

SYNTHESIS OF GRAPHENE OXIDE

ABSTRACT

Graphene is a single sheet of sp^2 bonded carbon having a two-dimensional (2D) layer. It has remarkable electronic, mechanical and thermal properties. In this paper, the graphene oxide (GO) was synthesized using improved Hummers method (Tour method) and then characterized by Raman spectroscopy. Raman spectroscopy results were showed that there are some defects or disorder present in the material's structure, but it is not highly disordered, thereby suggests a good degree of oxidation in the sample; thereby reconfirms the prepared sample is graphene oxide.

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CHAPTER 1: INTRODUCTION

Carbon, one of the earth's most abundant and intriguing elements, appears in different allotropes, has attracted research attention for centuries. Graphene is defined as a single atomic layer, two dimensional allotrope of carbon. It is the strongest known material to the mankind per unit size with incredible properties. Graphene is an extremely diverse material, and can be combined with other elements to produce different materials with various superior properties. Researchers all over the world continue to constantly investigate graphene to learn its various properties and various applications.

1.1 A BRIEF HISTORY OF GRAPHENE

It is well known that graphene's history spans more than a century of chemical research. Delving into its history reveals a tale of groundbreaking achievements that have shaped the course of modern technology.

- Graphite ore was found and mined in England in the sixteenth century.
- German scientist, Verner coined the name graphite (a Greek word for writing).
With the development of pencil industry, it has been used as a writing material in pencil since eighteenth century.
- The term “graphene” first appeared in 1987 to describe single sheets of graphite as one of the constituents. The term “graphite layers” was replaced with “graphene” by the IUPAC commission.
- In 1859, a British chemist, Benjamin Bordie, prepared a highly lamellar structure by thermally reducing graphite oxide by reacting graphite with potassium chlorate and fuming nitric acid, resulting in the formation of a suspension of graphene oxide crystallite.
- An early study of the properties of graphene oxide paper was completed by Kohlschutter and Haenni in 1919.
- Wallace (1947), while trying to study the electronic properties of three dimensional graphite, came up with the band theory of graphite.

- The next milestone work regarding graphene was the publication of the first TEM image of a few layers of graphene by Ruess and Vogt (1948).
- Hanns-Peter Boehm and his coworkers isolated and identified single graphene sheets in 1961.
- However, efforts to epitaxially grow few-layer graphene through the chemical vapor deposition of hydrocarbons on metal substrates (Land et al.1992 and Nagashima et al.1993) and on top of other materials (Oshima and Nagashima 1997) as well as by thermal decomposition of SiC have also been successful.
- There have been number of efforts to make very thin films of graphite by mechanical exfoliation from 1990 to 2004, but nothing thinner than fifty to 100 layers was produced during these years.
- In 2004, Andre Geim and Kostya Novoselov at Manchester University, UK; managed to extract single-atom-thick crystallites (graphene) from bulk graphite and transferred them onto thin silicon dioxide on a silicon wafer by a famous Scotch Tape technique. Though graphene was known earlier, it would not be an exaggeration to write that Geim and Novoselov rediscovered graphene in its new incarnation. They received the Nobel Prize in physics in 2010.
- In 2005 the Anomalous Quantum Hall Effect was detected, showing the massless nature of charge carriers in graphene by Novoselov et al. (2005) and Zhang et al. (2005).
- In 2008 Bolotin et al. demonstrated extremely high carrier mobility in suspended graphene.
- In January 2010, IBM researchers created a tuneable electrical band gap (up to 130meV) for their bi-layer graphene field-effect transistors (FET).
- Samsung, which started research and development on graphene in 2009, managed to fabricate a 30” graphene sheet by roll-to-roll process, and later in 2011, produced a 40” graphene sheet.
- In 2011 Vorbeck Materials made graphene-based ink to develop a Siren alarm (security) tag, the world’s first graphene-based ink product.
- 2011 saw another applicable output of graphene. Dickerson’s group created a film of graphene oxide that either causes water to bead up and “run off ” or alternatively be spread out in a thin layer. As graphene sheets are transparent, this film can be used in car windshields, water-repellent clothes, self-cleaning glasses, which were developed by Dickerson’s group.

- 2012 and 2013 saw much commercial growth and developments in Graphene technology:
 - Bluestone Global Tech started producing 24” by 300” Graphene films on copper.
 - HEAD developed a graphene racket.
 - Vorbeck and PNNL started marketing graphene-based Lithium-ion batteries
 - Cabot launched a graphene-based additive for high density Lithium-ion batteries
 - Durham graphene Science raised £1.2 million to commercialize graphene mass production.
 - IBM developed a graphene-based Terahertz frequency photonic filter and polarizer.
 - Sony could produce a 100 meter long graphene sheet with a new R2R method.
 - The National University of Singapore invested \$11 million in a graphene production facility.

1.2 STRUCTURE OF GRAPHENE AND GRAPHENE OXIDE

1.2.1 Structure of Graphene

Graphene is consisting of a single layer of carbon atoms arranged in a hexagonal lattice nanostructure. The name is derived from “graphite” and the suffix -ene, reflecting that the graphite allotrope of carbon contains numerous double bonds. Graphene is fundamentally one single layer of graphite; a layer of sp^2 bonded carbon atoms arranged in a honey comb (hexagonal) lattice. Each atom in a graphene sheet is connected to its three nearest neighbours by σ -bonds and a delocalised π -bond, which contributes to a valance band that extends over the whole sheet. This is the same type of bonding seen in carbon nanotubes and polycyclic aromatic hydrocarbons, and (partially) in fullerenes and glassy carbon. The valance band is touched by a conduction band, making graphene a semimetal with unusual electronic properties that are best described by theories for massless relativistic particles. Charge carriers in graphene shows linear, rather than quadratic dependence of energy on momentum; and field effect transistors with graphene can be made that show bipolar conduction.

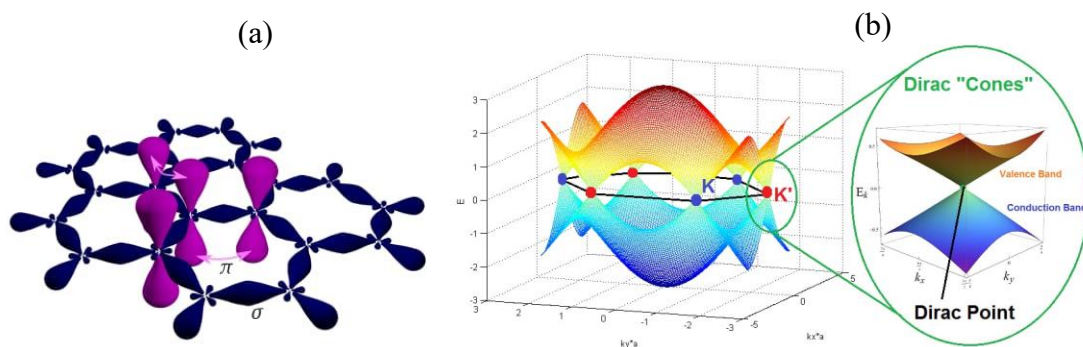


Fig 1.1 (a) Hybridisation in graphene,
(b) energy band diagram of graphene (Courtesy: Muonray)

Graphene is observed in the form of a plane of atoms with a molecular bond length of 0.142 nanometres. Three of the four outer-shell electrons of each atom in a graphene sheet occupy three sp^2 hybrid orbitals; s , p_x , and p_y ; that are shared with the three nearest atoms, forming σ -bonds. The length of these bonds is about 0.142 nanometres. The remaining outer-shell electrons occupies a p_z orbital that is oriented perpendicular to the plane (Fig 1.1a). These orbitals hybridize together to form two half-filled bands of free-moving electrons, π and π^* , which are responsible for most of graphene's notable electronic properties. Graphene sheets stack to form graphite with an interplanar spacing of 0.335nm. Several sheets stacked one on top of the other are regarded as multilayer graphene, up to the layer where the material becomes graphite. Graphite, a 3D crystal composed of weakly coupled graphene layers, is relatively common material – used in pencil tips, batteries and more.

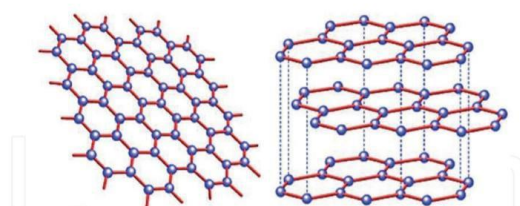


Fig 1.2 Structure of graphene sheet and stacked graphene (Courtesy: Neto, Guniea, Peres NMR; Drawing conclusions from graphene world. Physics World 2016)

The hexagonal lattice structure of isolated, single-layer graphene can be directly seen with transmission electron microscopy (TEM) of sheets of graphene suspended between bars of a metallic grid. Some of this image showed a “rippling” of the flat sheet, with an amplitude of about one nanometre. These ripples may be intrinsic to the material as a result of the instability of two dimensional crystals, or may originate from the ubiquitous dirt seen in all TEM images

of graphene. The hexagonal structure is also seen in scanning tunnelling microscope (STM) image of graphene supported on silicon dioxide substrates. The rippling seen in these images is caused by conformation of graphene to the substrate's lattice, and is not intrinsic.

Graphene is a zero-gap semiconductor, because its conduction and valence bands meet at the Dirac points (Fig 1.1 b). In order to get more insight into the electronic structure of graphene, which is the basic reason for its unusual behaviour, a more detailed consideration of the band structure is important. The hexagonal lattice of graphene is shown in the top of Fig. 1.3a, with a two-atom basis indicated by the diamond. The lattice thus has sublattices A and B.

Bonding in a graphene can be compared with its building block, a single benzene ring, where the in-plane bonding is due to bonds made from the p_{xy} orbitals, while the remaining p_z orbital, perpendicular to the plane and odd under inversion, forms the π and π^* bands. The presence of two sublattices leads to two sets of bands that cross at the K point; the crossing is not inhibited because they belong to different irreducible representations of the space group.

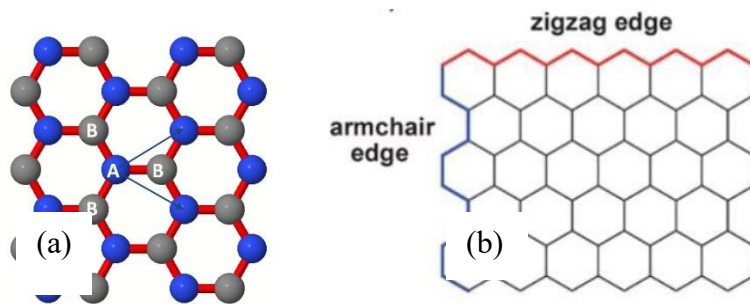


Fig 1.3 (a) hexagonal lattice of graphene with basis of two carbon atoms A and B, (b) two types of edges in graphene flake

It is also evidenced from STM analysis that edges of graphene can exhibit higher electronic density of states (DOS) near Fermi level than the basal planes. The edge configurations locally determine the distribution of electrons, and thus the selection of crystallographic orientation of graphene is of crucial importance for controlling its electronic properties in localized states. Zigzag and armchair are two main types of edges along the crystallographic directions in graphene (Fig 1.3 b).

The term graphene theoretically refers to monolayer graphene and sometimes also includes bilayer graphene, as both of them are semimetals with no overlap between the valence and conduction bands. The electronic structure of few-layer graphene (FLG, number of layers from 3 to < 10), is more complex because of the appearance of charge carriers. It has been shown

that the electronic structure of graphene rapidly evolves with the number of layers, approaching the 3D limit of graphite at 10 layers.

Graphene is one of the first and most famous examples of a 2D crystal. Two-dimensional materials and systems are fundamentally different from three-dimensional ones in many ways. Graphene can be used as a model system for studying two-dimensional physics and chemistry in general, and so has been attracting much academic interest since its isolation in 2004. It is also considered to have tremendous potential for a myriad of applications, like next-gen batteries, sensors, solar cells etc.

1.2.2 Structure of Graphene Oxide

Graphene oxide (GO) is a unique material that can be viewed as a single monomolecular layer of graphite with various oxygen-containing functionalities such as epoxide, carbonyl, carboxyl, and hydroxyl groups. Graphene oxide is an oxidized form of graphene, laced with oxygen containing groups. The key difference between graphene and graphene oxide is that graphene is a substance made of carbon atoms bonded to each other in a repeating pattern of hexagons, whereas graphene oxide is an oxidized form of graphene that is laced with groups having oxygen atoms.

Following oxidation of graphene, GO material (Fig 1.4) is found to be highly inhomogeneous with respect to structure. Three major features are present: holes (indicated in blue), graphitic regions (indicated in yellow), and high contrast disordered regions (indicated in red), indicating areas of high oxidation, with approximate area percentages of 2%, 16%, and 82%, respectively. Holes form in GO, as CO and CO₂ are released during the aggressive oxidation and sheet exfoliation, found here to be usually less than 5 nm. Although some high resolution electron microscopy studies have not reported holes in GO samples; a high resolution aberration corrected electron microscopy study of the reduced form of GO has observed similar holes. A closer examination of graphene oxide using TEM imaging gives a high contrast structure and 1.4 Å atomic spacing of graphene. The disordered, high contrast oxidized regions of the basal plane form a continuous network throughout the GO sheet.

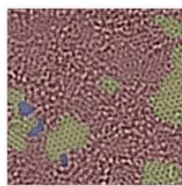


Fig 1.4 TEM image of single suspended sheet of GO (Courtesy: Determination of the Local Chemical Structure of GO & rGO; Erickson, Erni, Lee, Alem, Gannet, and Zettl)

The first model by Hofmann and Holst in 1939 describes a flat carbon sheet randomly bonded with epoxy groups with a C/O ratio of 2. Then in 1946, Ruess's group introduced the hydroxyl groups and 1,3-ether to the lattice. Scholz-Boehm model completely replaces the epoxide groups with hydroxyl groups. Nakajima and Matsuo 1994, built a lattice framework akin to poly (C₂F)_n which forms a stage-2 graphite intercalation compound. However, the latest two models proposed by Lerf-Klinowski and Dekany have become most popular because the SSNMR analysis was introduced into GO structure characterization. This new technique has improved the accuracy in detecting the functional groups on GO. In the Lerf-Klinowski (LK) model, tertiary alcohols and 1,2-ethers are dominant groups on the GO surface. The LK model discards the periodic crystal structure and substituted by the randomly distributed oxygen groups. They also suggested that the alkenes (C=C) in GO are probably either aromatic or conjugated and ketones are more preferable at the edge of GO. Later, Dekany proposed a model following the basic logic of Scholz-Boehm model, but adding 1, 3-ethers into the cyclohexane rings. Their conclusion indicates that only the LK model fits best with the experiment results while all other models were excluded due to their inconformity. But due to the computation complexity, the size of the LK model used in calculation was simplified and limited in size. Therefore, the precise distribution of functional groups and the edge structure are still controversial.

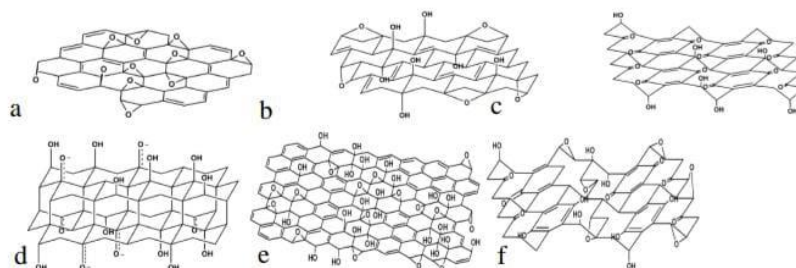


Fig 1.5 GO Structure models : (a) Hofmann model; (b) Ruess model ; (c) Scholz-Boehm model; (d) Nakajima-Matsuo model; (e) Lerf-Klinowski model; (f) Dekany model (Courtesy: T. Sazbo, Bereski, et al.; Evolution of Surface Functional Groups in a Series of Progressively Oxidised Graphene Oxides)

Apart from the experimental results, the theoretical characterization of the GO structure can give us a new perspective into the detail structure of GO. Lahaye et al. calculated the hydroxyl and epoxy system in 2×2 GO cell using density functional theory (DFT) where they found that the 1,3- ether are not likely to exist because of the joint binding energy and the single epoxy and hydroxyl prefer staying in close proximity. Boukhvalov and Katsnelson proposed a chainlike structure and found the band gap increased with the increasing oxygen coverage. They also discovered that graphene has a high flexibility as the chemisorption results in 5Å (radius) distortions of the graphene sheet for the presence of a single hydrogen atom. As for the chemisorption of two hydrogen atoms, the most energetic favourable configuration is that two hydrogen are bonded to neighbouring carbons from the opposite sheet sides. And the complete coverage of hydrogen atoms can minimize the total energy of graphene sheet . This result was also theoretically confirmed by Yan and Chou using MD (Molecular Dynamics) simulations and the transformation of hydroxyl and epoxy groups into carbonyl group during thermal annealing was revealed. The importance of hydrogen bonding was also proposed by Paci et al. in their Monte Carlo simulations. Also, epoxide groups were observed to migrate on the basal plane in processes often stabilized by hydrogen bonding or catalysed by hydrogen transfer reactions between the mobile epoxide oxygen and neighbouring functional groups. Li et al. found that epoxy pairs aligning in line in graphene oxide plane are likely to form carbonyl pairs and then lead to the “unzip” of the GO sheet. This result suggests a way to get a smooth GO edge by controlled oxidation process.

In spite of such many theoretical models, the real structure of GO still remains controversial. One reason may be that these models arrange the oxygen groups manually in a fixed cell within a limited scale. But the real GO is non-stoichiometric and non-periodic in the long range.

1.3 PROPERTIES OF GRAPHENE

There are many fascinating properties related with graphene that makes it different from other materials. The properties can be classified as electronic properties, mechanical properties, electrical properties, thermal properties, and optical properties.

1.3.1 Electronic Properties

As a consequence of the graphene structure, the first Brillouin zone has two conical points K and K' (called Dirac points), where a band crossing occurs. Near these crossing point, the

electron energy E is linearly dependent on the wave vector. Experimental observation of the cyclotron mass dependence on the square root of the electronic density in graphene was interpreted as evidence for the existence of massless Dirac quasiparticles in graphene. Dirac quasiparticles are low energy excitons described by pseudo-relativistic Dirac equation. As a zero band gap semiconductor, graphene displays an ambipolar electric field effect and charge carriers can be tuned continuously between electrons and holes in concentrations as high as 10^{13} cm^{-2} with room temperature mobilities of up to $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Moreover, the observed mobilities depend weakly on temperature, suggesting that an ultrahigh mobility could be realized in graphene at room temperature. The mobility in graphene remains high even at high carrier density in both electrically and chemically doped devices displaying the evidence of ballistic transport (unimpeded flow of charge carriers over long distances) on the sub-micrometer scale. Another measure of the electronic quality of graphene is whether the quantum Hall effect (QHE) can be observed at room temperature. QHE is the phenomenon of voltage changes in jumps, as the applied magnetic field changes.

The “half-integer” QHE observed in graphene (Figure 1.7a), with the Hall conductivity expressed as $\sigma_{xy} = \pm (4e^2/h) (N + (1/2))$ where N is the Landau level index, can be understood based on the massless Dirac fermions in graphene. The energy quantization of the graphene electronic structure in a magnetic field with a field strength B is described by

$E_N = \pm v_F \sqrt{(2\hbar B N)}$, where \pm refers to electrons and holes. Of particular importance is the existence of a zero-energy state at $N = 0$ (as shown in Figure 1.7c), which is shared by electrons and holes, leading to the QHE in graphene. From STM studies on graphene grown on SiC, the discrete, non-equally-spaced Landau level spectrum, including the hallmark zero-energy state of graphene, was observed.

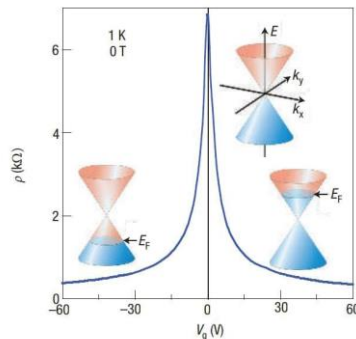


Fig 1.6 : Ambipolar electric field effect in single-layer graphene. The insets show its conical low-energy spectrum $E(k)$, indicating changes in the position of the Fermi energy E_F with changing gate voltage V_g . Positive (negative) V_g induce electrons (holes) in concentration

$n=\alpha V_g$. The rapid decrease in resistivity ρ on adding charge carriers indicates their high mobility. (Courtesy: *The Rise of Graphene*; Geim & Novoselov)

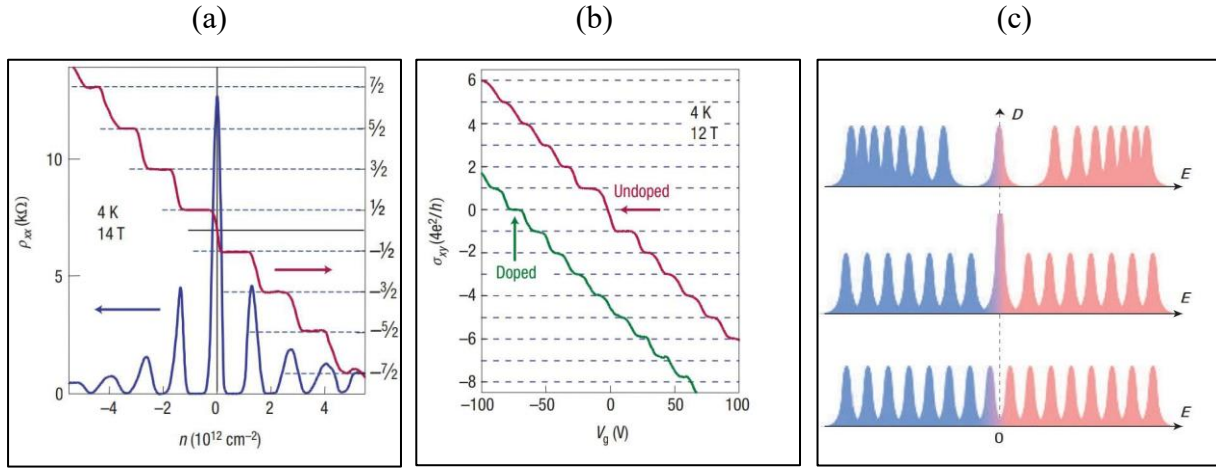


Fig 1.7

(a) The hallmark of massless Dirac fermions is QHE plateau in σ_{xy} at half integers of $4e^2/h$;
(b) Anomalous QHE for massive Dirac fermions in bilayer graphene is more subtle (red curve). σ_{xy} exhibits the standard QHE sequence with plateaux at all integer N of $4e^2/h$ except for $N=0$. The missing plateau is indicated by the red arrow. The zero- N plateau can be recovered after chemical doping, which shifts the neutrality point to high V_g so that an asymmetry gap ($\approx 0.1 \text{ eV}$ in this case) is opened by the electric field effect (green curve);
(c) Landau levels in the density of states D in graphene are described by E_N proportional to \sqrt{N} for massless Dirac fermions.

(Courtesy: *The Rise Of Graphene*; Geim & Novoselov)

1.3.2 Mechanical Properties

The mechanical properties of monolayer graphene including the Young's modulus and fracture strength have been investigated by numerical simulations. The Young's modulus of few layer graphene was experimentally investigated with force-displacement measurements by atomic force microscopy (AFM). Circular membranes of few-layer graphene were also characterized by force-volume measurements in AFM. Recently, the elastic properties and intrinsic breaking strength of free-standing monolayer graphene were measured by nanoindentation using an AFM. It was reported that defect-free graphene has a Young's modulus of 1.0 TPa and a fracture strength of 130 GPa. Monolayer GO (produced by a modified Hummer's method) with a Young's modulus of 207.6 GPa, with an error of 23.4 GPa still notably high. The Chemically

Modified Graphene (CMG) obtained by reducing graphene oxide with a hydrogen plasma exhibited a mean elastic modulus of 0.25 TPa with a standard deviation of 0.15 TPa. A ‘paper-like’ material made by flow-directed assembly of individual graphene oxide platelets has been reported. The average elastic modulus and the highest fracture strength obtained were ~ 32 GPa and ~ 120 MPa respectively. The mechanical properties of this ‘graphene oxide paper’ were improved by introducing chemical crosslinking between individual platelets using divalent ions and polyallylamine. In addition, a paper composed of stacked and overlapped reduced graphene oxide platelets was obtained by controlled reduction of graphene oxide dispersions with hydrazine. After annealing, its stiffness and tensile strength were higher than those of graphene oxide papers.

1.3.3 Electrical Properties

Graphene is an electrically conductive material with high electron mobility ($25\text{m}^2\text{V}^{-1}\text{s}^{-1}$) and electrical conductivity (6500Sm^{-1}). Graphene has been shown to greatly improve the electrical conductivity of polymers at low filler contents (e.g., 0.1Sm^{-1} at 1 vol% in polystyrene). In the general fabrication of GO, the process results in disruption of the sp^2 bonding orbitals of graphene and the addition of abundant surface groups that inhibit its electrical conductivity, making GO electrically resistive ($1.64 \times 10^4\ \Omega\text{m}$).

Upon reduction, the electrical conductivity of GO can be greatly improved and can be tuned over several orders of magnitude with conductivities ranging from $\sim 0.1\text{Sm}^{-1}$ to $2.98 \times 10^4\text{Sm}^{-1}$. Even after reduction, the reduced GO (rGO) contains residual sp^3 bonded carbon to oxygen, which disturbs the movement of charge carriers through the rest of the sp^2 clusters.

1.3.4 Thermal Properties

Like its electrical conductivity, synthesized GO from graphite has a low thermal conductivity of 0.5 to $1\text{Wm}^{-1}\text{K}^{-1}$ making it not an ideal option for most applications requiring good thermal properties. Graphene, on the other hand, has been shown to have one of the highest in-plane thermal conductivities of known materials, with a thermal conductivity of ~ 3000 to $5000\text{Wm}^{-1}\text{K}^{-1}$. As a result, reduction of GO is critical for incorporation of rGO into polymers to improve their thermal conductivity. Producing rGO films by annealing GO at high temperature (1000

°C) can significantly improve the in-plane thermal conductivity, showing an improvement from ~ 3 to $61 \text{ Wm}^{-1} \text{ K}^{-1}$. The films showed an interesting anisotropy in terms of thermal conductivity as the cross-plane thermal conductivity decreased to $\sim 0.09 \text{ Wm}^{-1} \text{ K}^{-1}$ and showed a ratio of the two (in-plane/cross-plane thermal conductivity) of 675. The incorporation of rGO into polymers has led to profound improvements in the thermal conductivity of the resultant nanocomposites. The enhanced thermal conductivity was believed to be a result of the high conductivity of the rGO, which was able to provide a path of lower thermal resistance for traveling phonons. Other important factors to improved thermal conductivity would be for high orientation of the rGO sheets and large sheet size that limits the thermal transfer along boundaries. rGO has also been shown to improve the thermal properties of many other polymer systems including PVA and styrene butadiene rubber. In some instances, it is useful to provide high thermal insulation properties such as in-home insulation and in flame retardants. GO has recently been shown to be an effective filler to improve the flame retardant properties of various polymer nanocomposites.

1.3.5 Optical Properties

The optical transmittance T and reflectance R for graphene are $T = (1 + 0.5\pi\alpha)^{-2}$ and $R = 1/4\pi^2\alpha^2 T$ for normal incidence light (where $\alpha = 2\pi e^2 / hc \approx 1/137$, e is the electron charge, c the light speed, and h Planck's constant); the opacity is $A = (1 - T) \approx \pi\alpha \approx 2.3\%$.

The optical absorption of graphene layers varies linearly to number of layers and each layer absorb 2.3%. The expression of T and R in terms of fundamental constants that do not directly involve material parameters is stated to be a result of the structure and electronic properties of graphene. The constant transparency ($\sim 97.7\%$) has been experimentally observed for graphene in the visible range and the transmittance linearly decreases with the number of layers for n -layer graphene.

Inter-band optical transitions in graphene also have been reported. The relaxation and recombination of photo-generated electron-hole pairs in graphene occurs on a timescale of tens of picoseconds, depending on the carrier concentration of graphene. Given the high carrier transport velocity even under a moderate electrical field, an ultrafast (up to 40 GHz) and efficient (6–16% internal quantum efficiency) photo response has been observed for graphene field effect transistors (FET), suggesting graphene-based highspeed optoelectronic devices for communications, detection, sensing, and so on.

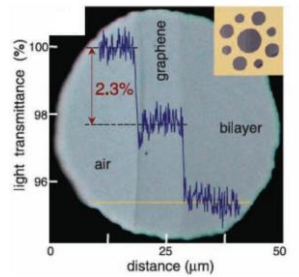


Fig 1.8 Photograph of graphene in transmitted light. This one atom thick crystal can be seen with the naked eye because it absorbs approximately 2.3% of white light. (Courtesy: 2008 American Asso. for the Advancement of Science)

1.4 APPLICATIONS OF GRAPHENE

The vast number of products, processes and industries for which graphene could create a significant impact all stems from its amazing properties. Some of the fields where these properties are applied are discussed below:

1.4.1 Electronics and Optoelectronics

Transistors: Traditional silicon transistors have limitations in terms of size and power consumption, which hinders the advancement of electronics. Graphene-based field-effect transistors (GFETs) offer a solution by providing excellent electron mobility, allowing for faster and more efficient switching of electrical signals. This property makes them suitable for high-speed electronics and potentially enables the development of faster and smaller electronic devices.

Flexible Electronics: Graphene's unique mechanical properties make it highly flexible, making it ideal for use in flexible displays and wearable electronics. These devices can be bent,

rolled, or stretched without compromising performance, opening up a new realm of possibilities for portable and wearable technology.

Sensors: Graphene-based sensors have garnered significant interest due to their high sensitivity and specific surface area. They can be designed to detect various substances, including gases, chemicals, and biological molecules. Such sensors find applications in environmental monitoring, medical diagnostics, and industrial safety. Graphene is utilized in biodevices as a sensor for single bacteria recognition, label-free DNA detection, and a polarity-specified molecular transistor for protein/DNA adsorption.

1.4.2 Energy Storage

Batteries: Graphene's high electrical conductivity and large surface area make it an excellent material for enhancing lithium-ion batteries' performance. By using graphene-based materials as an electrode, batteries can achieve higher energy density, faster charging times, and improved cycle life. Graphene enhanced Li-ion batteries show incredible characteristics such as longer lifespan, higher capacity, and faster time as well as flexibility and lightness, so that it could be used in wearable electronics.

Supercapacitors: Supercapacitors store energy through the adsorption of ions on their surface. Graphene's high surface area and electrical conductivity make it an ideal material for supercapacitors, providing rapid energy storage and release.

1.4.3 Composite Materials

Reinforcement: The addition of small amounts of graphene to composite materials, such as polymers or metals, can significantly enhance their mechanical properties. Graphene's inherent strength and stiffness improve the overall toughness and strength of the composite, making it suitable for a wide range of applications, including aerospace, automotive parts, and sports equipment.

Thermal Management: Graphene's exceptional thermal conductivity makes it a promising material for improving the thermal management of composites. By incorporating graphene into

materials used in electronic devices, such as smartphones or computers, heat dissipation can be more efficient, leading to improved performance and reliability.

1.4.4 Medical and Biological Applications

Drug Delivery: Graphene's large surface area and ability to be functionalized with various molecules make it a promising candidate for drug delivery systems. Drugs can be loaded onto graphene-based carriers, which can then be targeted to specific cells or tissues. This approach allows for controlled and targeted drug release, reducing side effects and improving treatment efficacy.

Water Filtration: Graphene-based membranes have shown great promise in water filtration applications. Their atomic thickness and excellent permeability allow them to selectively filter out contaminants, such as salts, heavy metals, and organic molecules, while allowing water molecules to pass through. This could potentially lead to more efficient and cost-effective water purification methods.

1.4.5 Aerospace and Defence

Lightweight Materials: Aerospace industries constantly seek ways to reduce the weight of aircraft and spacecraft to improve fuel efficiency and performance. Graphene's exceptional strength-to-weight ratio makes it an attractive material for developing lightweight components for aircraft and spacecraft, reducing fuel consumption and emissions.

Sensors: Graphene-based sensors have various applications in aerospace and defence, including aircraft structural health monitoring. These sensors can detect stress, strain, and other environmental changes in critical components, ensuring early detection of potential issues and enhancing safety.

1.4.6 Environmental Applications

Pollution Control: Graphene-based materials can be used for air and water purification. Graphene's large surface area and adsorption capacity enable it to effectively remove

pollutants, such as volatile organic compounds (VOCs), heavy metals, and other toxic substances from the environment.

Solar Cells: Graphene's electrical conductivity and light-absorbing properties have the potential to improve the efficiency of solar cells. By incorporating graphene into solar cell designs, it may be possible to enhance charge transport and light absorption, leading to more efficient energy conversion. In 2007, researches from MIT have managed to apply Graphene successfully on a solar cell.

1.5 SOME GENERAL APPLICATIONS OF GRAPHENE OXIDE

1.5.1 Environmental Applications of GO

One of the biggest threats to the environment is air pollution caused by the industrial release of harmful gases such as CO₂, CO, NO₂, and NH₃. GO is capable of covalent or noncovalent interactions with various molecules. GO can be employed in catalysis for converting polluting gases during industrial processing. The elimination of such harmful gases can be performed by capturing and storing gases, catalyst reactions of gas conversion, or direct utilization. Apart from gas pollution, water pollution also represents a very huge environmental problem. The approach of GO application in this area can be divided into two paths: pollutant adsorption and conversion.

1.5.2 Medical and Biological Applications of GO

The first possible application in this field is GO-based biosensors. GO-based biosensors rely on their preferred interaction with single-strand DNA (ssDNA) rather than double-strand DNA (dsDNA). This effect is caused by the effective hiding of nucleo-bases in dsDNA in a helical structure, which prevents GO from direct interaction with nucleo-bases.

Another interesting application is gene delivery, which is a promising way to treat genetic disorders, including cancer. The therapy uses gene vectors protecting DNA from nuclease degradation. GO sheets have been covered by polyethyleneimine (PEI) as a surface modifier for gene delivery into the cells. The delivery runs through complexation by electrostatic interaction and covalent conjugation for the loading of plasmid DNA (pDNA).

1.5.3 GO Membranes

GO membranes may be used as ionic and molecular sieves or for selective gas transport. It was reported that a membrane of pure graphene oxide can block everything except for water vapour. Nair et al. claimed that a GO membrane allows only water vapour to pass through, while ethanol and other alcohol molecules are blocked from passing through. Others reported a study exploring the dependence of gases that pass through on the number of layers of GO. In other words, the selective diffusion of gases can be accomplished by the regulation of gas flow pores and channels by various stacking strategies.

1.5.4 High-Temperature Materials and GO

Graphene and graphene oxide are very promising materials for the reinforcement and general enhancement of mechanical properties of high-temperature materials. Some researchers studied the effects of graphene oxide on high-temperature materials such as metal alloys and ceramics. The mechanical resistance can be significantly improved by only 1 vol.% of GO.

1.5.5 Building Materials and GO

Researchers have attempted many times to enhance the properties of cement-based materials by admixtures, and supplementary cementitious materials. In more recent studies, newly produced nanomaterials such as nano-titanium oxide, nano-silica, nano-iron oxide, carbon nanotubes, and graphene oxide have been incorporated into the cement-like structures to enhance the mechanical properties of such materials. Such nanoparticles are able to fill even the smallest pores in the cement, providing a compact structure. The large surface area and the presence of functional groups make GO a highly reactive material. Mechanical properties of graphene are degraded by functionalization, meaning that GO shows lower elastic modulus and tensile strength than graphene. However, GO's tensile strength and elastic modulus are still superior to those of cement—adding GO to cement-like materials enhances the mechanical properties of such building materials. Introducing small amounts of GO (0.05 wt.%) increases the flexural strength by 40–60% and compressive strength by 15–33%.

Besides these applications, there is a vast world of graphene oxide, where it is used in energy storage devices. Those energy storage applications are discussed below.

1.6 ENERGY STORAGE APPLICATIONS OF GRAPHENE OXIDE

1.6.1 Graphene Oxide in Batteries

GO can be coated on the cathode materials so as to construct the advantageous architectures to improve the performance of lithium ion batteries (LIBs). The GO-coated cathode exhibited a discharge capacity of 185 mA h g^{-1} at 100 mA g^{-1} , which was higher than that of the carbon-coated vanadium oxide electrode (135 mA h g^{-1}). Significantly, GO can be used as an active cathode material in the LIBs. A theoretical calculation shows that Li ions can attach to GO either by forming bonds with oxygen-containing groups that is prevalent at high and medium oxygen coverages or by forming LiC_6 rings that is dominant at low coverage. This suggests a new application of GO as a cathode material in lithium storage. GO has also been extensively used in the production of anode materials for LIBs. Although the GO is reduced eventually in the most cases, the functions of the pristine GO still cannot be negligible. More importantly, GO can be directly used in the anodes without being reduced, as it can provide additional Li ion storage through surface oxygen-containing functional groups and nanocavity and also provide LiC_2 storage through the graphite layers and aromatic ring occurring in the GO. Continuing interest for the use of GO in LIBs is further related to its strong affinities to polar components, capability to be reduced and repulse against negative charges. The electrolyte–electrode or current collector interfaces can thus be modified with the assistance of GO to improve the battery performance. GO has been explored as a filler material for various polymer matrices to develop the solid-state electrolytes of LIBs. The incorporation of GO into the polymers, on one hand, can enhance the mechanical stability of the polymer electrolytes. On the other hand, GO can improve the ionic conductivity of the electrolytes, because the interactions between the functional groups of GO and Li ions can accelerate the dissociation of the lithium salt. Also, the interface of GO and polymer matrix creates a new pathway for fast Li ion transport.

A typical Li air battery is composed of a metallic Li anode, an organic electrolyte and a porous airbreathing cathode. However, the cathode materials of Li-air cells have met a huge challenge, which includes transport of oxygen through the pores and the deposition of insulating products on active sites for oxygen reduction and evolution. GO shows some potential in the Li-air

batteries. A free-standing GO paper was used as a O_2 -breathing cathode without binder or other additives. The specific capacity of the Li-air cell using the GO derived porous carbon cathode reached as high as $11,060 \text{ mA h g}^{-1}$ at a current density of 280 mA g^{-1} , as the hierarchically porous structure promoted a continuous oxygen flow in the O_2 -breathing electrode as well as provided sufficient void space for Li_2O_2 deposition.

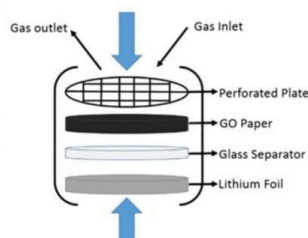


Fig 1.9 Schematic illustration of the Li-air battery assemblies with the GO cathode (Courtesy: GO: An Emerging electromaterial for energy storage & conversion; Tian, et al.)

An innovative design of metal/GO batteries, in light of the spontaneous redox reaction between the metals and the GO, was proposed. As displayed in Fig 1.10, the metals, including Li, Na, Zn, Fe and Cu, acted as anode and the GO functioned as both cathode and separator. When the GO contacted the metal, the reduction of GO happened along with the formation of metal oxides. A specific capacity of about 1604 mAhg^{-1} was observed for the Li/GO battery.

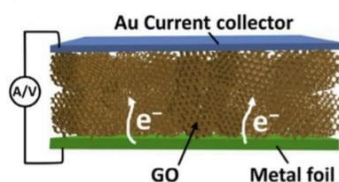


Fig 1.10 schematic illustration of metal/GO battery (Courtesy: J. Gao, et al.; Carbon N.Y.)

1.6.2 Graphene Oxide in Capacitors

A dielectric capacitor is composed of two conducting electrodes separated by an insulating dielectric spacer. Such dielectric medium is required to have a high dielectric constant and low dielectric loss for the maximum capacitance. It was presented that a GO-encapsulated CNT hybrid possessed not only a high dielectric constant and low dielectric loss, but also a highly enhanced breakdown strength and maximum energy storage density. The GO shells effectively enhanced the dispersion of CNTs; served as insulation barriers to decrease dielectric loss; and increased the charge scattering due to their ultra-thin structure and insulating property; resulting in an increase of breakdown strength. Supercapacitors (SCs), also called electrochemical

capacitors, are the high-performance energy storage devices with excellent power capability, short charge–discharge time, and long cyclic life. Charge storage in SCs is principally based on either the electrostatic charge accumulation at the electrode–electrolyte interface, i.e., electrical double layer capacitance, or the fast and reversible faradaic processes on the electrode surface, i.e., pseudo-capacitance. GO, in virtue of its unique physicochemical properties, has been applied to enhance the performances of SCs.

On the other hand, GO with other conducting materials; e.g. carbonaceous materials, transition metal oxides/nitrides/sulphides, and conducting polymers; play a synergistic effect to electrodes, which include increasing the surface area, providing anchor sites for formation of nano-sized composite electrodes, inhibiting the aggregation of active materials during cycling and etc. Additionally, the hydrophilic functional groups endow GO with a highly ionic conducting property, which facilitates its use as the solid-state electrolyte for all-solid-state SCs.

1.6.3 Graphene Oxide in Fuel Cells

A fuel cell is an electrochemical conversion device that generates electricity via chemical redox reactions when supplied with a fuel, e.g., hydrogen, natural gas, or methanol, and an oxidant, e.g., oxygen or air. Platinum (Pt) has been widely used as an effective electrocatalyst in fuel cell technology for the electro-oxidation of fuel at the anode and electro-reduction of oxygen at the cathode. The addition of small amount of GO greatly increases the durability of commercial Pt/C catalyst without sacrificing initial electrochemical active surface area. This is because the GO can provide the anchoring sites of eluted metal ions, thereby inhibiting the Pt agglomeration in Pt/C catalyst.

Owing to a high proton conduction, GO has been widely explored as a promising membrane/seperator in various fuel cells. The introduction of GO into the membranes not only increases the ion-exchange capacity, water uptake, proton conductivity and mechanical properties, but also improves the selectivity of the membrane.

1.8 RECENT WORKS ON GRAPHENE

Ultra-Thin Light-Weight Laser-Induced-Graphene (LIG) Diffractive Optics

To provide higher design flexibility, lower process complexity, and chemical-free process with reasonable investment cost, direct laser writing (DLW) of laser-induced-graphene (LIG) is actively being applied to the patterning of Planar Diffractive Lens (PDL). It can be useful in future micro electronics surface inspection, biomedical, and other industries.

Investigation of Boron-Doped GO Anchored with Copper Sulphide Flowers as Visible Light Active Photocatalyst for Methylene Blue Degradation

The non-biodegradable nature of waste emitted from the agriculture and industrial sector contaminates freshwater reserves. Fabrication of highly effective and low-cost heterogeneous photocatalysts is crucial for sustainable wastewater treatment. The present research study aims to construct a novel photocatalyst using a facile ultrasonication-assisted hydrothermal method. Metal sulphides and doped carbon support materials work well to fabricate hybrid sunlight active systems that efficiently harness green energy and are eco-friendly. Boron-doped graphene oxide-supported copper sulphide nanocomposite was synthesized hydrothermally and was assessed for sunlight-assisted photocatalytic degradation of methylene blue dye.

Fast Synthesis of Large-Area Bilayer Graphene Film on Cu

Bilayer graphene (BLG) is intriguing for its unique properties and potential applications in electronics, photonics, and mechanics. However, the chemical vapor deposition synthesis of large-area high-quality bilayer graphene on Cu is suffering from a low growth rate and limited bilayer coverage. Herein, we demonstrate the fast synthesis of meter-sized bilayer graphene film on commercial polycrystalline Cu foils by introducing trace CO₂ during high-temperature growth.

A Reconfigurable Graphene Patch Antenna Inverse Design at Terahertz Frequencies

The inverse design of a reconfigurable multi-band patch antenna based on graphene is for terahertz applications to operate frequency range (2–5THz). The simulation results show that it is possible to achieve up to 8.8 dB gain, 13 frequency bands, and 360⁰ beam steering. The proposed antenna finds many potential applications in the THz frequency band.

Robust Microscale Structural Superlubricity between Graphite and Nanostructured Surface

Structural superlubricity is a state of nearly zero friction and no wear between two contacted solid surfaces. However, such state has a certain probability of failure due to the edge defects of graphite flake. Here, we achieve robust structural superlubricity state between microscale graphite flakes and nanostructured silicon surfaces under ambient condition. We find that the friction is always less than 1 μN , the differential friction coefficient is on the order of 10^{-4} , without observable wear. This is attributed to the edge warping of graphite flake on the nanostructured surface under concentrated force, which eliminate the edge interaction between the graphite flake and the substrate.

Unconventional Correlated Insulator in CrOCl-Interfaced Bernal Bilayer Graphene

The realization of graphene gapped states with large on/off ratios over wide doping ranges remains challenging. Heterostructures based on Bernal-stacked bilayer graphene (BLG) atop few-layered CrOCl, exhibiting an over-1-G Ω -resistance insulating state in a widely accessible gate voltage range. The insulating state could be switched into a metallic state with an on/off ratio up to 10^7 by applying an in-plane electric field, or by heating.

Phonon-Mediated Room-Temperature Quantum Hall Transport in Graphene

The quantum Hall (QH) effect in two-dimensional electron systems (2DEs) is conventionally observed at liquid-helium temperatures, where lattice vibrations are strongly suppressed and bulk carrier scattering is dominated by disorder. However, due to large Landau level (LL) separation (~ 2000 K at $B = 30$ T), graphene can support the QH effect up to room temperature (RT), concomitant with a non-negligible population of acoustic phonons with a wave-vector proportional to the inverse electronic magnetic length. Here, we demonstrate that graphene

encapsulated in hexagonal boron nitride (hBN) realizes a novel transport regime, where dissipation in the QH phase is governed predominantly by electron-phonon scattering.

Staggered Circular Nanoporous Graphene Converts Electromagnetic Waves into Electricity

Harvesting largely ignored and wasted electromagnetic (EM) energy released by electronic devices and converting it into direct current (DC) electricity is an attractive strategy not only to reduce EM pollution but also address the ever-increasing energy crisis. Here we report the synthesis of nanoparticle-templated graphene with monodisperse and staggered circular nanopores enabling an EM–heat–DC conversion pathway. The staggered circular nanoporous graphene exhibits an anomalous combination of properties, which lead to an efficient absorption and conversion of EM waves into heat and in turn an output of DC electricity through the thermoelectric effect.

Mixed-Modality Speech Recognition and Interaction Using a Wearable Artificial Throat

Researchers have recently been pursuing technologies for universal speech recognition and interaction that can work well with subtle sounds or noisy environments. Multichannel acoustic sensors can improve the accuracy of recognition of sound but lead to large devices that cannot be worn. To solve this problem, we propose a graphene-based intelligent, wearable artificial throat (AT) that is sensitive to human speech and vocalization-related motions. Its perception of the mixed modalities of acoustic signals and mechanical motions enables the AT to acquire signals with a low fundamental frequency while remaining noise resistant. Its feasible fabrication process, stable performance, resistance to noise and integrated vocalization make the AT a promising tool for next-generation speech recognition and interaction systems.

From Nanohole to Ultralong Straight Nanochannel Fabrication in GO with Swift Heavy Ions

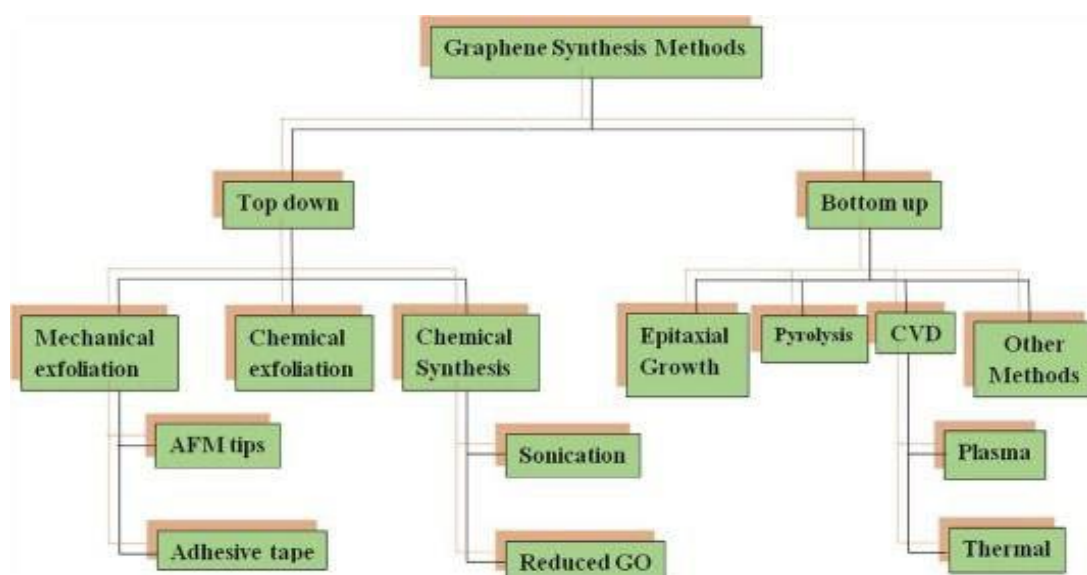
Porous architectures based on graphene oxide with precisely tailored nm-sized pores are attractive for biofluidic applications such as molecular sieving, DNA sequencing, and recognition-based sensing. Uniform 6–7 nm-sized holes and straight, vertical nanochannels can be formed by simply irradiating graphene oxide (GO) films with high-energy heavy ions. Long

penetration depths of energetic ions in combination with localized energy deposition and effective self-etching processes enable the creation of pores even in 10 μm -thick GO films. This fully scalable fabrication provides a promising possibility for obtaining innovative GO track membranes.

CHAPTER 2: DIFFERENT SYNTHESIS METHODS

2.1 DIFFERENT METHODS OF GRAPHENE SYNTHESIS

Synthesis process is known as extracting graphene depending on the purity and the desired product. After the discovery of graphene, different techniques were developed to produce layers and thinfilms of graphene. Chemical vapour deposition (CVD), chemical exfoliation, chemical synthesis, and mechanical cleaving are some of the commonly used methods of graphene synthesis. Top-down and bottom-up synthesis methods are determined by the number of layers, thickness, the nature and average size of the graphene materials. In top-down growth mechanism process, graphene sheets are produced by exfoliation/separation of graphite and its derivatives including graphene oxide (GO).



2.1.1 Chemical Vapour Deposition (CVD)

CVD is one of the most common methods for synthesizing large-area, high-quality graphene films. In this method, a carbon-containing gas is introduced into a high-temperature furnace, and the carbon atoms deposit onto a substrate to form graphene layers. The choice of substrate

and growth conditions can influence the quality and properties of the synthesized graphene. CVD is a process where one or more gaseous adsorption species react or decompose on a hot surface to form stable solid products. The main steps that occur in the CVD process can be summarized as follows:

- a. Transport of reacting gaseous species to the surface
- b. Adsorption of the species on the surface
- c. Heterogeneous surface reaction catalysed by the surface
- d. Surface diffusion of the species to growth sites
- e. Nucleation and growth of the film
- f. Desorption of gaseous reaction products and transportation of reaction products away from the surface

CVD is a more complicated method than PVD for the formation of thin films and coatings,

▪ Thermally activated CVD:-

This is the conventional CVD technique where the resistive heating of hot wall reactors gives sufficiently high temperatures for the dissociation of gaseous species. This leads to the heating of the entire substrate to a high temperature before the desired reaction is achieved. It precludes the use of substrates with melting points much lower than the reaction temperature. Hot tungsten filament is also used to heat the reacting gases in the vicinity of the substrate. Recently, hot filament CVD was used to grow one-dimensional SiC nanorods. Due to high hardness, high thermal stability, wide band gap and high electron mobility, SiC nanorods are potential materials for structural and electronic applications.

Carbon, silicon and silicon dioxide powders, compacted in the form of a plate, are used as the silicon and carbon sources. The chamber was filled with hydrogen gas and a tungsten filament was used to activate the hydrogen gas. The filament and substrate temperatures used are 2570 and 1373 K, respectively. The hot filament causes dissociation of molecular hydrogen to atomic hydrogen.

Advantages:-

- Produces high-quality, continuous graphene films.
- Offers control over layer thickness and properties.
- Suitable for large scale production.

Disadvantages:-

- Requires specialized equipment and high temperatures.

- Substrate choice can affect the quality of graphene.

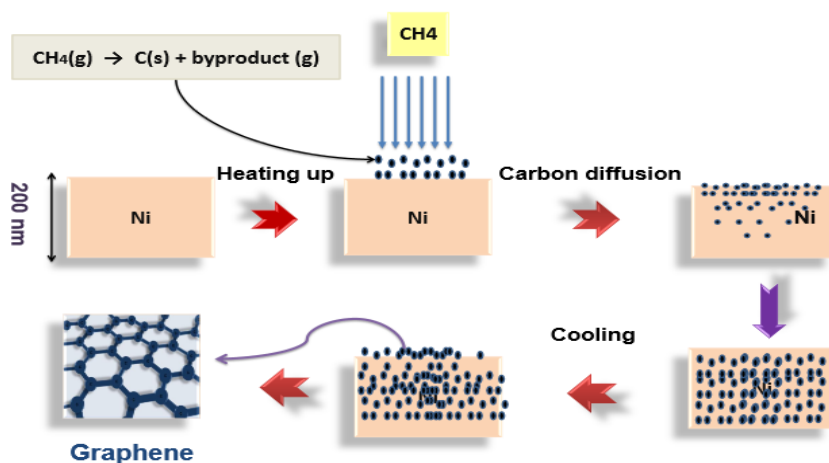


Figure:- CVD graphene growth on Nickel

2.1.2 Chemical Exfoliation (Liquid phase exfoliation)

Method involves exfoliating graphite flakes into individual graphene layers using a solvent or surfactant. This can yield graphene dispersions that can be deposited onto various substrates. The degree of exfoliation and resultant graphene quality can be influenced by the choice of solvent and processing conditions. Graphite exfoliation by electrochemical techniques has become a simple but yet high yielding method in recent times for the mass production of graphene. This method involves the use of various forms of graphite such as graphite foils, plates, rods and graphite powders as electrodes in an aqueous or non-aqueous electrolyte and electric current to bring about the expansion of electrodes. The electrodes could be of two types based on the power applied, that is, Cathodic (Negative) and Anodic (Positive) electrodes . [Wang et al in their study used Pure Graphite as electrodes and PSS (Polysodium-4-styrenesulfonate) solubilized in deionized water to incarnate the electrolyte. They accommodated the graphite rods in an electrochemical cell which was filled with the electrolyte. A persistent current of 5 V was applied. Few minutes of electrolysis resulted in the accumulation of a black material at the anode. The exfoliation process was carried on for 4 h to isolate the product from the cell. It was then centrifuged at 1000 rpm and then the product was gradually poured out. The dispersion obtained was found to be extremely stable. Powdered dry graphene was achieved by washing the dispersion with deionized water and alcohol

followed by vacuum drying. Then the yield was calculated by weighing the dry powder and sediment.]

Advantages:-

- Relatively simple process.
- Can produce graphene dispersions for various applications.
- Scalable for moderate quantities.

Disadvantages:-

- Quality of exfoliated graphene may vary.
- Requires post-processing to remove residual solvent.

2.1.3 Chemical synthesis (Graphene oxide reduction)

This approach involves chemically reducing precursor molecules to form graphene. One common example is the reduction of graphene oxide (GO) to produce reduced graphene oxide (rGO), which retains some functional groups. While the resulting material may not be as pristine as CVD-grown graphene, it can still exhibit useful properties and is easier to produce in bulk.

Advantages:-

- Can be produced from low-cost graphite or graphene oxide.
- Functional groups on graphene oxide can be tailored.
- Easier to produce in bulk compared to CVD.

Disadvantages:-

- Resulting graphene may have defects due to functional groups.
- Not as high quality as CVD graphene.

2.1.4 Mechanical exfoliation/cleaving (Scotch Tape Method)

This method, famously used by the Nobel Prize-winning researchers Andre Geim and Konstantin Novoselov in their discovery of graphene, involves repeatedly peeling off layers of graphite using adhesive tape. This manual process results in very thin flakes of graphene. While not scalable for large-scale production, it was essential in the early days of graphene research.

Mechanical exfoliation is also known as Scotch tape or peel-off method. It was the first method to be used by Novoselov and Geim for the production of graphene with the help of an adhesive tape to force the graphene layers apart. In this method, multiple layers of graphene remain on the tape after peeling off, but with recurrent peeling, it splits open into a handful of graphene flakes. For detachment, the tape is attached to a certain substrate (acetone) and a final peeling by using a fresh tape is carried out to obtain flakes different in both size and thickness which can be observed under a light microscope on SiO₂/Si substrates. This process is slow and imprecise, hence the material produced is most often used to study the properties of graphene rather than actually using it commercially. This method can also be performed by using different agents such as electric field, epoxy resin, and by transfer printing technique.

Advantages:-

- Simple and low-cost method.
- Suitable for research and initial graphene isolation.

Disadvantages:-

- Not scalable for commercial production.
- Inconsistent graphene quality and thickness.



2.1.5 Pyrolysis

The word pyrolysis originated from the Greek-derived element pyro and lysis. Pyro means fire and lysis stand for separating. Synthesized carbon atom on a metal surface is a simple procedure used to fabricate few-layer graphene. One of the common techniques of graphene synthesis is the thermal decomposition of silicon carbide (SiC). At high temperature, Si is desorbed leaving behind C atom which forms few graphene layers. This technique has received a significant

improvement through the continuous production of graphene films in mm scale at a temperature of 750 °C on a thin film of nickel coated on SiC substrate. The advantage of this method is the continuous production of graphene films over the entire SiC coated surface. However, this method cannot be used in the synthesis of graphene in large scale. A similar approach is applied in the thermal decomposition of ethylene at 1000 K. The advantage of this synthesis method is the production of high purity graphene mono-layer.

Advantages:

- Scalability: Easily scaled for large-scale production of graphene.
- Cost-Effective: Simple equipment and potentially lower production costs.
- Versatility: Works with various precursor materials, offering flexibility.
- Control over Properties: Parameters can be adjusted for desired graphene characteristics.
- High Purity: Inert atmosphere minimizes impurities in the final product.

Disadvantages:

- Limited Control: Achieving precise control and uniformity is challenging.
- Defects and Imperfections: Process can introduce defects and imperfections in the graphene lattice.
- Energy-Intensive: High temperatures used, leading to energy consumption.
- Resource Consumption: Dependent on non-renewable resources in some cases.
- Layer Control Challenges: Difficulty in precisely controlling the number of graphene layers.
- Safety Concerns: Involves high temperatures and potential hazards.

The terms “top-down” and “bottom-up” refer to the growth mechanisms of these methods.

➤ TOP-DOWN METHOD

In this approach, bulk graphite or graphite-derived materials (like graphene oxide) are broken down into smaller graphene layers through processes like exfoliation or mechanical cleaving.

➤ BOTTOM-UP METHOD

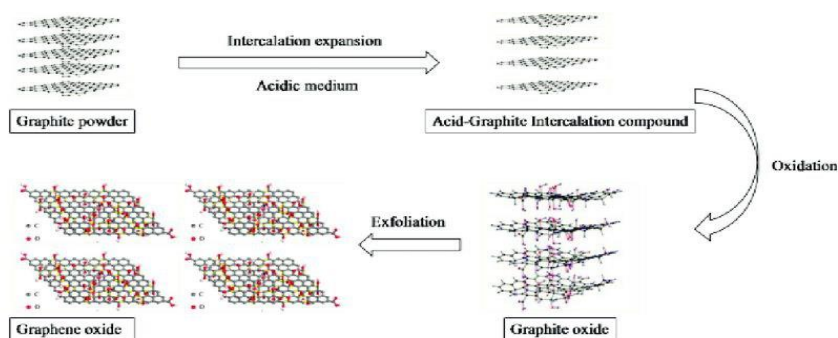
This method involves building up graphene layers atom by atom or molecule by molecule. CVD is an example of a bottom-up method as it involves the deposition of individual carbon atoms to form graphene layers.

Each method has its advantages and limitations in terms of scalability, graphene quality, and the specific applications they are best suited for. The choice of synthesis method often depends on the desired properties and scale of production required for a particular application, such as electronics, sensors, composites, and more.

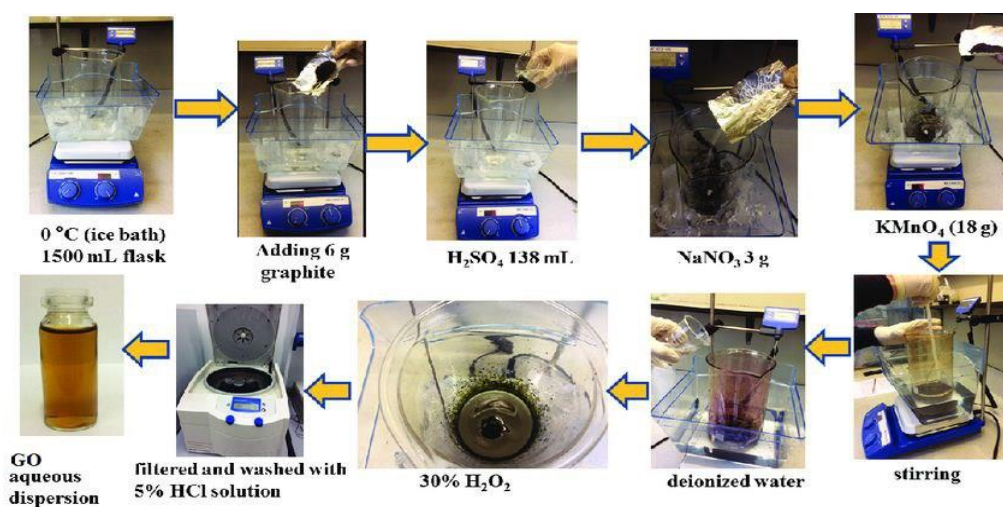
2.2 DIFFERENT METHODS OF GRAPHENE-OXIDE SYNTHESIS

2.2.1 HUMMERS METHOD

Synthesis of graphene oxide (GO) from graphite using the Hummers method in which the graphite surface is modified with such strong acids as H_2SO_4 , HNO_3 , KMnO_4 promoted the formation of hydroxyl and epoxy groups on the main plane, as well as carbonyl and carboxyl groups at the edges. Obtained results of the synthesis of GO with the oxidation of bulk graphite with strong oxidants, then with subsequent separation into few-layer graphene sheets, contributes to the production of graphene, graphene-like materials in large quantities, with a low cost, a fairly simple synthesis method and the possibility of converting it into graphene. The elemental composition of the obtained GO were studied by the energy dispersive X-ray spectroscopy (EDX) analysis and the structural characteristics were investigated by the Raman spectroscopy. The thermal stability and chemical functionalisation of GO were determined by the thermogravimetric analysis. The structural and crystal features of the obtained GO from graphite were studied using an X-ray diffractometer (XRD).



Main stages of synthesis of GO



Synthesis of GO using Hummers method

Advantages:

- Widely used and well-established.
- Produces highly oxidized GO with abundant functional groups.

Disadvantages:

- Harsh chemicals are used, posing safety and environmental concerns.
- Difficult to control the degree of oxidation.

2.2.2 IMPROVED HUMMERS METHOD

An improved method for the preparation of graphene oxide (GO) is described. Currently, Hummers' method (KMnO₄, NaNO₃, H₂SO₄) is the most common method used for preparing graphene oxide. We have found that excluding the NaNO₃, increasing the amount of KMnO₄, and performing the reaction in a 9:1 mixture of H₂SO₄/H₃PO₄ improves the efficiency of the oxidation process. This improved method provides a greater amount of hydrophilic oxidized graphene material as compared to Hummers' method or Hummers' method with additional KMnO₄. Moreover, even though the GO produced by our method is more oxidized than that prepared by Hummers' method, when both are reduced in the same chamber with hydrazine, chemically converted graphene (CCG) produced from this new method is equivalent in its

electrical conductivity. In contrast to Hummers' method, the new method does not generate toxic gas and the temperature is easily controlled. This improved synthesis of GO may be important for large-scale production of GO as well as the construction of devices composed of the subsequent CCG.

Take 120 ml of concentrated H_2SO_4 in a beaker and place it on a magnetic stirrer at moderate speed. Add 13 ml of H_3PO_4 to it and mix thoroughly. Then, add 1 g of graphite to the mixture. Gradually add potassium permanganate, pinch by pinch. The mixture will turn green, followed by the evolution of purple fumes. Let the mixture stir for two and a half hours. It will eventually turn into a greyish-brown colour. Add approximately 130 ml of distilled water and a few drops of H_2O_2 (1 ml). The colour will change from brown to yellow. Stop the stirring and allow the mixture to settle for some time. Next, wash the solution with distilled water and 1 molar HCl (6 ml), allowing the mixture to settle again. Repeat the washing process with distilled water until the pH reaches neutral (pH 7). Then, dry the mixture. The resulting material can be powdered using a mortar, and you will obtain a brown powder. For characterisation we are using Raman spectroscopy. The resulting data is taken and compared with standard data.

2.2.3 STAUDENMAIER METHOD

Similar to the Hummers method, this approach uses a mixture of concentrated sulfuric and nitric acids along with potassium chlorate (KClO_3) as the oxidizing agent to produce GO. Perform the synthesis in a well-ventilated fume hood with proper safety gear. Start with natural graphite flakes. Combine graphite with concentrated nitric acid and potassium chlorate. Place the mixture in an ice bath and allow it to oxidize for several hours. Dilute the mixture with deionized water until it reaches neutral pH. Filter the mixture to separate GO from impurities and wash the GO product. Collect and dry the GO material. Disperse the dried GO in a suitable solvent.

Advantages:

- Similar to the Hummers method but may be slightly milder.

Disadvantages:

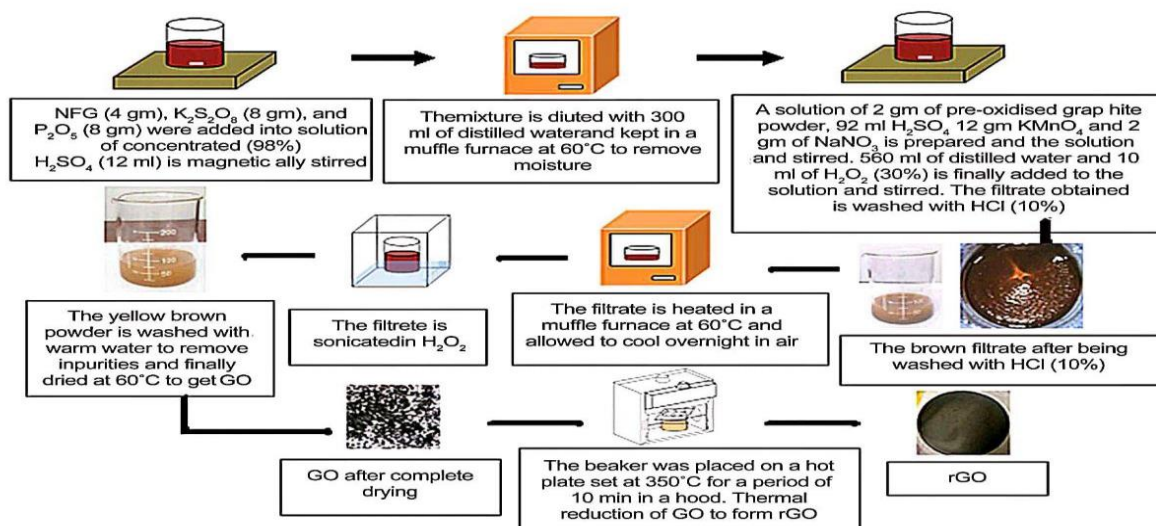
- Still involves the use of strong acids and oxidizing agents.

2.2.4 MODIFIED HUMMERS METHOD

Synthesis of Graphene oxide (GO) by modified Hummers Method and its Thermal Reduction to obtain reduced Graphene Oxide (Rgo).

Graphene oxide (GO) has been initially prepared by a modified Hummers method. Subsequently reduced graphene oxide (rGO) having few layer graphene is extracted from GO by the thermal reduction of GO. Natural flake graphite (NFG) was procured from LOBA Chemie India having a mean size of 60 mesh and purity of 98%. Sulfuric acid (H_2SO_4) and phosphorous pentaoxide (P_2O_5) were procured from Merck India. All reagents used were of analytical grade and had the highest commercially available purity. A mixture of 4 gm of NFG, 12 ml H_2SO_4 and 8 gm of P_2O_5 was prepared. The solution was subjected to magnetic stirring for a period of 6 h. 12 ml of H_2SO_4 was again added to the filtrate along with 8 gm of $\text{K}_2\text{S}_2\text{O}_8$. This mixture was magnetically stirred for 6 h. After cooling the mixture to the room temperature, it was diluted with 300 ml of distilled water. The filtrate was then dried overnight in air and later heated in a muffle furnace in air at 60°C for 2 h in order to remove the moisture. 2 gm of the preoxidised graphite powder is then added to the mixture of 92 ml H_2SO_4 and 12 gm KMnO_4 under continuous stirring in a water bath. 2 gm of NaNO_3 is then added to the solution after 15 mins. This solution is then stirred at room temperature for 2 h. Later 200 ml of distilled water is added to the solution and stirred for 15 mins. 10 ml of 30% H_2O_2 and 560 ml of distilled water is added to the solution. The filtrate obtained is washed with HCl (10%). The brown suspension obtained is heated in a muffle furnace for 30 mins at 60°C and then allowed to cool overnight in air. The brown dispersion is dialyzed extensively to remove residual metallic ions and acids with distilled water for 1 week. Finally, the filtrate was air dried overnight and sonicated for 5 with H_2O_2 . The yellow-brown residual powder was washed with warm water for upto 3 times to remove the impurities. The dry GO powder is finally obtained after heating the filtrate at 60°C for 4 h. To obtain rGO from GO, 100 mg of the dried GO powder is taken in an empty beaker. The beaker was covered with aluminium foil that had many punched pores and was placed on a hot plate set at 350°C for 10 mins in a hood. The resulting black powder of rGO was then collected from the beaker. Figure 2 shows the various steps that have been undertaken for the synthesis of rGO from NFG. Various analyses including FTIR, XRD, SEM, FESEM, Micro-Raman, DSC, TGA, BET, and AFM, were performed to characterize the materials. GO prepared by oxidizing NFG via modified Hummer's method;

stacks of GO sheets, 1-2 μm thick, with thicker edges due to oxygen-functional groups. GO is hydrophilic and dissolves in water, while NFG and rGO are hydrophobic. rGO has higher thermal stability due to lower defect density. FTIR spectra show effective reduction of GO to rGO through thermal treatment. rGO has a smaller average particle size compared to GO.



Advantages:

- Offers some degree of control over oxidation level through variations in reaction conditions.

Disadvantages:

- Still employs hazardous chemicals.

2.2.5 TOUR'S METHOD

James Tour's method for synthesizing graphene oxide (GO) is a multi-step process that involves the oxidation and exfoliation of graphite to produce GO. Mix 9 grams of graphite flakes with 230 mL of concentrated sulfuric acid (H_2SO_4) in a glass container. Slowly add 4.5 grams of potassium permanganate (KMnO_4) to the mixture while stirring continuously. The mixture will heat up and turn brown. Stir for several hours at around $50\text{--}60^\circ\text{C}$, or until the colour becomes olive green. Dilute the mixture by adding approximately 500 mL of deionized water slowly, while stirring. This step should be done with caution as it can produce heat and gas. The solution will turn bright yellow. Filter the yellow solution using a filter paper to remove solid residues. Wash the filtrate with deionized water until it becomes neutral (pH 7). Acidify the solution by adding hydrochloric acid (HCl) dropwise while monitoring the pH until it reaches

around 3. Collect the solid material by filtration and wash it thoroughly with distilled water. Disperse the purified material in a mixture of DI water and ethanol (typically 3:1 ratio) by sonication or mechanical stirring. Add hydrogen peroxide (H_2O_2) to the dispersion to initiate exfoliation and reduce GO to some extent. The amount of H_2O_2 can vary depending on the desired properties. Allow the mixture to react for a specified time (typically a few hours) while maintaining a controlled temperature (e.g., ice bath) to prevent overheating. After the reaction, centrifuge the dispersion to separate the thinner GO sheets from unexfoliated material. Wash the separated GO sheets with DI water and ethanol multiple times to remove excess chemicals and by-products. Collect the GO sheets and dry them, often under vacuum or in an oven.

Advantages:

- Effective in producing GO with low defects.

Disadvantages:

- Initial oxidation step requires strong acids and oxidizing agents

2.2.6 Brodie Method

In this method, graphite is oxidized with a mixture of concentrated nitric acid (HNO_3) and potassium chlorate (KClO_3). It typically results in less oxidation compared to the Hummers method.

Advantages:

- Gentler than the Hummers method.

Disadvantages:

- Lower oxidation level and functionalization compared to other methods.

2.2.7 Microwave-Assisted Synthesis

Microwaves can be used to accelerate the oxidation process, reducing the reaction time required for GO synthesis.

Advantages:

- Rapid and energy-efficient.

Disadvantages:

- Limited control over oxidation and functionalization.

2.2.8 Electrochemical Exfoliation

GO can be obtained through electrochemical methods, where a voltage is applied to graphite electrodes in an electrolyte solution, causing the exfoliation and oxidation of the graphite layers. Prepare an electrolyte solution, typically using concentrated sulfuric acid (H_2SO_4) or another suitable acid. The concentration and type of acid can vary depending on the desired properties of GO. Set up this step in a well-ventilated area or fume hood due to the use of corrosive acids. Assemble an electrochemical cell with three electrodes: a working electrode (graphite), a counter electrode (typically another graphite electrode), and a reference electrode (e.g., Ag/AgCl). The working electrode should be loaded with natural graphite flakes or be made from graphite foil. Submerge the working and counter electrodes in the prepared electrolyte solution. Ensure that the electrodes are properly positioned and that there is a suitable gap between them. Apply a voltage (typically between 1 and 10 volts) to the working electrode relative to the reference electrode. This potential difference induces an electrochemical reaction at the surface of the graphite, causing exfoliation of the graphite layers and oxidation to form GO. If necessary, use a magnetic stirrer to agitate the electrolyte solution gently during the electrochemical process to enhance exfoliation. Monitor the electrochemical process closely, controlling the voltage, current, and duration to achieve the desired degree of exfoliation and oxidation. The process may take several hours to complete, depending on the parameters and the starting material. After the electrochemical exfoliation, collect the GO suspension from the electrolyte solution. Wash the collected GO suspension multiple times with deionized water to remove excess acid and impurities. Use techniques like centrifugation to separate GO from unexfoliated material. Dry the purified GO, typically in an oven or under vacuum, to obtain solid GO material.

Advantages:

- Allows for fine-tuning of GO properties.

Disadvantages:

- Requires specialized equipment and expertise.

2.2.9 Oxidation by Peroxides

GO can also be synthesized by using hydrogen peroxide (H_2O_2) or other peroxides as oxidizing agents under suitable conditions.

Advantages:

- Uses milder oxidizing agents.

Disadvantages:

- Limited control over the degree of oxidation.

2.2.10 Photochemical Oxidation

Ultraviolet (UV) light can be employed to initiate the oxidation of graphite in the presence of a suitable oxidizing agent.

Advantages:

- Mild and selective oxidation under controlled conditions.

Disadvantages:

- Requires UV light sources and specialized equipment.

CHAPTER 3: EXPERIMENTAL DETAILS

3.1 MODIFIED HUMMERS METHOD

Graphene oxide (GO) has been initially prepared by a modified Hummers method.

A mixture of 4 gm of natural flake graphite (NFG), 12 ml H_2SO_4 and 8 gm of P_2O_5 was prepared. The solution was subjected to magnetic stirring for a period of 6 h. 12 ml of H_2SO_4 was again added to the filtrate along with 8 gm of $\text{K}_2\text{S}_2\text{O}_8$. This mixture was magnetically stirred for 6 h. After cooling the mixture to the room temperature, it was diluted with 300 ml of distilled water. The filtrate was then dried overnight in air and later heated in a muffle furnace in air at 60°C for 2 h in order to remove the moisture. 2 gm of the pre-oxidised graphite powder is then added to the mixture of 92 ml H_2SO_4 and 12 gm KMnO_4 under continuous stirring in a water bath. 2 gm of NaNO_3 is then added to the solution after 15 mins. This solution is then stirred at room temperature for 2 h. Later 200 ml of distilled water is added to the solution and stirred for 15 mins. 10 ml of 30% of H_2O_2 and 560 ml of distilled water is added to the solution. The filtrate obtained is washed with HCl (10%). The brown suspension obtained is heated in a muffle furnace for 30 mins at 60°C and then allowed to cool overnight in air. The brown dispersion is dialyzed extensively to remove residual metallic ions and acids with distilled water for 1 week. Finally, the filtrate was air dried overnight and sonicated for 5 with H_2O_2 . The yellow-brown residual powder was washed with warm water for upto 3 times to remove the impurities. The dry GO powder is finally obtained after heating the filtrate at 60°C for 4 hr.



3.2 IMPROVED HUMMERS METHOD (TOUR METHOD)

An improved method for the preparation of graphene oxide (GO) is described. Currently, Hummers' method (KMnO_4 , NaNO_3 , H_2SO_4) is the most common method used for preparing graphene oxide. We have found that excluding the NaNO_3 , increasing the amount of KMnO_4 , and performing the reaction in a 9:1 mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ improves the efficiency of the oxidation process. This improved method provides a greater amount of hydrophilic oxidized graphene material as compared to Hummers' method or Hummers' method with additional KMnO_4 . Moreover, even though the GO produced by our method is more oxidized than that prepared by Hummers' method, when both are reduced in the same chamber with hydrazine, chemically converted graphene (CCG) produced from this new method is equivalent in its electrical conductivity. In contrast to Hummers' method, the new method does not generate toxic gas and the temperature is easily controlled. This improved synthesis of GO may be important for large-scale production of GO as well as the construction of devices composed of the subsequent CCG.

Procedure

Take 120 ml of concentrated H_2SO_4 in a beaker and place it on a magnetic stirrer at moderate speed. Add 13 ml of concentrated H_3PO_4 to it and mix thoroughly. Then, add 1 g of graphite to the mixture. Gradually add potassium permanganate, pinch by pinch to produce a slight exotherm about $35 - 40^\circ\text{C}$. The mixture will turn green, followed by the evolution of purple fumes. Let the mixture stir for two and a half hours. It will eventually turn into a greyish-brown colour. Add approximately 130 ml of distilled water and a few drops of H_2O_2 (1 ml) and stirred for 20 more minutes. The colour will change from brown to yellow. Yellow colour indicates high level of oxidation. Stop the stirring and allow the mixture to settle for 12 hrs.

Next, wash the solution with distilled water and 1 molar HCl (6 ml), allowing the mixture to settle again. Repeat the washing process with distilled water until the pH reaches neutral (pH 7). Each washing process has been done by adding distilled water upto 80% of the beaker and stirring for 20 mts. Then, dry the mixture at 60°C . The resulting material can be powdered using a mortar, and you will obtain a brown powder.

For characterisation we are using Raman spectroscopy. The resulting data is taken and compared with standard data.



H₂SO₄, H₃PO₄ and graphite mixture stirring. Solution subjected to 6hr magnetic stirring. Add potassium permanganate pinch by pinch.



Mixture turns green with purple fumes. Adding 130 ml distilled water and 1ml H₂O₂.



Colour changes from brown to yellow



Drying the mixture with neutral pH.



After drying. Resulting material powdered by mortar.



A Brown powder is obtained

CHAPTER 4: RESULT AND DISCUSSION

4.1 X-RAY DIFFRACTION (XRD)

X-ray diffraction (XRD) is a widely-used analytical technique in materials science, chemistry, and various scientific disciplines. It allows researchers to determine the atomic and molecular structure of crystalline materials with high precision. Here's a more detailed explanation of how XRD works.

Principle of XRD: XRD is based on the principle of X-ray scattering. When a crystalline material is exposed to a beam of X-rays, the X-rays interact with the electrons in the atoms of the crystal lattice. This interaction causes the X-rays to scatter in different directions. The scattered X-rays interfere with each other, creating a pattern of constructive and destructive interference known as a diffraction pattern.

Bragg's Law: The key equation in XRD is Bragg's Law, which relates the angles at which X-rays are diffracted to the spacing between the crystal lattice planes and the wavelength of the X-rays. Mathematically, it is expressed as:

$$\lambda = 2d * \sin(\theta)$$

Where:

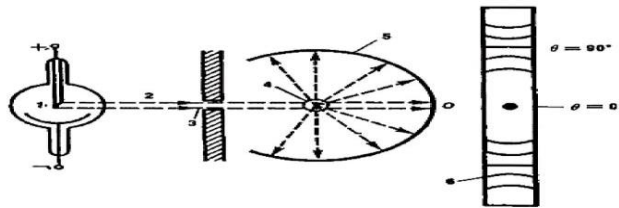
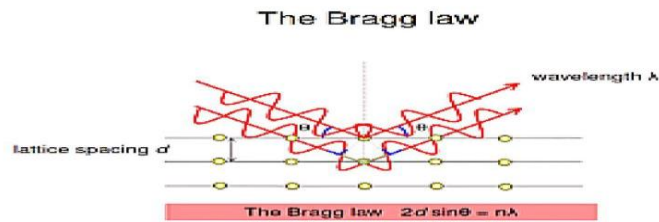
λ is the wavelength of the X-rays.

d is the spacing between crystal lattice planes.

θ is the angle of diffraction.

By measuring the angle θ at which X-rays are diffracted and knowing the wavelength of the X-rays, researchers can determine the lattice spacing (d) of the crystal.

XRD Instruments: XRD experiments are typically performed using specialized XRD instruments, which consist of an X-ray source (often a rotating anode or sealed tube) that emits X-rays, a sample holder, and a detector. The sample is mounted in the instrument, and the detector records the intensity of diffracted X-rays at various angles.



Data Analysis: The recorded diffraction pattern is a plot of intensity (y-axis) against the diffraction angle (θ , x-axis). By analyzing this pattern, researchers can:

Identify the crystal structure: The positions and intensities of the diffraction peaks provide information about the arrangement of atoms within the crystal lattice. This helps in identifying the crystal structure of the material.

Quantify crystalline phases: XRD can determine the relative amounts of different crystalline phases present in a sample.

Measure lattice parameters: Precise values of lattice parameters (e.g., unit cell dimensions) can be determined.

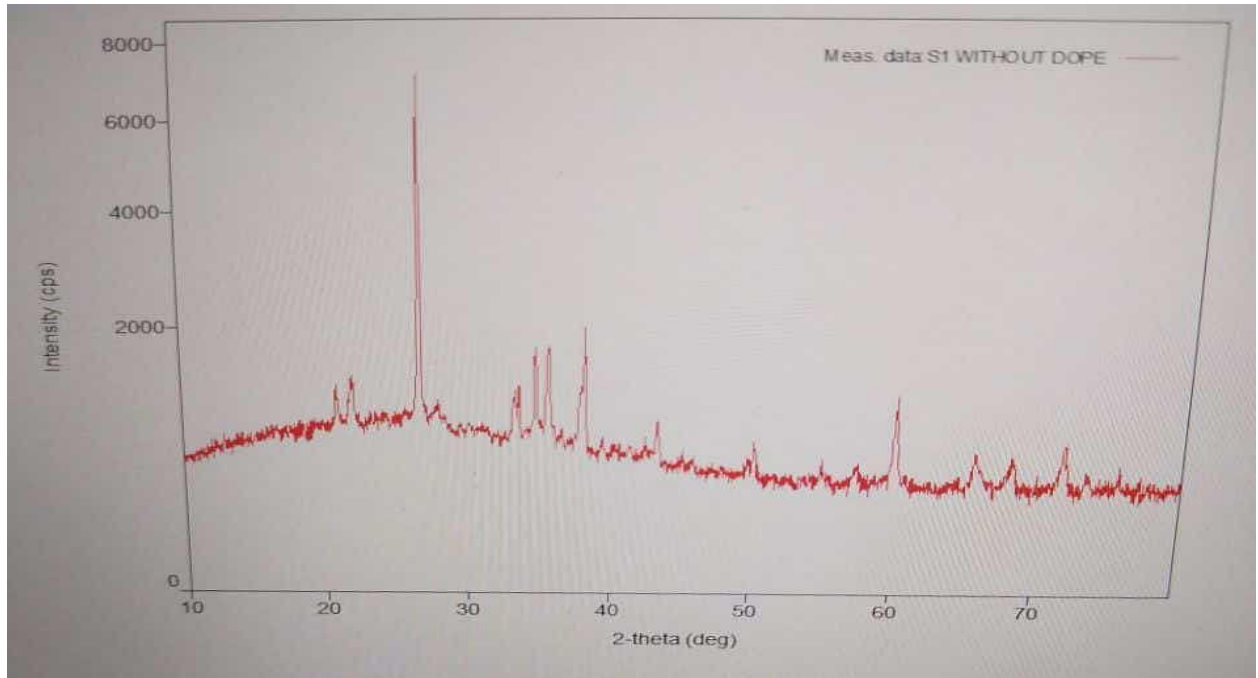
Study defects and strains: XRD can reveal information about defects, strains, and microstructural characteristics within the crystal.

Determine crystal orientation: It can be used to determine the orientation of a single crystal or the preferred orientation (texture) in a polycrystalline sample.

In summary, X-ray diffraction is a versatile and non-destructive technique that provides detailed information about the atomic and molecular arrangement in crystalline materials. Researchers use XRD to understand the properties, composition, and structural characteristics of a wide range of materials, from metals and ceramics to pharmaceuticals and geological samples.

SAMPLE ANALYSIS

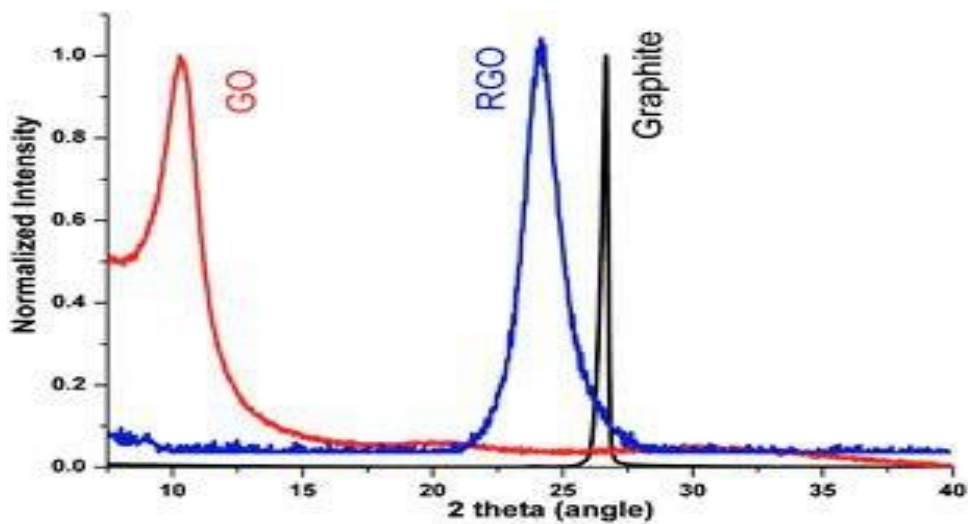
XRD ANALYSIS



Graph obtained by the Modified Hummer's Method

- This is the graph we obtained. We get the peak between 20 to 30 for the sample. This is XRD peak of graphite. Thus the sample contain graphite and rGO.

INFERENCE



- This is the XRD graph of Graphene oxide.
- Generally for graphene the peak is between 10 and 20.
- For graphite it is between 20 and 30

Preparation of graphene from graphite is not completed. We get the XRD peak between 20 and 30 which is the peak of graphite. But there is another two peaks formed near 20 to 25, where one can be Reduced Graphene Oxide. We are not sure about the results so we used another synthesis method for the preparation of graphene oxide.

4.2 RAMAN SPECTROSCOPY

Raman spectroscopy is a molecular spectroscopic technique that utilizes the interaction of light with matter to gain insight into a material's make up or characteristics, like FTIR. The information provided by Raman spectroscopy results from a light dispersion process, whereas IR spectroscopy relies on absorption of light. Raman spectroscopy yields information about intra- and inter-molecular vibrations and can provide additional understanding about a reaction. Both Raman and FTIR spectroscopy provide a spectrum characteristic of the specific vibrations of a molecule ("molecular fingerprint") and are valuable for identifying a substance. However, Raman spectroscopy can give additional information about lower frequency modes, and vibrations that give insight into crystal lattice and molecular backbone structure.

Inline Raman spectroscopy is used to monitor crystallization processes and reveal reaction mechanisms and kinetics. Combined with analysis tools, this data enables informed reaction understanding and optimization.

When light interacts with molecules in a gas, liquid, or solid, the vast majority of the photons are dispersed at the same energy as the incident photons. This is described as elastic or Rayleigh scattering. A small number of these photons, approximately 1 photon in 10 million will disperse at a different frequency than the incident photon. This process is called inelastic scattering, or the Raman effect, named after Sir C.V. Raman who discovered this and was awarded the 1930 Nobel Prize in Physics for his work. Since that time, Raman has been utilized for a vast array of applications from medical diagnostics to material science and reaction analysis. Raman allows the user to collect the vibrational signature of a molecule,

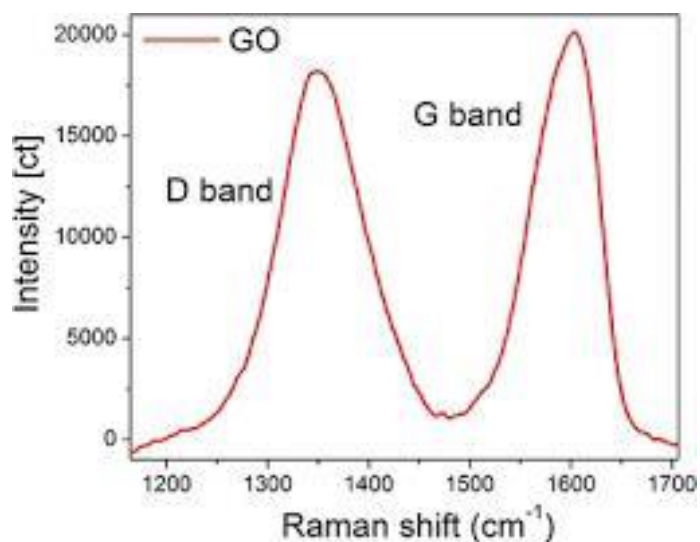
giving insight into how it is put together, as well as how it interacts with other molecules around it.

Raman spectroscopy looks at changes in a molecular bonds polarizability. Interaction of light with a molecule can induce a deformation of its electron cloud. This deformation is known as a change in polarizability. Molecular bonds have specific energy transitions in which a change of polarizability occurs, giving rise to Raman active modes.

Raman spectroscopy is a popular technique for characterization of carbon-based materials, especially C=C double bonds which result in high Raman intensities. Raman spectroscopy is an essential tool for the study on structural and electronic properties of graphene, including disorder and defect structures, defect density, and doping levels apart from electron paramagnetic resonance (EPR) and photoluminescence.

Raman spectroscopy of graphene is generally characterized by two main features: the G-peak, resulting from first-order scattering of the E_{2g} phonon from sp² carbon atoms, which is known to appear at 1575–1583 cm^{−1} for bulk graphite. The band is resonant, which means that it is much more intense than we would expect it to be otherwise. The band position is pretty much independent of excitation laser frequency though, making it different from the other graphene bands that will be discussed. The position of the band and to a certain extent the shape can provide you with more information.

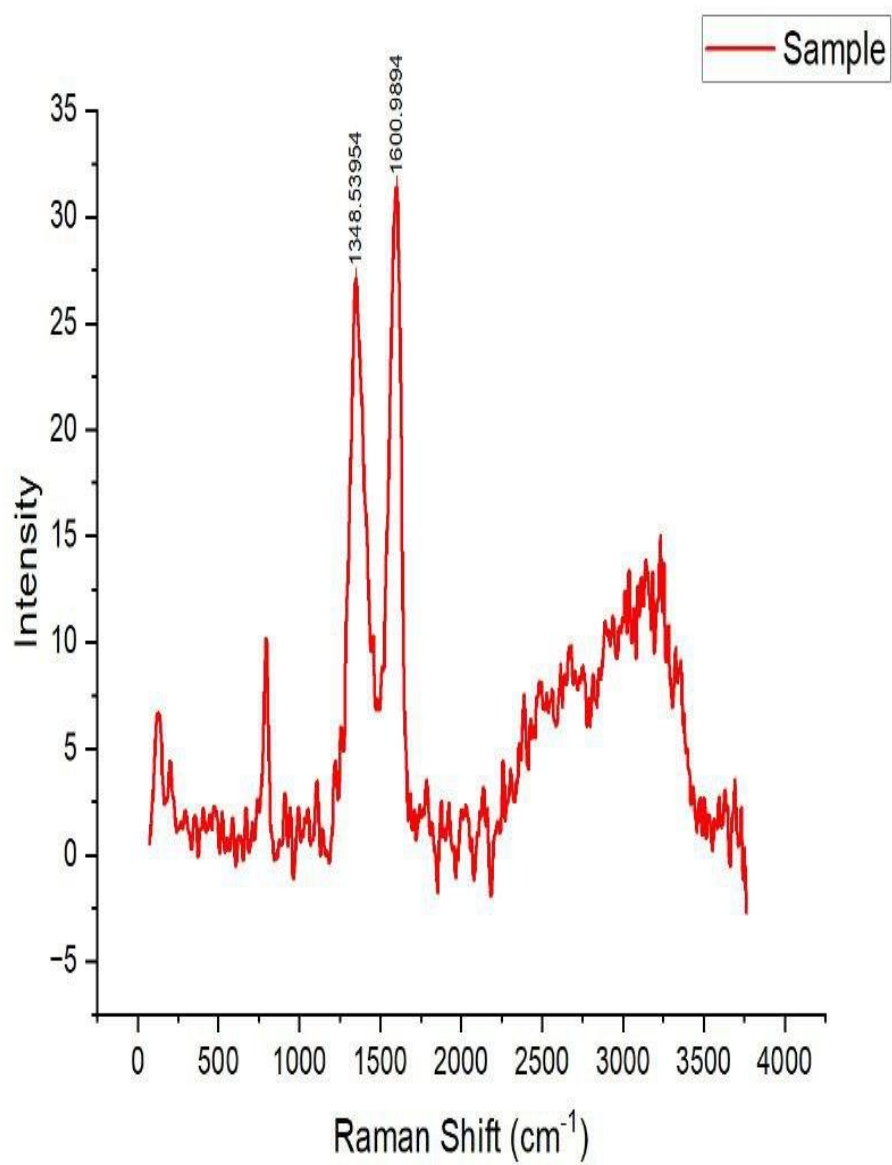
D-peak (at ~1350 cm^{−1}), resulting from breathing mode of κ-point phonons of a 1g symmetry. The D-band is known as the disorder band or the defect band. It represents a ring breathing mode from sp² carbon rings, although to be active the ring must be adjacent to a graphene edge or a defect. The band 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. The intensity of the D-band is directly proportional to the level of defects in the sample. The last thing to note about the D-band is that it is a resonant band that exhibits what is known as dispersive behavior. This means that there are a number of very weak modes underlying this band and the choice of excitation laser used will enhance different modes. The consequence of this is that both the position and the shape of the band can vary significantly with different excitation laser frequencies, making it is important to use the same excitation laser frequency for all measurements when characterizing the D-band.



Instrument description

The instrument is a WITec alpha300RA (WITec GmbH, Ulm, Germany) AFM, SNOM & RAMAN combined system. The laser is coupled into the microscope using a single mode optical fiber coupling and the RAMAN signal is collected into a multimode optical fiber which is connected to the UHTS 300 spectrograph equipped with a back illuminated CCD with better than 90% QE in the visible region.

RAMAN SPECTROSCOPY ANALYSIS



Graph obtained from Improved Hummer's Method

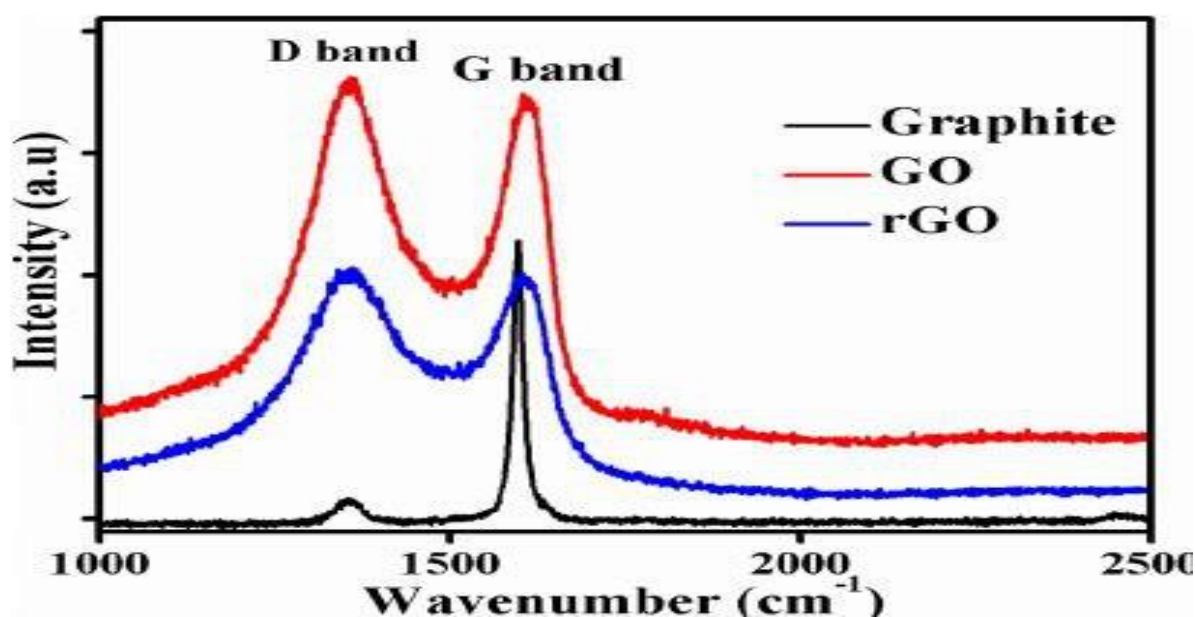
Raman Shift (cm ⁻¹)	Intensity (a.u.)	Raman Shift (cm ⁻¹)	Intensity (a.u.)
1315.38356	18.70571709	1584.939612	29.64798164
1319.535449	19.48816299	1588.955085	30.17841339
1323.685223	20.24738693	1592.96854	30.84924698
1327.832884	21.57080078	1596.979978	31.3995285
1331.978433	23.34583282	1600.989401	31.40737534
1336.121871	24.95365524	1604.996809	30.72434235
1340.263201	26.12545395	1609.002205	29.67072678
1344.402422	26.88459778	1613.005589	28.51057434
1348.539538	27.11071014	1617.006964	26.97824669
1352.674549	26.74278831	1621.00633	24.78935814
1356.807458	26.06983566	1625.003689	22.23295593
1360.938264	25.45273209	1628.999043	19.68090439
1365.066971	24.90705299	1632.992392	17.07226563
1369.193579	24.22962189	1636.983739	14.31640053
		1640.973084	11.51017189

Fig 4.2 Table of Raman intensity versus Raman shift; near G and D bands

Moreover, the intensity ratio of D band and G band (I_D/I_G) indicates the oxidation degree and the size of sp^2 ring clusters in a sp^3/sp^2 hybrid network of carbon atoms. From intensity data (fig 4.2), the (I_D/I_G) intensity ratio of the GO sample is $(27.1101/31.4073) \approx 0.86$

A value of 0.86 suggests that there are some defects or disorder present in the material's structure, but it is not highly disordered, thereby suggests a good degree of oxidation in the sample; thereby reconfirms the prepared sample is graphene oxide.

INFERENCE



Raman spectroscopy is an efficient technique to determine the number of graphene layers and the change of crystal structure of GO and rGO. There are two main bands, the D band and the G band together with weak 2D (also called the G') band. The D band is related to disorders and defects in graphene. The G band is Raman active for sp^2 hybridized carbon-based material. The 2D (the G') band is used to determine whether the graphene is single or few layered.

The two main bands in the graphite spectrum are known as the G band at 1582 cm^{-1} and the 2D band at 2685 cm^{-1} . On the other hand, The Raman spectra of graphene oxide displays a D band at $1348.53954\text{ cm}^{-1}$ and a broad G band at 1600.9894 cm^{-1} . The D band of the Raman spectrum of graphene oxide is prominent. This results in the degradation of the in-plane sp^2 domain in graphene oxide owing to the extensive oxidation.

CONCLUSION

Modified Hummers method:

The preparation of graphene from graphite remains incomplete, as evidenced by the XRD peak observed between 20 and 30 degrees, which corresponds to the peak of graphite.

Therefore the sample contain graphite and a small peak is obtained, which can be reduced graphene oxide. Additionally graphene oxide where not formed, that is why we didn't detect the corresponding peak

Improved Hummers method (Tour method):

The comparative analysis of structural properties of Graphene oxide samples synthesized accordingly to Tour method was done. In summary, this project, which centres on graphene oxide, has yielded invaluable insights into the synthesis, properties, and prospective applications of this remarkable material. The research has showcased graphene oxide's remarkable adaptability across diverse domains, spanning from electronics to biomedical engineering. Through the effective synthesis and meticulous characterization of graphene oxide, the project has established a strong foundation for future investigations and inventive developments. The project's discoveries underscore the extraordinary attributes of this material, positioning it as a highly promising candidate for tackling a wide array of technological challenges. The post-treatment of graphene oxide can enhance its properties and tailor its applications.

Finally, with the broadening of the spectrum of graphene-based materials and processes, recently initiated efforts to standardize the definition of different types of graphene will certainly help speed up the commercialization of graphene.

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