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Functionalization of Graphene using Carboxylation process

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Abstract

Graphene, the starting material for all the carbon nanostructures has attracted strong scientific and technological interest in recent years. It has shown great promise in many applications, such as electronics, energy storage and conversion (super capacitors, batteries, fuel cells, solar cells, and bioscience/biotechnologies. Graphene is a zero-gap semiconductor material, which is electroactive and transparent. Because of its interesting properties, graphene has found its way into a wide variety of biosensing schemes. It has been used as a transducer in bio-field-effect transistors, electrochemical biosensors impedance biosensors, electrochemiluminescence, and fluorescence biosensors, as well as bimolecular labels.so Functionalization and dispersion of graphene sheets are of crucial importance for their end applications. In our article, we have functionalized Graphene using carboxylation process for its application in biosensors.

*Keywords:-*Graphene, functionalization, carboxylation, FTIR, Raman.

1. Introduction

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. The current interest in graphene can be attributed to three main reasons. First, its electron transport is described by the Dirac equation and this allows access to quantum electrodynamics in a simple condensed matter experiment [1–5]. Second, the scalability of graphene devices to nano dimensions [6–10] makes it a promising candidate for applications, because of its ballistic transport at room temperature combined with chemical and mechanical stability. Remarkable properties extend to bilayer and few-layers graphene [4–6, 8, 11]. Third, various forms of graphite, nanotubes, buck balls, and others can all be viewed as derivatives of graphene and, not surprisingly, this basic material has been intensively investigated theoretically for the past 60 years [12]. These properties have result in the application of graphene in different areas like field effect transistor, spin electronics, biosensors, lasers, photo detectors, as MRI contrast agent etc. [13-17]. Carbon might be the most widely-used material in electroanalysis and electro catalysis. For example, carbon nanotubes have shown excellent performance in biosensors, biofuel cells, and polymer electrolyte membrane (PEM) fuel cells. Graphene-based electrodes have shown superior performance in terms of electro catalytic activity and macroscopic scale conductivity than carbon nanotubes based ones. These indicate that the opportunities in electrochemistry encountered by carbon nanotubes might be available for graphene. Graphene exhibits excellent electron transfer promoting ability for some enzymes and excellent catalytic behaviour toward small biomolecules such as H_2O_2, NADH, which makes graphene extremely attractive for enzyme-based biosensors, e.g. glucose biosensors and ethanol biosensors [18].

Functionalization and dispersion of graphene sheets are of crucial importance for their end applications. Chemical functionalization of graphene enables this material to be processed by solvent-assisted techniques, such as layer-by-layer assembly, spin-coating, and filtration. It also prevents the agglomeration of single layer graphene during reduction and maintains the inherent properties of graphene [19].

Because of its interesting properties, graphene has found its way into a wide variety of biosensing schemes. It has been used as a transducer in bio-field-effect transistors, electrochemical biosensors impedance biosensors, electrochemiluminescence, and fluorescence biosensors, as well as bimolecular labels. In our work, we have functionalized Graphene using process of carboxylation for its application in biosensors

In this paper we are functionalizing graphene by the use of 2 type of carboxylation process and the success of process is confirmed by Fourier transform infrared spectroscopy and Raman spectroscopy. After this graphene has been utilized to explore its application in electrochemical biosensors.

2. Experimental

There are two methods that we have used for the carboxylation of graphene.

In first process of carboxylation we used technique that will give us required COOH group for carboxylation. So for that we used 10 mg of graphene 7 mg of which was added to added 30 ml H_2SO_4 and remaining 3mg was added to 10 ml HNO_3 (3:1 ratio 30 ml of H_2SO_4 and 10 ml of HNO_3). And then both were mixed together and left for 10min then this process was followed by sonication for 3-4 hours. Next step was of centrifugation for 1 hour at 22000 rpm, and then we decanted the supernatant and added distilled water to the graphene pellets. Now again we centrifuged for 1 hour at 2200 rpm, and this process was repeated five times so that ph. 7 is achieved then we decanted the supernatant and added ethanol to the graphene pellets. Again centrifuged and decanted the supernatant and allowed the graphene to dry.

Graphene produced was stored in room temperature and its characterization was carried out using techniques of Fourier transform infrared spectroscopy and Raman spectroscopy.

In second process 10 mg of graphene oxide was taken that was sonicated for 3 hours with excess of Trichloroacetic acid. After this solution was diluted by adding D.I. water upto five times the amount of acid taken so to balance ph. range for further process. Solution was then filtered through hydrophilic 0.2μ Millipore filter paper and washed 5 times with distilled water the filtration process took 2hours. Carboxylated graphene was dried under vacuum at 50°C.The powder of graphene was stored at room temperature. Further characterization was carried out using techniques of Fourier transform infrared spectroscopy and Raman spectroscopy.

3. RESULTS & DISCUSSIONS

Fourier Tranform Infrared Spectroscopy(FTIR): When infrared 'light' or radiation hits a molecule, the bonds in the molecule absorb the energy of the infrared and respond by vibrating. Commonly, scientists call the different types of vibrations bending, stretching, rocking or scissoring.an IR spectrometer has a source, an optical system, a detector and an amplifier. The source gives off infrared rays; the optical system moves these rays in the correct direction; the detector observes changes in the infrared radiation, and the amplifier improves the detector signal [20].

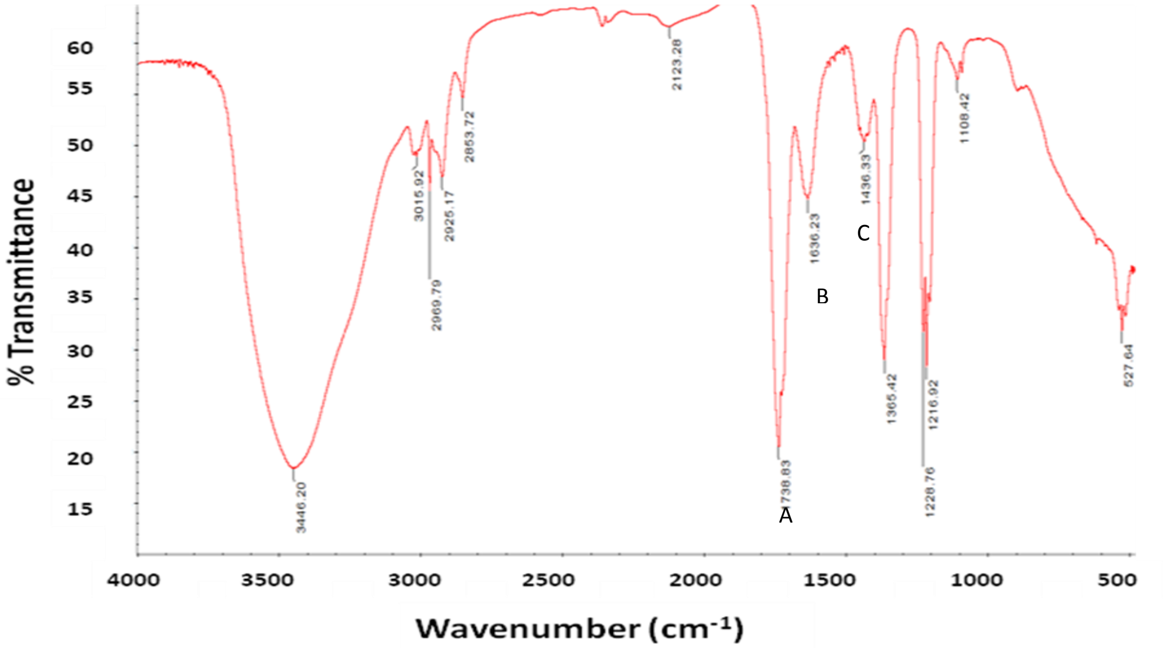

Figure. 1 FTIR spectrum of carboxylated graphene (A) C=O stretch 1700-1740 cm $^{-1}$ (B) N-H bend 1640-1550 cm^{-1} (C) O-H bend 1440-1400 cm^{-1}

Table 1. showing most common IR frequencies and bond stretches [20]. IR spectroscopy identifies molecules based on their functional groups. The chemist using IR spectroscopy can use a table or chart to identify these groups.

IR Frequency	Bond and functional group
3500–3200	O–H stretch in phenols
3400–3250	N–H stretch in amines, amides
3300–2500	O–H stretch in carboxylic acids
3330–3270	–C?C–H (alkyne H)
3100–3000	=C–H stretch (alkene H)
3000–2850	-C–H stretch (alkane H)
2830–2695	C–H stretch in aldehydes
2260–2210	C?N stretch (nitrile)
2260–2100	–C?C– stretch in alkynes
1760–1665	C=O stretch carbonyls (general)
1760–1690	C=O stretch in carboxylic acids
1750–1735	C=O stretch in esters
1740–1720	C=O stretch in aldehydes
1715	C=O stretch in ketones
1680–1640	–C=C– stretch in alkenes

Raman spectroscopy: This is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system[20]. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down[21]. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line due to elastic Rayleigh scattering [22] are filtered out while the rest of the collected light is dispersed onto a detector.

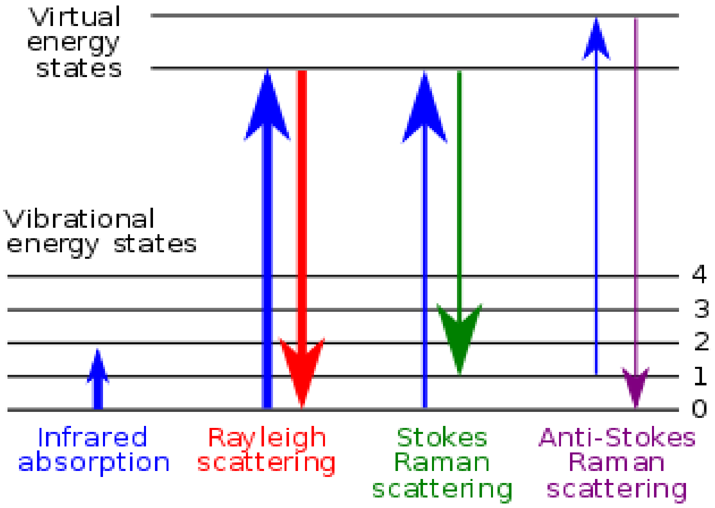

Figure.2 Energy level diagram showing the states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.

G-band is the primary mode in graphene. It represents the planar configuration sp2 bonded carbon that constitutes graphene. As the layer thickness increases, the band position shifts to lower energy representing a slight softening of the bonds as the layer thickness increases.

The D-band is known as the disorder band or the defect band. The band is the result of a one phonon lattice vibrational process. The band is typically very weak in graphite and is typically weak in graphene as well. If the D-band is significant, it indicates that there are a lot of defects in the material.

2D band is sometimes referred to as the G′-band when discussing similar materials such as carbon nanotubes. It is the result of a two phonon lattice vibrational process.

G Band

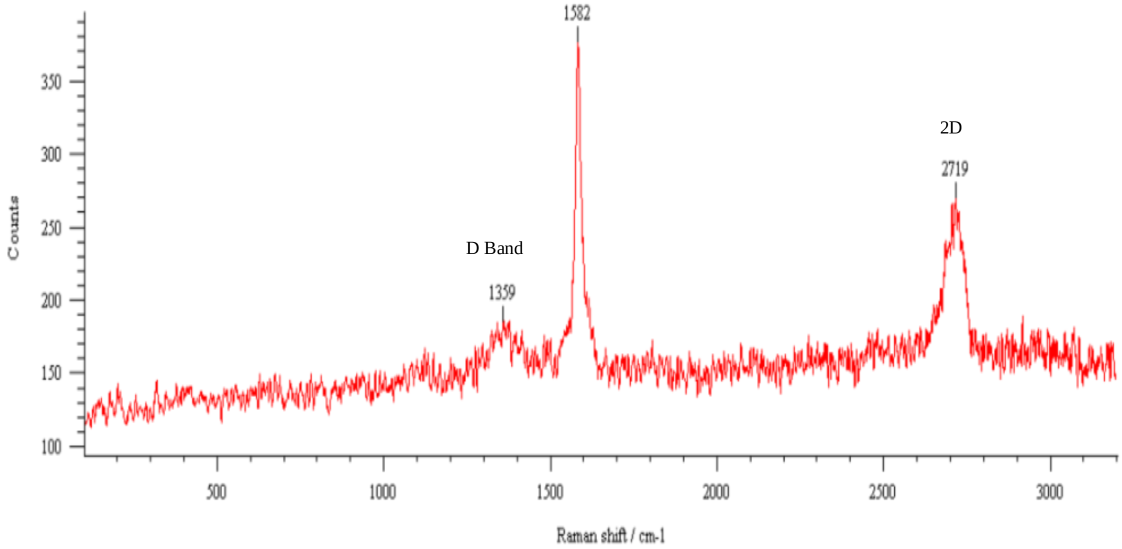

Figure.3 Raman spectroscopy of pristine graphene. Here G-band shows primary mode in graphene and D-band is minimum.

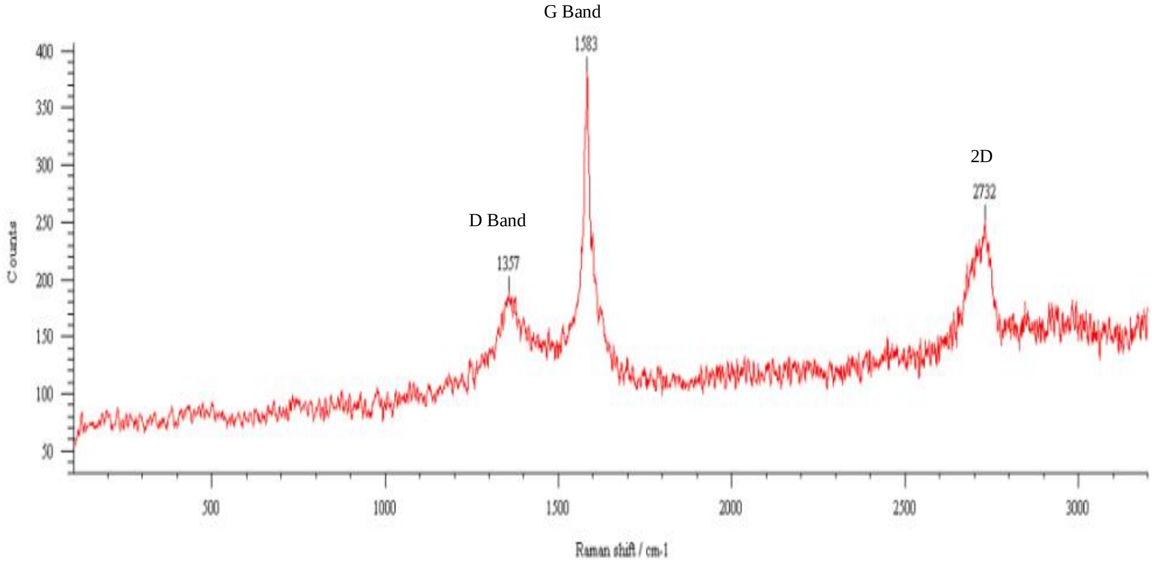

Figure 4 Raman spectroscopy of carboxylated graphene Here G-band shows primary mode in graphene and D-band is significant showing that defects in graphene are present which confirms the functionalization of graphene.

4. CONCLUSIONS

We have presented the carboxylation of graphene with the help of 2 processes and received the same results of characterization confirming that carboxylation is possible with both the methods but out of the two methods first process is better because it has more yield of carboxylated graphene. The research signifies that carboxylated graphene produced can be successfully used further for its application as a sensitive electrochemical biosensor.

This method is suitable for carboxylation of graphene at large-scale production using relatively inexpensive technology. And graphene produced can be stored easily at room temperature

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