

Applications for the Synthesis, and Properties of Graphene Oxide Detailed Analysis*

Swati Burade

Department of Chemistry,
Kamla Nehru Mahavidyalaya, Sakkardara
square, Maharashtra, Nagpur-440024, India
E-mail: swati.buradeparlewar82@gmail.com,

W. B. Gurnule

Department of Chemistry
Kamala Nehru Mahavidyalaya Sakkardara
square, Maharashtra, Nagpur-440024
Email: wbgurnule@gmail.com

Rashmi R. Dubey

Department of Chemistry,
Kamla Nehru Mahavidyalaya,
Nagpur- 440024, Maharashtra, India

Uma S. Purohit

Department of Chemistry,
Kamla Nehru Mahavidyalaya,
Nagpur- 440024, Maharashtra, India

Swati S. Nagare

Department of Chemistry,
Kamla Nehru Mahavidyalaya,
Nagpur-440024, Maharashtra, India

ABSTRACT

The research community has become interested in graphene oxide (GO) due to its special features, and efficient production methods are being looked into. The sheet's carbon content, determined by synthesis method and also determines what type of oxygen and what are the proportions of oxygen groups used to embellish sheets of Graphene Oxide. The reaction in which reduction of Graphene oxide gives the final product i.e. Reduced Graphene oxide, but elimination of oxygen groups from graphene oxide (tpGO) can also be done by thermal procedure. This chapter contains information on graphene, the substance that forms the basis of graphene oxide (GO), as well as GO synthesis and attributes. It also exposes the reader to the various carbon allotropes. In this chapter we discuss how graphene and graphene oxide are synthesized by modified Hummer's method. There are so many applications of Graphene Oxides but out of those biomedical applications few applications of graphene oxide like in medical field, in water treatment, supercapacitor and gas sensor.

Keywords: Graphene, Graphene oxide, properties, synthesis, Hummer's method, application

I. INTRODUCTION

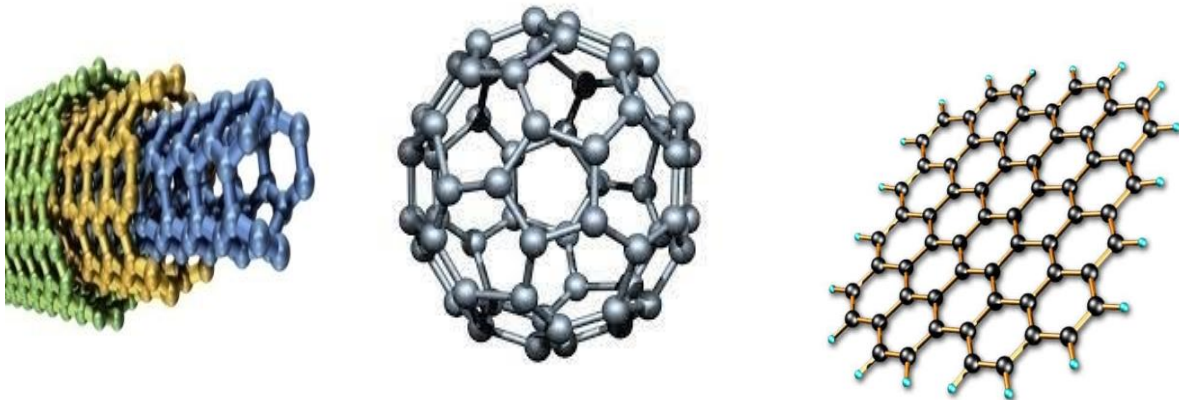
We know Carbon as a chemical element having atomic number 6, chemical symbol C, and atomic weight 12.011 u. It is a non-metal and in the periodic table Carbon belongs to IV th A group. Carbons having 4 valency as it has 4 bonded electrons. In nature carbon is one of the most prevalent elements, and is involved in numerous essential structures and activities, including DNA creation and photosynthesis [1]. Carbon is one of the most common elements in nature, and its atoms can arrange themselves into complex networks that are necessary for organic chemistry and the development of life.. The only substance that can exist in forms ranging from zero dimensions (0-D) to three dimensions (3-D) is carbon. The qualities of carbon's many allotropes range from hard (diamond) to soft (graphite), insulative (diamond) to semi-conductive (graphite) and conductive (graphene), as well as from light-absorbing (graphite) to diaphanous (diamond) [2].

For discovering fullerene, Kroto, Smalley, and Curl received the Noble Prize in Chemistry in 1996. These days, we are aware that fullerenes exist in both nature and space. In the past, fullerene was named Molecule of the Year in 1991 and attracted the majority of research initiatives compared to other scientific fields, to the point where the average publication frequency in the first few years following its discovery was every thirteen hours. With its distinctive sp² carbon structure, fullerene exhibits a high symmetric cage with various sizes (C₆₀, C₇₆, and so on). The most prevalent fullerene in the composition as it was made is C₆₀, whose molecular structure, together with that of C₇₀, [3]. The carbons in fullerenes are joined in groupings of five to six numbered rings, which are polyhedral nanostructures, Fullerenes exhibit little aggregation propensity despite being exceedingly insoluble in water and organic media, which makes it easier for them to be used as sorbent in miniaturized SPE processes [4]. The corannulene, sometimes referred to as bucky bowl and the smallest curved subunit of

fullerene, is a new derivative of fullerene. It has 20 carbons (C₂₀H₁₀)[1]. Sumio Iijima found CNOs in 1980 [9], but CNTs, which were also found at the same time, attracted more attention. Surprisingly, attention to alterations of these nanostructures just started to gain traction at the beginning of the year 2000. In the hexagonal and pentagonal rings that make up the CNOs' structure, in which the carbon at the points form one double and two single bond with adjacent carbon atom, which are distributed throughout the molecule in delocalized -electrons [5].

Three groups reported the field emission from carbon nanotubes (CNTs) at low-turn-on fields and high current densities in 1995, four years after Iijima's discovery of CNTs (1991). [6]. Since their discovery, carbon nanotubes have attracted a lot of attention because of their distinctive physical characteristics. Nanotubes as fillers in polymer or epoxy matrix composite materials with improved mechanical, electrical, and thermal qualities have been the subject of extensive research. Most importantly, they are regarded as the best options for polymer mechanical reinforcement. The tensile strength of 2 CNTs is known to be close to 60 GPa, and their Young's modulus can reach 1 TPa. [7]. The seamless cylinders known as carbon nanotubes (CNTs) are made of one or more layers of graphene (also known as single-wall, SWNT, or multiwall, Open or closed ends, MWNT (1, 2). On the other hand, flaws in mass-produced CNTs include pentagons, heptagons, and other faults in the sidewalls that typically reduce desired qualities. Perfect CNTs have all carbons connected in a hexagonal lattice except at their ends. Although MWNT diameters can surpass 100 nm, SWNT and MWNT diameters are typically 0.8 to 2 nm and 5 to 20 nm, respectively. CNT lengths span the molecular and macroscopic scales, ranging from less than 100 nm to several metres [8].

The oxidation of graphite yields graphene oxide (GO), a nanostructured carbon-based substance. It has several applications in supercapacitors, pollutants degradation, medicine, and composite manufacturing. 10-12 GO The substance can be dispersed in water, numerous organic solvents, and polymers due to the presence of functional groups such as carboxylic acid and hydroxyl groups. Furthermore, these functional groups have the ability to create appropriate bonds with the polymer matrix. Two-dimensional materials, such as GO, have a variety of functional groups, such as hydroxyl and carboxyl, available on their surface and edges. By carefully targeting these functional groups, a strong link can be formed between the filler and the matrix. [9] The oxidation of graphite, graphene oxide (GO) has been regarded as the only intermediate or precursor for producing the latter on a wide scale was first reported by English chemist Sir Brodie. [10] In addition to being an important additive and performance enhancing material in composites, graphene oxide (GO), the oxygen-functionalized and solution-processable form of graphene, has also gained popularity as a structural reinforcement agent in fibers, energy storage devices, molecular sieves, liquid crystal optical materials, and fibers[11]. In graphite the thin layer found, which consists of carbon that have undergone sp² hybridization and are arranged in a honeycomb lattice, was given the name "graphene" about 30 years ago. This gave it a significant surface area and some promising mechanical, electrical, and thermal properties. Because it is difficult to create structured structures on a large scale, pure single-layer graphene has only had modest success in real-world applications despite its outstanding features. The ability of the precursor GO to exfoliate bulk graphite oxide produced by the oxidation of graphite has allowed it to advance significantly in recent years in both academia and industry[10].



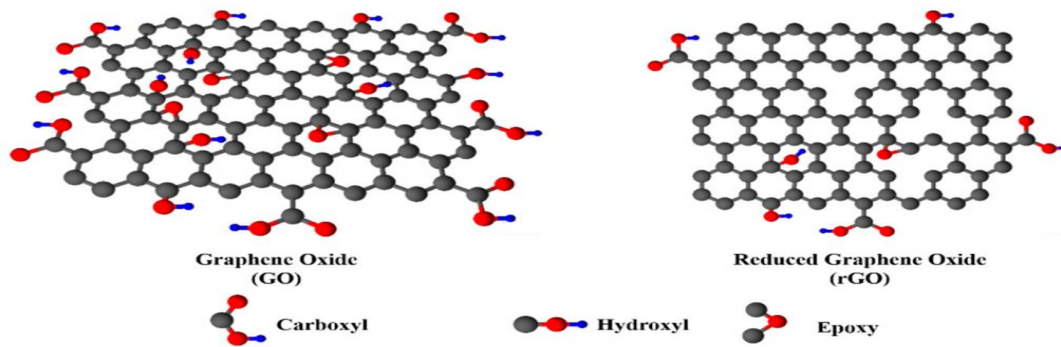


Figure1 Structures of 1) Carbon nanotubes 2) Fullerenes, 3) Graphene 4) Grapheme oxide and reduced graphene oxide

II. PROPERTIES OF GRAPHENE OXIDE

Two-dimensional carbon nanomaterial with carbon atoms having sp^2 hybridization is Graphene. Researcher has gained too much attention for its best electrical, thermal and mechanical properties [12].

A. Mechanical Properties

It has been well documented that pristine monolayer graphene has good mechanical properties, with a break strength of 42 N m⁻¹, 1.0 TPa Young's modulus, and an inherent tensile strength of 130.5 GPa. In an effort to attain these qualities, GO and rGO blends are created, with values varying based on the number of surface groups and flaws left behind from oxidation or other treatment procedures. According to Suk et al. monolayer GO (made using a modified version of Hummer's approach) had a Young's modulus of 207.6 23.4 GPa, a significant decrease in magnitude. Similar to this, Gomez-Navarro et al. reported a rGO monolayer with a Young's modulus of 250 150 TPa that was made using the original Hummer's process and thermal annealing in a hydrogen atmosphere [13]. Different graphene oxide (GO) dosages of 0.01wt%, 0.02wt%, 0.03wt%, and 0.04wt% by the weight of cement, with an oxygen concentration of 28.95%, were introduced in the cement composites to improve their mechanical properties. On the microstructural condition of hydration crystals in the cement composites mechanical property improvement depends mostly. There would be determination of microstructural analysis, microstructure and strength interrelationship of cement mixes [14].

B. Electrical Properties

Several variables affect how electrically conductible graphene oxide sheets are. The planar construction was used to record electrical measurements such as electrical current-voltage. A DC power supply of (0–30) V was used to record the data, and a Keithly Electrometer type 4830 was used to record the output current [15]. High electron mobility ($25 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) and electrical conductivity (6500 S m^{-1}) are characteristics of the electrically conductive substance known as graphene, which is composed of two atomically thin layers of sp^2 carbon. Because of its been demonstrated to significantly increase polymers' electrical conductivity at low filler contents, such as 0.10 S m^{-1} at 1% in polystyrene (PS)[13]. In adequate proportions, silica fume can greatly improve the electrical characteristics of composites with high Graphene contents. This addition aided in the composites' improved electrical conductivity qualities [16].

C. Thermal Properties

Recent research has shown that the heat conductivity of graphene nanoribbons is substantially dependent on their length due to phonon scattering. Under varied length conditions, the thermal conductivity of a functionalized graphene sheet with variable oxidation levels is determined. The influence of sheet length on heat conductivity is studied. For comparison, the thermal conductivity obtained for the pristine graphene sheet with zero oxidation level is also provided. The phonon mean free path in graphene is quite vast in comparison to the length of the functionalized graphene sheet, making thermal conductivity highly reliant on sheet length [17]. The thermal stability of polymer nanocomposites containing GO was demonstrated using the PerkinElmer TGA 4000 thermal analyzer. Weight % loss was detected from 30C to 600C at a heating rate of 10C min⁻¹ with respect to temperature [18]. In the air atmosphere size of Graphene Oxide, Graphene and Graphite were varying by thermal degradation and was used to investigate how that particle size dependant on thermal characteristics [19]. The brief idea about Graphene, Graphene Oxide and Reduced graphene oxide and its properties are given by the table no. 1[20].

Table no.1 Graphene , Graphene oxide, Reduced Graphene oxide and their general characteristics

Sr.No.	Characteistics	Graphene	Graphene oxide	Reduced Graphene oxide
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1	Electrical conductance	$\sim 6.5-10 \text{ S m}^{-1}$	$5.71 \times 10^{-6} \text{ S m}^{-1}$	$10^3-10^6 \text{ S m}^{-1}$
2	Sheet resistance	$210 \Omega \text{ sq}^{-1}$	$\sim 10^9-10^{10} \Omega \text{ sq}^{-1}$	$\sim 10^2-10^6 \Omega \text{ sq}^{-1}$
3	Carbon- carbon bond length	0.142nm	NA	NA
4	Mobility of electrons	$\sim 201,000-255,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.12-10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$1.9-220 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
5	Thermal conductance	$\sim 4900 \text{ W m}^{-1} \text{ K}^{-1}$	$0.51-19 \text{ W m}^2 \text{ K}^{-1}$	$1400-2272 \text{ W m}^{-1} \text{ K}^{-1}$
6	Specific capacitance	551 F g^{-1}	$216-256 \text{ F g}^{-1}$	$215-427 \text{ F g}^{-1}$
7	Surface area	$2632 \text{ m}^2 \text{ g}^{-1}$	$736.7 \text{ m}^2 \text{ g}^{-1}$	$468-759 \text{ m}^2 \text{ g}^{-1}$

III. GRAPHENE SYNTHESIS, GRAPHENE OXIDE SYNTHESIS, AND REDUCED GRAPHENE OXIDE SYNTHESIS

A. Graphene Synthesis

On the efflorescence of individuals result, required size and purity generation or extraction of Graphene procedure depends is referred as Graphene synthesis. Earlier there was discovery of numerous strategies for producing thin graphite film. In the late 1970 the transition metal has thin Graphite coating of carbon precipitate. On the single crystal platinum surface graphite layer was synthesized by using chemical composition method in 1975, but due to a deficiency of characterisation techniques or may be due to its restricted potential applications, it was not identified as Graphene. Several strategies for graphene production have been developed in recent years. Mechanical cleaving (exfoliation), chemical exfoliation, chemical synthesis, and thermal chemical vapor deposition (CVD) synthesis are, nonetheless, the most commonly utilized processes today. Other approaches, such as unzipping nanotubes and microwave synthesis, have also been reported.[21]

a. Synthesis by Top down method

An attack approach based on powdered raw graphite can be defined as top down method. Graphene sheet was form by the attack which finally splits into its layer. Mechanical or chemical exfoliation, as well as chemical synthesis, are examples of Top-Down strategies[22].

Mechanical Exfoliation

Mechanical exfoliation is a famed but unusual practice for extracting monolayer of graphene fragments on chosen surfaces. This is original recorded process of producing graphene. The approach was used in nanotechnology when the surface of material's layer is subjected to either longitudinal stress or transverse. Graphite is formed by the collecting of single layer of Graphite atom due to weak van der Waals forces. The distance 3.34 and bond energy 2 eV/nm² values for the interlayer data. But, for mechanical cleaving, an external force of up to 300nN/mm² is required in order to separate a single atomic layer from graphite. Sheet stacking is caused by partially filled p orbital overlaps perpendicularly on the plane of the sheet, which involves van der Waals forces. There was low bonding and large vertical lattice spacing due to exfoliation. The hexagonal lattice plane has superior bonding and narrow lattice spacing[22].

Chemical Exfoliation

Chemical synthesis is one of the most appropriate methods for producing graphene. In a chemical technique, colloidal suspension is produced that modifies graphene from graphite and graphite intercalation compound. Various forms of paper, such as polymer composites, energy storage materials, and transparent conductive electrodes, have already employed a chemical process to produce graphene. Chemical exfoliation consists of two steps. firstly to enhance interlayer space by the interlayer van der Waals forces. Using rapid heating or sonication for the preparation of graphene intercalated compound one or few layers of graphene exfoliates. Polycyclic aromatic hydrocarbons (PAHs) have been utilized in the manufacturing of graphene to disperse single layer graphene sheets[21].

Electrochemical Exfoliation

In an aqueous or non-aqueous electrolyte conversion of graphite into graphene by electrochemical exfoliation applying carbon source as an electrode. Recently, researchers divulge that by the method in which graphite rod exfoliate electrochemically in acidic electrolytes, a simple, low-cost electrochemical method used for production of graphene. The researcher created graphene nanosheets by exfoliating a graphite rod in a single step and then gold nanoparticles attached to the surface of graphene. Then the resulting material used to alter a glassy electrode of carbon, and in the presence and absence of interfering species hydroquinone's electrochemical behaviour was investigated. In the aqueous medium on the basis of electrochemical

delamination of graphite with sodium halides as an electrolyte Munuera et al. analysed a simple approach for the production of accessible low oxygen graphene[23].

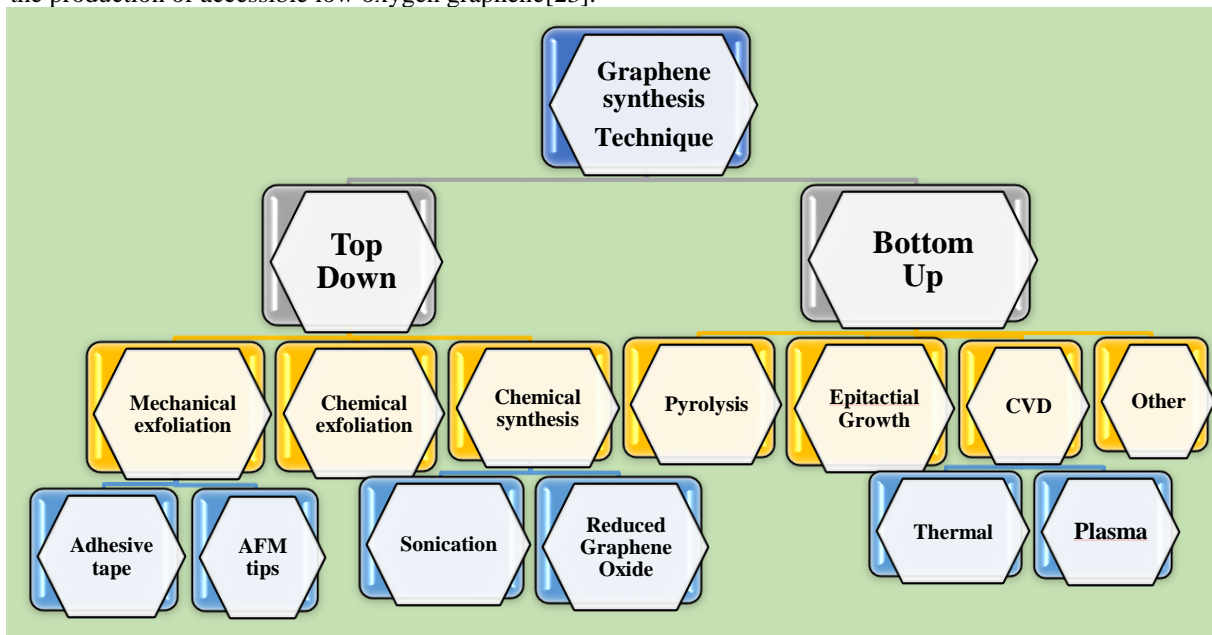


Figure 2 Flow chart of synthesis techniques of Graphene

b. Bottom Up Synthesis

Pyrolysis

For the production of highly graphitic carbon materials pyrolysis has been studied as safe method. It is primarily a bottom-up approach to produce graphene derivatives in a high-temperature, non-oxidizing environment. The creation of graphene-derived products has been demonstrated by pyrolysis of waste precursors. Wang et al. created graphene using a single stage of AC arc plasma pyrolysis. The approach used a combination of methane and hydrogen gas in the presence of a carrier gas (Ar) to synthesized graphene with low layer under ideal circumstances for application lithium battery. Other recent waste pyrolysis sources have been exploited to scale-up graphene production. For example, under Ar, coffee waste can be converted into graphene at 800 °C for 1 hour. At 900 °C through pyrolysis lignin-based graphene produced for application of energy storage for 3 h and 5 °C/min, through pyrolytic optimization for waste-water treatment elephant grass was prepared from graphene derived material and for industrial applications there was synthesis of plastic waste into graphene nanosheets via pyrolysis. Solvothermal techniques have been used to aid pyrolysis in some circumstances [24].

CVD (Chemical Vapour Deposition)

CVD is a chemical reaction-based technology for the deposition material a on substrates from vapour species as a thin film. Many complex factors govern the procedure and kinds of chemical reactions that can exist in a CVD reactor, which include system setup, configuration of reaction, gas feedstock, ratios of gas, combination of both pressures i.e. reactor and gas, temperature of reactions, growth time, temperature, and so on. CVD is a popular bottom-up method for creating few and single graphene layer films. In 1966 on metals the thermal CVD was used to create films of crystalline graphite on Ni substrates was originally reported. At 530°C using a CVD technique by hydrocarbon breakdown, a graphite layer was deposited on the platinum surface. In 2004, By utilizing lp CVD to build graphene on Iron, G graphene films was completed lucratively by research of potentials of chemical vapour density [20]. Because it is simple to set up in research facilities, has a proven track record of success in industrial settings, and can be scaled up, the CVD approach is attractive for the development of graphene. In CVD reactor carbon sources in different precursors, such as solid, liquid, and gaseous, were suitable for formation of graphene which was described earlier. In the reactor chamber there was direct loading of solid precursor. As previously stated, for the generation of thin film deposition CVD procedures are classified on the basis of energy method which was used in the reactor. The extremely common route are (1) hot-wall CVD, For adjust growth substrate and subsequent feedstock decomposition, furnace heated whole reaction chamber to provide energy which was needed (2) cold-wall CVD, in which In an unheated reaction chamber, to the desired growth temperature the growth substrate is directly heated (3) plasma-enhanced CVD (PECVD), plasma ignite to low pressure gas by high frequency voltage [25].

Epitaxial growth

The starting material for graphene epitaxial growth is commonly SiC. First, SiC is heated to a high temperature in a vacuum chamber, where thermal breakdown occurs and Si sublimates. The dissolved SiC is then subjected to an annealing process, which comprises slow cooling following heating. This permits the sublimation Si to be reconstructed as an interfacial layer on SiC, and the C to deposit as an epitaxial layer on the Si face to generate graphene. However, Si could still evaporate during C deposition. Because the heating temperature is managed, this approach has good control over the quantity of graphene layers generated, resulting in graphene with promising electrical properties. However, the homogeneity of graphene produced by this energy-intensive process is uncommon. The formation of a C-polar face rather than the S-polar face, which favors homogenous graphene growth, could further impair graphene quality [26].

Other Methods

There are some additional methods for the production of graphene such as of graphite's arc discharge, irradiation of electron beam of PMMA nanofibers, and nanodiamond conversion. For the generation of graphene nanoribbons utilizing mixture of Conc. H₂SO₄ and extremely oxidative KMnO₂, irradiation of laser, Lithium in liquid ammonia, and etching plasma unzipped by multi-walled carbon nanotubes, which can then be used to make graphene. Boron- and nitrogen-doped graphene is frequently produced using arc discharge techniques. An arc discharge in presence of nitrogen between pyridine or ammonia and carbon electrodes was utilized to produce Nitrogen-doped graphene sheet. Boron-doped graphene sheets have been created in the presence vapour mixture of hydrogen-diborane or graphite electrode filled by boron.[27]

B. Synthesis of Graphene Oxide

In the bottom-up methods, for production of Pristine Graphene basic molecules of carbon are utilized. In the "top-down" methods, from a carbon source, frequently graphite, graphene derivatives layers were recovered for the preparation of GO these were two primary categories. There was very consumption of time and prone to scalability issues in bottom-up synthesis. The synthesis of graphene oxide and/or reduced graphene oxides first are increasingly common meant for producing derivatives of graphene in top-down approach, particularly for application in nanocomposite materials. Brodie, Staudenmaier, and Hummers and Offeman are frequently credited with the first GO synthesis [28].

In 100 mL of concentrated sulfuric acid in a jar took graphite fragment (10 g), KMnO₄ (6 g), and K₂FeO₄ (4 g) as oxidants were propagated at less than 5 °C. Shaken for 1.5 hours. Then again add 5 g of KMnO₄ at 35 °C the beaker was kept in water bath and again shaken for another 3 hrs to complete the oxidation. After progressively addition of 250 mL of deionized water, heated up to 95 °C for 15 minutes, until brown colour suspension indicating hydrolysis and intercalated Graphite Oxide was removed. Lastly, intercalated Graphite Oxide was reacted with 12 mL H₂O₂ to convert the residual oxidants and intermediates to soluble sulfate, then for 20 minutes it centrifuged at 10000 rpm to eliminate the residual graphite, repeatedly cleaned through 1 mol/L HCl and distilled water, forming the terminal graphene oxide. In comparison to this using Kovtyukhova's enhanced Hummers method 20, another GO (named GO1) was prepared [29].

Graphite powder was treated with NaNO₃, KMnO₄, conc. H₂SO₄ mixture this was another process for oxidation of graphite in 1958 demonstrated by Offeman and Hummers.

First, powdered graphite and sodium nitrate 100 g and 50 g respectively were reacted in 2.3 litres of Sulfuric acid and at 0 °C in an ice bath. Then to the suspension, mix 300 g of KMnO₄. Stirred the suspension thickened after that then by adding hot water it became diluted and added with H₂O₂ (3%) to convert the permanganate residue and manganese dioxide to form soluble manganese sulphate which was colourless. Lastly, for the elimination of soluble salt of mellitic acid gave washing to diluted suspension many times. Then dehydration occurred at 40 °C after centrifugation in vacuum yielded the dry form of graphitic oxide over phosphorus pentoxide. Recently Hummers' improved approach have been exploited by many researchers for production Graphite oxide [30].

Graphene Oxide was synthesized from graphite powder by a modified Hummer's technique 0.5 g graphite and 0.5 g NaNO₃ were added to 24 ml concentrated sulphuric acid (H₂SO₄) in a conventional synthesis. The mixture was ultrasonicated for 1 hour while being kept at 5 °C in an ice bath. Then three g of Potassium permanganate was progressively mixed. The reaction mixture was then ultrasonically agitated for 2 hours using an ultrasonic bath with required power and frequency to get a homogenous mixture. 50 ml distilled water was gradually mixed to the mixture, then by 1 hour of ultrasonication. Brown coloured mixture was detected, heated to 35 °C the mixture was withdrawn from the ice bath and agitated by magnetic stirrer for one hour. The mixture's colour shifted to pale brown. Following that, another 100 cc distilled water was added to the mixture, and the temperature was raised to 90 °C and agitated for 1 hour. Finally, a 10 mL hydrogen peroxide and 100 mL distilled water solution was added to create a pale yellow suspension.

To remove any metal ions, the resulting suspension was thoroughly filtered using a premium Wattman filter

before being rinsed with 10% HCl. The suspension was then thoroughly rinsed with distilled water till the pH was neutral. To create a well-dispersed graphene oxide solution, distilled water was added to the resultant filtrate, subjected to ultrasonication for an hour [31].

Without any further modification all the analytical reagent grade chemicals graphite powder, NaNO₃, KMnO₄, H₂SO₄, NaOH, H₂O₂, concentrated HCl utilized and received. Graphite powder was used as a reactant in the modified hummer's method for the production of graphene oxide. Added 0.5 g powdered graphite and 23 ml of concentrated H₂SO₄ and 0.5 g NaNO₃ in this preparation. For abt four hrs in an ice bath the mixture vigorously stirred into the mixture slowly added approx. 3 g of KMnO₄ with 10 minutes of interval then again stirred for 1 hr. At 35°C mixture was heated and cooled at room temp. 45 ml of dist. Water added and continued stir continuously for one hour. Up to 90°C for 2 h mixture was heated with stirring, into that 100ml distilled water added. To stop the reaction abt 13 ml 30% H₂O₂ added. For two days the mixture was kept for settle down by washed with 100 ml of 5% HCl solution and. Then for many times mixture was washed to discard all the impurities with DW, centrifuged continuously for 10 minutes at 5000 rpm. Then powdered form obtained by drying at 60 °C centrifuging too[32].

For the making of graphene oxide from natural graphite enhanced hummers' method was used. In order to get rid of graphite which was not reacted and inorganic salts, the pure suspension of graphene oxidewas cleaned and purified and slightly removed by centrifuging it five times (7000g) with 1 M HCl and six to nine times (15100g) with doubly distilled water. A light brown liquid with a 1 w/w% of graphene oxide nanoparticle was obtained then washed finally and centrifuge [33].

Using a modified Hummers technique, sample of graphene oxide was created. 1 g of coconut charcoal on graphite base added in 25 mL of H₂SO₄, and for 30 minutes this reaction mixture churned in an ice bath. After solution was stirred, gradually added 3 g KMnO₄ and stirred for a three hrs. and maintained temp of ice bath between 20°C to 30°Cstirring was stopped when it became dark green. After this solution was taken out of the ice bath, continued stirring at 35°C for an hr. Then, slowly added 50 ml deionised water, and for 1 hour the mixture was stirred. Again added 100 ml distilled water and sterilized for one hours. For the removal of excess KMnO₄ solution sterilized for 30 min. before being progressively infused with 5 ml hydrogen peroxide. After this, neutral pH was maintained by adding distilled water before centrifugation was used to eradicate the ppt from the liquid. For creation graphene oxide powder, for 12 hour the ppt was baked in an oven at 110⁰ C [34].

C. Synthesis of Reduced Graphene Oxide

Vitamin C was used to decrease a diluted 2 mg/mL graphene oxide solution. Ascorbic acid was present in the combination at a 20 mM concentration in 1 mL of cc. In order to set a basic pH and prevent the precipitation of the reduced GO (rGO), NH₃ was added to a 15 mL reaction mixture. For one hour, the mixture was refluxed at 95 °C while being stirred. It was then centrifuged and washed several times water to maintained neutral pH. The rGO was finally air dried[35].

Hydrazine monohydrated was used as the reduction agent in this chemical reduction (ratio: 1.1). Before centrifugation, graphene oxide 800 ml (1 g/L) and 800 ml of hydrazine monohydrated were combined to accomplish the task. For three hours, the mixture was continuously stirred at 90°C in a closed stirring reactor. After the allotted time had passed, for precipitation of product the solution was centrifuged for 30 minutes at 10,000 rpm (RGO-F/ RGO-H). The remaining hydrazine was then removed from the precipitate, for maintained pH washed with water. That finished product was kept in a drying oven for four hours at 80 degrees [36].

500 ml of DI water and 1.5g of GO powder were combined to create the combination. To create GO dispersion, the liquid was agitated for 30 minutes. It was then time to add 0.5 cc of hydrazine hydrate to the diffusion. After that solution was heated in oil bath upto 80°Cand then continuously stirred the solution for 72 hours. The liquid was divided into six individual 50 ml centrifuge tubes for washing after 72 hours. The cleaning process involved adding DI water and centrifuging for 15 minutes at 5000 rpm. Before drying for 24 hours at 80 degrees Celsius in an oven, these steps were performed twice [37].

Hydrazine hydrate is used to reduce GO in a process. To ensure uniform dispersion in the solvent, 1 g of GO is placed in a beaker with 100 ml of distilled water and allow for 2 hours through sonication. after ultrasonication 0.4 cc hydrazine hydrate was mixed and held at 60°C for12 hrs. magnetic stirring. The resulting solution underwent vacuum filtration and many rounds of ethanol and water washings. To produce a dry product, the filtered paste was dried for 24 hours at 40°C in a vacuum oven[38].

Table 2 Exemplify outline of Graphene, Graphene Oxide, Reduced Graphene Oxide

Characteristics	Graphene	Graphene Oxide	Reduced Graphene Oxide
Electrical conductivity	7200	$1-6 \times 10^{-5}$	$2-8 \times 10^{-3}$
Electron mobility $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	10,000-50,000	Insulator	0.06-200
Thermal Conductivity	$4.85-5.30 \times 10^3$	1500-5810	0.2-2
Cost of product	High	Low	Low
Young's Modulus	1-3	2-5	2-4
C:O Ratio	No oxygen	2-4	8-247
Synthesis	Chemical Vapour deposition and Graphite Exfoliation	Oxidation of Graphite followed by Exfoliation	Thermal or chemical reduction of graphite oxide

IV APPLICATION OF GRAPHENE OXIDES

Applications of graphene oxides in biomedical field

Graphene derivative separated into graphene oxide and reduced graphene oxide which have comprehensive potential uses in biomedicine, including phototherapy, drug delivery systems, polymer composites, biological sensors, and biomolecule detection [39]. Couple of years back graphene took lead position in scientific inquiry. The new technology to synthesize graphene has made this material widely available on the market. GO and rGO, two of graphene's derivatives, have fascinated too much of interest for usage in technology [40]. With its potential for use in biomedical sectors like drug/gene delivery, parasitology, tissue engineering, antimicrobial treatment, cancer therapy, and other biomedical imaging and diagnostics, Astounding GO has drawn attention ever since it was first developed. In the field of clinical research the usage of graphene oxide requires thorough studies employing specific cell lines, theoretical models, and animal models to establish its toxicity and biocompatibility [41]. Several groups have documented the usage of GO in medication, delivery, cancer therapy in recent years. GO has proven to make apoptosis in human liver cancer cells (HepG2 cells) and could be used to treat human hepatocellular carcinoma (HCC)[42]. But we are discussing some more biomedical applications here.

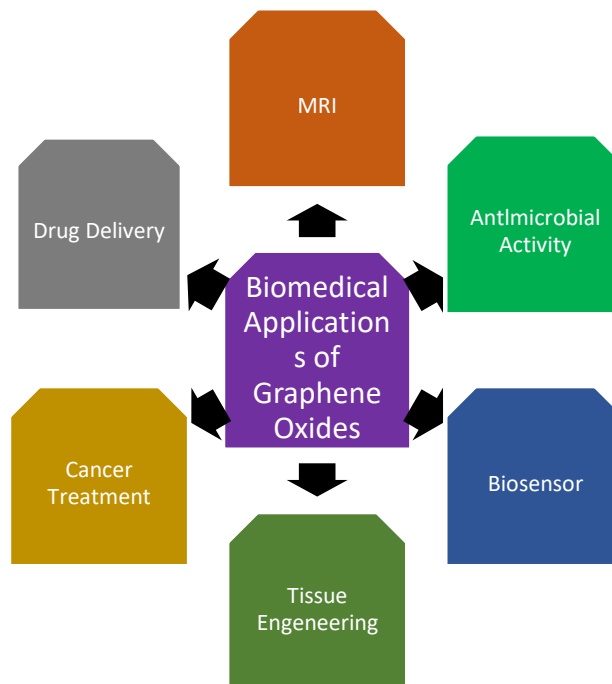


Figure 3 Biomedical application of Graphene Oxide

A. Application of GO in MRI

In clinical biomedicine, magnetic resonance imaging (MRI), a non-invasive diagnostic technique with extremely high temporal-spatial resolution, is frequently used. The position, size, and boundary of diseased regions, such as tumors, can be plainly seen all the time the obvious contrast with normal tissues [43]. Based on how water protons relax, T1 and T2 are two categories of MRI contrast agents. Water protons' ability to relax into their spinlattices and spinespins could both be improved by T1 contrast agents and T2 contrast agents, respectively[44]. Gd, Mn, and Fe-based materials are the most frequently employed contrast agents (CAs) for MRI. CAs must build up in the tumor location during blood circulation for an effective MRI. Therefore, there is a pressing demand for carriers with specialized tumor targeting properties and lengthy blood circulation times[43]. The majority of magnetic nanomaterials, including the non-toxic γ -Fe₂O₃, α -Fe₂O₃, and Fe₃O₄ nanoparticles, were investigated for use as T2 contrast agents. Since Fe₃O₄ nanoparticles are likely to aggregation, precipitation in real-world applications, that limits their usability, that is vital to provide them the proper capabilities in order to create magnetic hybrids. Because of its substantial surface area, several oxygenation function, biocompatibility, and on the graphene oxide sheet that have ability to control the creation of spreading of Fe₃O₄ that may have the potential to operate as MRI contrast agents, GO was used as a platform [44]. For MRI application the application of Fe₃O₄ modified graphene oxide was initially reported by the Yu group. On poly(sodium 4-styrenesulfonate) modified graphene oxide Fe₃O₄ was decorated using a high-temperature thermal decomposition process in a controlled manner, and the magnetic GO as made demonstrated exceptional in vitro T2-weighted MRI effect and good water solubility. Later, Chen et al. created a GOPEG--FeOOH-based MR conversion agent with enormously high transverse relaxivity (r_2) value. The r_2 value of GO-PEG-FeOOH in this study was $303.81 \text{ mM}^{-1} \text{ s}^{-1}$. Which was higher than other reagents. The efficient buildup of GO-PEG--FeOOH in liver tissue was also responsible for the outstanding in vivo T2 weighted MRI effect of the liver. MRI applications also use Gd and Mn based CAs. For use in T1 weighted MRI, Yang and associates created a Gd modified GO (Gd-NGO). Compared to Gd-DTPA, the as-prepared Gd-NGO had a substantially greater r_1 value and contrast of the in vivo T1 weighted MR picture. Zhang and colleagues reported using GO-DTPA-Gd ($r_1=10.8 \text{ mM}^{-1}\text{s}^{-1}$) as a contrast agent for MRI and found improved T1 MRI effects for HepG2 cells in another piece of literature. For T2 weighted MRI, Peng et al. created a modified MnFe₂O₄ GO and obtained a high r_2 value of $256.2 \text{ mM}^{-1}\text{s}^{-1}$ [43]. After receiving an intravenous injection of CAD/MGO, the MRI signals of the tumour greatly improved, and the tumour boundary was easier to see, indicating that CAD/MGO was rapidly enhancing in the tumour area. Additionally, 15 minutes after injection, the liver, kidney, muscle, and heart's MRI signals showed only a negligible improvement; in contrast, the bladder's MRI signals exhibited continuous elevation and peaked 30 minutes after injection. Normal organs and the signal-to-noise tumor ratios (SNR) were clearly visible by MR image, indicating that the CAD/MGO composites might used as effective contrast agents for T1-weighted positive MRI of tumours[44]

B. Application of GO in Drug Delivery

A remarkable collection of material properties are displayed by GO and its functional analogues, which are frequently employed to transport various treatments like DNA, antibodies, proteins, genes, and tiny medicinal molecules. Special and innovative characteristics of GO sheets that are important for drug delivery are their dimensions laterally, surface area, layer count, and surface chemistry. These characteristics provide a wide range of customizability to controlled drug-release platforms. Changes in the shape, drug load, and drug-release properties of nanocomposite films can be generated by varying the dimensions and width of the GO nanosheets. GO may enable the loading of a variety of biomolecules onto the film due to its role as a nanocarrier[41]. Graphene oxide loaded and released anticancer drug after some important work, there are too much work had been published which was on controlled drug loading and targeted delivery of drugs through graphene and its derivatives this was also use for cancer therapy as well as other non-cancer treatments as biodelivery carriers. For example, for targeting agents towards tumour cells a superparamagnetic GO-Fe₃O₄ nanohybrid is used as the delivery carrier, however the drug release is measured by pH values.[45].

Through electrostatic self-assembly, Lei and co-worker using GO adapted with CS and SA created a drug delivery system (SA-sodium alginate). DOX was added to the nanocomposite through π -stacking and electrostatic interactions. Self-assembly was used to create the nanocomposite by means of layers, and the positively charged CS there was electrostatic interactions between CS which was positively charged GO and SA(sodium alginate). FTIR was used to validate the attachment of both the CS and the SA. According to atomic force microscopy dimensions the width 2 nm for GO, 6 nm for GO-CS, and 60 nm for GO-CS-SA composites. DOX was added to GO-CS/SA nanocomposites. Additionally, a fluorescent marker called fluorescein isothiocyanate was used to track the absorption of DOX by cells. the DOX's earlier issue in reply to the GO-CS-SA-DOX's amazing cytotoxicity[42].

Camptothecin (CPT), an anticancer medication, was fixed onto drug delivery system of the GOPEG-FA with the addition of GO-PEG-FA solution and agitating it for entire night. Repeated washings at 9000 rpm at

RT for twenty minutes and filtration through 100 KDa filter paper were used to remove the unbound CPT. The GO-PEG-FA-CPT complex that created was re-suspended and set aside at 4°C. Phosphate buffer saline was used for dilution and calibrations at 7.4 pH. Following is how the loading efficiency was determined:

Loading effectiveness is equal to $(\text{total CPT} - \text{unbound CPT}) / \text{total CPT} \times 100\%$. At pH 5.3 and 7.4 allowed researchers to calculate the release rate of CPT-loaded GO-PEG-FA departing the sample against 50 ml PBS at 37 °C. A UV-visible spectrophotometer set to 365 nm was used to measure the concentration of medication released after 6 hours of dialysate replacement with PBS [46]. Researchers have worked very hard in recent years to modify graphene-based nanomaterials in the right ways to upsurge their efficiency for chemotherapeutic applications as well as cancer cell testing. As an illustration, Zhang and colleagues created a useful NGO for the loading and precise anticancer medications delivery. For targeted and controlled release of drug, a drug delivery system of mediating graphene was discovered by Depanet al. Doxorubicin was attached to graphene oxide using chitosan conjugated by Folic acid to create nanocarrier system. Functionalization noncovalent type which allows regulated drug release and drug loading known as "stacking" [47].

C. Application of GO in Cancer treatment

Every year, millions of individuals worldwide are affected by cancer, which is the unchecked cell proliferation that kills. Cancer of breast is the most common aggressive malignancy in women globally, out of nine one woman in worldwide imagining to acquire cancer of breast throughout their whole life and young woman in the age of 29 died from it [41]. Treatment outcomes may be enhanced by giving cancer cells medication combination with synergistic effects. Given the synergistic potential of this medication mixture, the DOX-TOS content added to nanomaterials in the literature was not optimized. Instead, based on the physicochemical characteristics of the produced materials, the DOX:TOS mixture ratios full in the nanomaterials were chosen. Moreover, depending on the fraction affected (Fa) that is being examined, various drug ratios may had diverse cojunctional effects. Researcher therefore first identified the DOX:TOS molar ratio that displays the best synergy athwart many Fa before loading the DOX-TOS mixture in POx-GO. To do this, MCF-7 cells were treated with DOX:TOS at their different molar ratios like 5:1 to 1:5, [48]. More than 570,000 cancer-related deaths are anticipated in the United States in 2011. The creation of new diagnostic techniques that enable the early detection of disease is the best way to stop the spread of cancer. Finding the biomarkers of specific cancers is one of the most promising strategies. Graphene's remarkable physical characteristics and its oxide are enabling the creation of novel optical, platforms for electrochemical, FET-based biosensors and diagnosis that, as we'll see in the section below, were started to make it possible to diagnose diseases [49]. The amino-modified graphene oxide and carboxymethyl cellulose were joined to generate the graphene oxide - carboxymethyl cellulose complex, which served as a carrier for the tumour-specific medication doxorubicin hydrochloride (DOX) after Rao et al. recognized that an acidic tumour environment facilitated tumour-specific drug release. In order to create a hybrid for the treatment of Non-Muscle Invasive Bladder Cancer (NMIBC), Durán et al. loaded DOX and small interfering RNA (siRNA) onto scaffold made of one-layer GO with a purity of 99%. Sixty percent of the rats showed NMIBC recovery during in vivo tests. It can be assumed that GO had a good chance of successfully treating NMIBC [39]. Hyaluronic acid, also known as hyaluronan (HA), is polymer that controls a number of physiological processes that are normal while also promoting the development of chronic and acute diseases, like cancer. HA family members, including HA synthases, HA receptors, and HYAL-1 hyaluronidase, have been experimentally demonstrated to support growth of tumour and are overexpressed in a number of carcinomas, for cancer cells it was used as potential target. Additionally, graphene oxide nanocarriers had altered so that cancer cells can be recognized using the HA receptors and then brought inside the cell through endocytosis. A graphene oxide functionalized with adipic acid dihydrazide was employed by Wu et al. [46] to create amine groups that permitted HA binding covalently. The resultant GO-HA demonstrated very minimal cytotoxicity toward HeLa and L929 cells and barely any hemolytic activity. In the GO-HA DOX was added to the carrier to create GO-HA/DOX, which was shown to be endocytosis that is efficiently mediated by receptors in cancer cells [50].

D. Application of GO in tissue Engineering

Nanotheranostics is the term for the treatment and diagnostic process combined. On the basis of the utilization of nanomaterials, it entails integrating treatment and diagnosis into a single platform. It enables early disease identification, leading to more effective therapy. One of the popular therapeutic methods that links numerous specialists from various scientific fields is tissue engineering. These days, creating a scaffold that is suitable for supporting growth of cell and has enough mechanically stable to complete a course of rejuvenation and maintain surgical settlement is a fascinating task, particularly when it comes to the treatment of orthopedic and cardiovascular injuries [51]. By creating biological replacements and secure materials, tissue engineering can replace or repair damaged human tissue or scaffolds. Due to its capacity to interact with another biomolecules for reformative medicine, graphene nanomaterial is now extensively used in the medical and tissue engineering industries.

Recently, fresh inventions have been drawn to graphene and its byproducts, which have been used in biocompatible systems. In a recent study, the electrospinning process was used to modify CHI/Poly(vinyl alcohol) (PVA)/GO composite nanofibre. The findings showed that 6 wt% CHI/PVA/GO composite was more ecologically friendly against the proliferation of ATDC5 cells than was 4 wt% CHI/ PVA/GO composite. They concluded that additional research into 6 weight percent CHI/PVA/GO nanofibre for artificial cartilage was warranted[52].The topic of skin and muscle tissue engineering is another significant application of tissue engineering in relation to mechanical enhancement of graphene-based materials. It is crucial to use biomaterials to replicate the mechanical milieu of native extracellular matrix (ECM) in order to promote skin and skeletal muscle regeneration. But most biomaterials now in use are unable to duplicate the mechanical properties of ECM [49]. Because of their hydrophilic polymeric network structure, which resembles ECM, and the ease with which their physicochemical properties might be altered, hydrogels, for instance, were frequently used as a class of ECM-mimicking materials[53]. It has been shown that the distinction of mouse embryonic stem (ES) cells into both nascent, ultimate haematopoietic cells has been greatly abetted by GO-coated substrates. GO has no impact on differentiated cells' ability to proliferate or survive. GO speedily converted haemangioblasts into haemogenic endothelial cells, which is thought to be a crucial stage in the process of defining the hematopoietic system. Additionally, GO enhances the development of human ES cells into blood cells[54].

E. Application of Graphene Oxide as Biosensor

The Graphene derivative has very distinctive characteristics of are widely utilized as biosensors [47].Biosensors are analytical indicators that are hypersensitive to very low concentrations of the drug being studied and accept a quantifiable physicochemical indication. Because of its inherent advantages, photoelectrochemical sensing method had gathered considerable interest as auspicious analytical tool[44]. Biosensors built on GBMs are flexible diagnostic tools with quicker discovery than conventional techniques. They can identify detected compounds at femto- or pico-molar concentrations.

There was device that can transform quantitatively or semi-quantitatively chemical's detection into an evaluable signal known as chemical device . These sensors typically consist of a receptor and a transducer. The receptor might be any organic or inorganic compound that has the ability to interact with a specific species or set of species. Chemical information is converted into a signal by the transducer. Field-effect transistors, resonant biosensors, optical-detection biosensors, ion-sensitive biosensors, electrochemical biosensors, and thermal-detection biosensors are some of the different types of biosensors that can be categorized based on the transducer system. Electrochemical and surface plasma resonance (SPR) sensors on the basis of metal nanoparticles should also be mentioned, as should optical sensors based on metal NPs or chromophores. According to what we know, the electrical, structural, and thermal characteristics of GBMs make them upright contenders for the sensing of biomolecules[51].Because various compounds oxidize or decrease at distinct potential windows, electrochemical biosensors are unique to those potential windows. For biomolecular detection the researcher have very sensitive platform thanks to fluorescence spectroscopy. The ability of field effect transistors (FET) to provide fully automated electronic finding that is totally combined with the electronic chips made by semiconductor firms has recently attracted too much consideration in biosensing field. Therefore, there is an raising attention from industry as well, not just academia, in these devices [47]. For the purpose of developing PEC sensing system for prostate specific antigen testing, reduced GO-BiFeO₃ nanocomposites with enhanced PEC performance were successfully produced. For the analysis of vascular endothelial growth factor Modified graphene oxide-modified Au electrode served as a rapid, reliable, extremely specific, and precise identifying method in human plasma for cancer diagnosis. At the same time, the results from this electrochemical biosensor did not significantly differ from those from the ELISA test [44]. GO has also been employed to identify glucose. Because of its biocompatibility with GOx, a stable glucose sensor with a sensitivity of 8.045 mA cm⁻² M⁻¹ 132 was created. In a different study, Niu and colleagues uncovered a unusual glucose biosensor based on the graphene ionic liquid glucose oxidase system's direct electron transfer process[133]. Up to 14 mM, their system responded linearly. With a linear response between 2 and 16 mM, the CdS nanocrystal-based graphene system provides an extremely low detection limit of 0.7 mM[47].

F. Application of Graphene Oxide as Antimicrobial activity

Preparation of silver nanoparticles and their antibacterial impact on GO sheets have been documented .Graphene Oxide has made by using sodium nitrate and silver citrate. Through the use of thermogravimetric analysis (TGA), XRD, TEM, UV-Vis, and Raman's spectroscopy, GO was physically and chemically characterized. It was discovered that GO and GO-Ag had antibacterial properties that are effective against microorganisms using the conventional counting plate methods. GO-Ag compound shown significant antibacterial activity while GO dispersion had minimal antimicrobial effect against the microorganism. When exposed to the GO-Ag nanocomposite, *Pseudomonas aeruginosa* displayed antibiofilm activity on the surface of stainless steel with a 100% inhibition rate[40].For assessing different categories of graphene-based materials antibacterial properties, *Escherichia coli* was utilized as a perfect bacterium for evaluating four different ways of material with antibacterial properties which was graphene based. The same concentration of Graphite, Graphite

oxide, graphene oxide, and reduced graphene oxide distributions in isotonic saline solution (40 g/mL) was gestated with Escherichia coli cells (106 to 107 CFU/mL) for 2 hours, respectively. Using the colony counting technique outlined in the Materials and Methods section, the mortality rate of bacterial cells was calculated. As a control, isotonic saline solution devoid of materials based on graphene was utilized[54].

V. CONCLUSION

There have been tremendous progress in the use of nanomaterials for biomedical uses over the last few decades. Graphene oxide has recently appeared as auspicious material in nanomedicine. Future applications of GO will benefit greatly from the proper synthesis. A substantially Reduced Graphene Oxide, with a resembling bottom-up generated Graphene, is appreciated in biosensors and electronics. A less decorated Graphene Oxide is excellent in capacitors and filtering applications. The existence of functional groups form it invaluable in sorption and reinforcing applications. The inexpensive charge of the substrate and their accessibility for mass manufacturing are significant advantages in GO synthesis. The mechanical, electrical, and thermal properties of graphene oxide are all the emphasis of this chapter, along with a discussion of the parameters for graphene and reduced graphene. The synthesis of graphene, graphene oxides, and reduced graphene oxide is also mentioned here, especially by Humer's modification techniques. There are numerous applications for graphene and its derivatives, but we only elaborate one of them here, i.e. the biomedical application of graphene oxides.

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