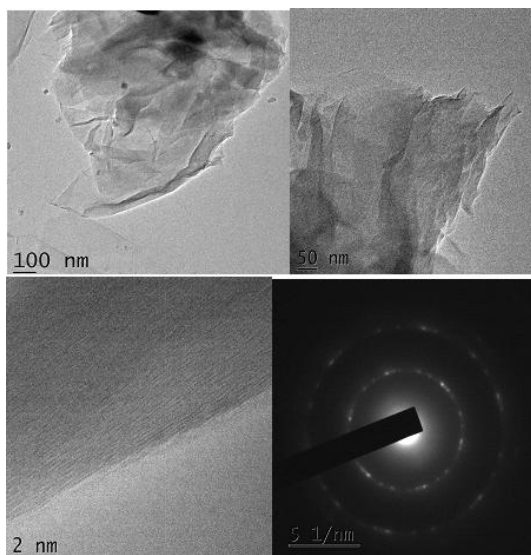


Figure 6: TEM Micrograph of Fluorographene (FG)

The change of ac conductivity (σ_{ac}), dielectric constant (ϵ') and dielectric loss ($\tan \delta$) of GO and FG on frequency are measured at a frequency range of 1000Hz to 1MHz. (Equation 1 to 4) and is presented in Figure 7. The $\tan \delta$ value of GO is 153.37 at low frequency and changes to 100.92 for FG composite. The conductivity of FG is 0.559×10^{-4} mho m^{-1} and GO is 1.705×10^{-4} mho m^{-1} . The dielectric loss represents the energy dissipated from the dielectric system. One could observe the variation of $\tan \delta$ with the frequency. The value of dielectric loss increases with the frequency at room temperature. The dielectric constant (ϵ') and dielectric loss ($\tan \delta$) show the same frequency response. Space charge polarisation is the dominant factor for higher values of ϵ' at a lower frequency. As the frequency changes, the contribution of electronic and atomic contribution dominates [23-28]. Due to this, the dielectric constant is constant after a certain frequency (as the electronic and atomic contributions become most prominent). The ac conductivity also shows high variation with frequency. The incorporation of fluorine in the graphene matrix alters the electrical behaviour drastically; lowering of $\tan \delta$, dielectric strength, and conductivity is noticed.

These findings are in agreement with the energy gap studies. The energy gap is found to be high for Fluorographene compared to graphene oxide. The addition of Fluorine and oxygen tailor the properties of the graphitic system and changes the dielectric behaviour. From the results, we can conclude that the ac conductivity of GO decreases with respect to

functionalisation. These GO and FG can act as an alternative for silicon capabilities which need further studies.

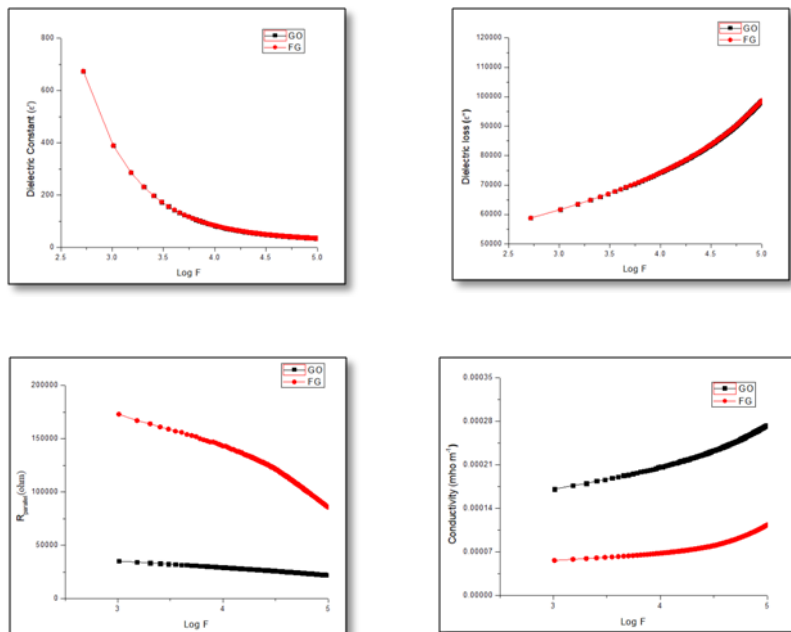


Figure 7: Variation of Different Electrical Parameters with Frequency

5. Conclusion

Graphene Oxide (GO) and Fluorinated graphene are synthesised by modified Hummer's Method and through adeoxyfluorination reaction. The structural characterisation and chemical composition of samples were investigated with XRD and FTIR analysis. The Fourier transfer infrared spectroscopy (FTIR) analysis confirms the formation of Fluorographene. The peak at 1216 cm^{-1} and the shoulder at 1312 cm^{-1} are ascribed to the stretching vibration of covalent C-F bonds and C-F₂ bonds, respectively. The XRD analysis shows a shift in 002 peaks from $2\theta = 26^\circ$ to 11.314° with the incorporation oxygen atom which shows successful oxidation and the new 001 peaks is observed for fluorographene which shows the effective fluorination. The introduction of band gap energy suggests that GO and FG can act as an effective semiconductor and

whose electro-chemical applications are worth investigating. The surface morphology of both functionalised graphene derivatives shows the formation of the layered structure. The present study demonstrates that the change in the conductivity value depends upon the functionalisation of graphene.

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