

GRAPHENE: SYNTHETIC AND REDUCTION APPROACHES

Abstract

Carbon community substrates such as carbon nanotubes, graphene oxide (GO), and carbon nanoparticles have been of great interest to the scientific community for the last three decades due to numerous potential applications. Graphene oxide is an oxidized derivative of graphene and is obtained from the severe oxidation of graphite powder. This process introduces oxygen-containing functional groups to the surface of GO. Chemical species both organic and inorganic molecules can be attached to the surface of graphene oxide via these functional groups. Also, functional groups on its surface can serve as nucleation and growth sites for metal nanoparticles. GO high surface area can serve as nucleation sites for metal nanoparticles, it can be used as a substrate to deposit metal nanoparticles. Graphene and its derivative materials have shown great potential applications in numerous research fields such as material science, chemical science, physical science, and nanoscience platforms, which are assumed to improve modern and multifunctional strategies.

Keywords: Graphene, nanoparticles, Development.

Authors

Dr. Chandra Mohan Kurmarayuni

Department of Chemistry
Acharya Nagarjuna University
Guntur, Andhra Pradesh, India

P. Krishna Kumari

Department of Chemistry
Mrs. A.V.N College
Visakhapatnam, Andhra Pradesh, India

Dr. B. Srikanth

Lecturer in Chemistry
Government Degree College
Cumbum, Prakasam, Andhra Pradesh, India

Dr. Swarnalatha Kurapati

Department of Chemistry
Ch. S.D. St. Theresa's College for Women
Eluru, Andhra Pradesh, India.

I. INTRODUCTION

Since the sixteenth century graphite has been well known and used commonly in various industries to make steel, brake lining, telephones, pencils and dry lubricant, just to name a few.¹ Graphite is a stacked layer made up of graphene which is a one atom thick sheet of sp^2 hybridized carbon atoms arranging hexagonally.^{2,3} These features give a two-dimensional geometry to graphene. In addition, graphene possesses excellent electronic properties due to its delocalized π bonds and high quality crystal structure.³ Graphene is very attractive to researchers and engineers due to its high electron mobility and ballistic conduction which was first recognized when graphene's charge carriers had zero rest mass and migrated quickly at nearly 0.003 the speed of light across its hexagonal structure.³⁻⁵ Graphene also exhibits quantum hall effect at room temperature,^{4,6,7} tunable band gap,⁸ and excellent elasticity.⁹ Graphene is considered the parent of all graphitic materials since it is the building block of important allotropes of carbon. Graphene is versatile and can be stacked to form three-dimensional graphite, as stated earlier, rolled to form one dimensional carbon nanotubes and wrapped into zero dimensional fullerenes.¹⁰

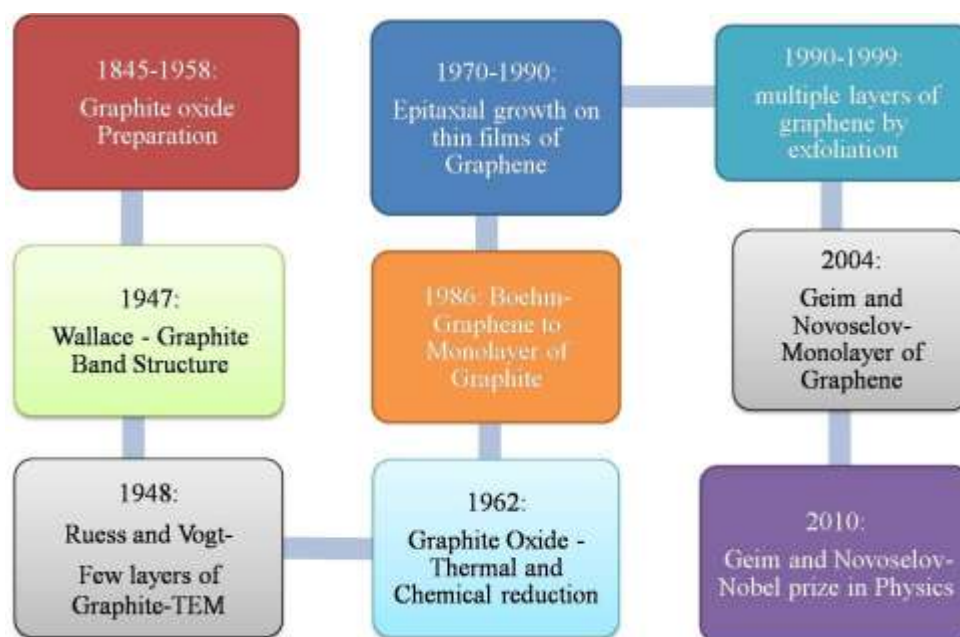


Figure 1: The Timeline Development of Graphene

Due the fame of graphite since the sixteenth century it was the main form of carbon known. It was not until the year of 1985, when Kroto *et al.* during their investigation of the formation mechanisms of long-chain carbon molecules in interstellar space and circumstellar shells, discovered fullerenes during the laser vaporization of graphite. Fullerene was a superstable species, with its geometry determined to be of the soccer ball shape and comprised of sixty carbon atoms with 32 faces.¹¹ This discovery stimulated the scientific community to investigate other structures which can be formed from the graphitic sheet graphene. As a result, fullerenes discovery was shortly followed by the observation of carbon nanotubes in 1991 by a Japanese scientist, Lijima. Lijima's investigation was performed using an arc-discharge procedure like the laser vaporization used to make fullerenes. However, during arc-discharge, needle-like carbon structures grew on the negative electrode.

These carbon needles were later called carbon nanotubes which are single sheet of graphene rolled to form a tube.¹² These two advancements in science lead to the vast increase in the number of carbon allotropes known today in the scientific community.¹ The major developments regarding the graphene are depicted in **Figure 1**.

Synthetic Studies of Graphene: Various novel synthetic approaches are developed for the synthesis of graphene. Graphene possesses many excellent properties as stated earlier. As a result, there are myriad of potential utilizations in devices. These may include sensors, transparent electrodes for solar cells, future generations of high-speed and radio frequency logic devices and reinforced composites that are electrically and thermally conductive.¹⁰ Despite these potential benefits of graphene, its widespread use has been impeded by its availability which is due to the challenge in synthesizing graphene from graphite or using bottom-up techniques. The most common methods for the synthesis of graphene are micromechanical cleaving of graphite, chemical cleaving, or “exfoliation” of graphite, epitaxial growth, and chemical vapor deposition (CVD). In 2004, a group of scientists in Manchester Britain made a significant discovery. They used adhesive tape to repeatedly remove layers of fragmented graphite. Raman spectroscopy, optical microscopy and atomic force microscopy were used to identify these fragments as single and few layer graphenes.⁵ This method is commonly referred to as micromechanical cleaving of graphite.

The exposure of graphite to strong acidic solution results in the chemical exfoliation of stacked graphite sheets to single and few-layer graphenes. This chemical treatment introduces oxygen-containing groups to the sheets of graphene, which results in the synthesis of graphite oxide and graphene oxide.¹³ The presence of these functional groups increases the solubility of graphene oxide in various solvents. However, unlike graphene, graphene oxide has disruption in its sp^2 hybridized bonding network due to the acid treatment. This renders graphene oxide an electrical insulator. Therefore, to restore the sp^2 network present in pristine graphene, graphene oxide is usually reduced thermally or chemically, which removes most of the oxygen functional groups. This material may contain structural defects and it is not the same as pristine graphene, hence the name is reduced graphene oxide.^{3,14,15}

The epitaxial growth of graphene can be achieved by heating of hexagonal crystals of silicon carbide at high temperatures.^{3,16} As an example, Berger *et al.* in 2006 synthesized epitaxial graphene by vacuum graphitization during the thermal decomposition of silicon carbon crystals at 2400 K.¹⁷ Decomposition of the silicon carbon crystal at 1200 °C results in the formation of millimetre-size continuous graphene planes after the vaporization of silicon.^{18,19} However, this method has a disadvantage due stacking faults and other disorders introduced from the substrate, which results in poorer electronic properties than pristine graphene.²⁰ Synthesis of graphene by chemical vapor deposition is achieved in the presence of a metal substrate. During this process, a vapor-rich hydrocarbon is heated at approximately 800 °C, allowing graphene to deposit on the surface of a metal substrate, nickel or copper for example. Continuous planes of graphene with centimeters dimension can be obtained. However, this method also has challenges in preventing metal substrate contaminants. In addition, it is a challenge to control the number of layers of graphene deposited on the metal substrate.²¹⁻²³

II. GRAPHENE OXIDE (GO)

The enlargement of Graphene Oxide (GO) is a great achievement and numerous research work is reported on this man-made material (**Figure.2**). Graphene oxide (GO) is not a naturally occurring compound. It is composed of carbon, oxygen, and hydrogen atoms. GO, is an exfoliated form that is an intermediate between graphite and graphene, which is chemically similar to Graphite oxide (multilayer) but structurally different. GO, largely consists of mono-, bi-, or few layers with oxygen functionalities, which are corresponding to the exfoliated form of graphite oxide, a lamellar structure (multilayer). In GO having known oxygen functionalities encompass with the oxygen functional groups are mostly hydroxyl and epoxy groups present on the basal plane, with small quantities of carbonyl, carboxy, phenol, quinone, and lactone functional groups present at the sheetedges.²⁴

The most potential method for obtaining graphene is chemical exfoliation of graphite to obtain graphite/graphene oxide and subsequent reduction to graphene. The chemical exfoliation of graphite was first performed by Brodie in 1859.²⁵ In a typical synthesis, graphite was oxidized upon exposure to potassium chlorate and nitric acid. In the following years, other reports of the synthesis of graphite oxide were published. In 1958, Hummers and Offerman synthesized graphite oxide using potassium permanganate and sulfuric acid as oxidizing mixture.²⁶

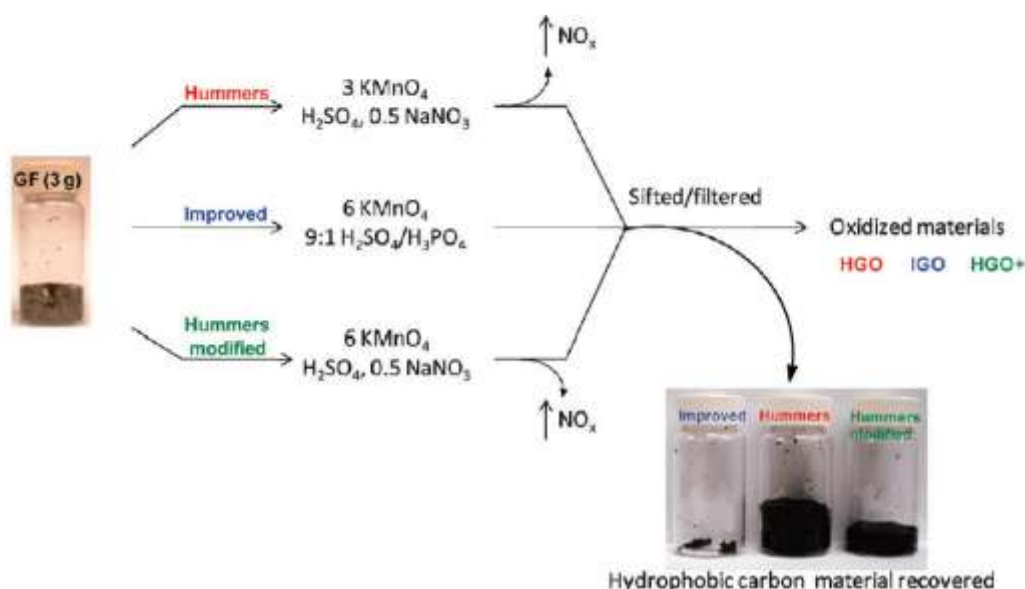


Figure 2: Three different techniques to synthesize GO from graphite source. Reprinted with permission from <https://pubs.acs.org/doi/10.1021/nn1006368> copyright@2010. American Chemical Society

Chemically modified graphene or graphene's derivatives, such as graphene oxide (GO) for example, have been intensely studied recently for many applications.²⁷ They have been used in nanocomposites' synthesis for applications such as transparent conducting films,²⁸ catalysis,²⁹ fuel cell,²⁹ light energy conversion,³⁰ and sensing.^{31,32} According to Bananni *et al.*, graphene oxide is the oxidized form of graphene sheet with oxygen functional groups, such as hydroxyl, peroxy, carbonyl, carboxyl, aldehyde and epoxy.^{27,33,34} Currently, GO is commonly synthesized using the previously mentioned modified Hummers method

which involves the chemical exfoliation of graphite either thermally or ultrasonically in the presence of strong acids and oxidizing agents.^{26,35,37-40} This covalent functionalization results in the disruption of the sp^2 network forming sp^3 bonds rendering GO as an excellent electrical insulator.^{36,41,42} On the other hand, the oxygen functional groups on the basal plane and edges enable the dispersibility of GO in polar solvents such as water.^{43,44}

1. Structure of Graphene Oxide: According to Dreyer *et al.*, there is no definitive structure representative of graphene oxide. This is mainly due to several reasons, including variation in each sample synthesized, as evidenced in the berthollide and amorphous structure, and inadequate techniques for analyzing this material. As a result, there have been uncertainties about the structure of graphene oxide sheets.²⁷ Regardless of these uncertainties, there has been significant progress in determining graphene oxide's structure. The earliest structural model suggested by Hofmann and co-workers were believed to have a chemical formula of C_2O . The structure they suggested was comprised of oxygen-containing groups (epoxy) attached to the basal plane of a graphitic lattice with sp^2 hybridization.⁴⁵ A more detailed model which was proposed in 1946 by Ruess, was supported later by Marmoux.^{46,47} This structural model was sp^3 hybridized with both epoxy and hydroxyl functional groups on the basal planes of the carbon lattice. Furthermore, a structural model made of a corrugated backbone with only quinodal species was proposed by Scholz-Boehm in 1969.⁴⁸ Scholz and Boehm's model was followed by Nakajima and Matsuo's. They suggested a structural model similar to poly(dicarbon monofluoride) with a chemical formula of $(C_2F)_n$. This poly(dicarbon monofluoride) structure arranges in a stage 2 graphite intercalation compound in order to form GO.⁴⁹ A stage 2 graphite intercalation compound has every two layers of graphite followed by an intercalating molecule. This alternation continues throughout the structure.⁴⁹ To date, the most common structural models of GO used in the scientific community are the ones proposed by Lerf and Klinowski's in 1996 and 1998. They were able to determine the structure of GO by analyzing the reactivity of the materials through its products. They have performed numerous in depth analyses on graphite oxide's structure and its hydration behavior. The analyses dismissed the lattice model previously proposed. Instead, they suggested an amorphous and nonstoichiometric model. They first proposed a sheet of six membered rings of carbon atoms with epoxides on the basal planes and carboxylic functional groups at the edges of the sheets.⁵⁰ Their characterization was supported by the use of nuclear magnetic resonance spectroscopy to obtain the structure of GO. This was the first of its kind to be used in the scientific community for such structural analysis as other researches mainly utilized reactivity, x-ray diffraction and elemental composition to support their structural models of GO. The second model proposed by Lerf and Klinowski in 1998 had only epoxy and hydroxyl functional groups on the surface of the carbon sheet they previously proposed. This model was proposed after NMR analysis of GO heated at 100°C showed none of the previous signals at 60 and 70 ppm. However, a signal at 120 ppm was present which was ascribed to phenol and aromatic species.^{51,52}

In 2008, Cai *et al.* performed an investigation with the objective of understanding the structure of GO. They utilized solid-state nuclear magnetic resonance (SSNMR) which can provide structural information of materials. During their synthesis and solid-state NMR structural characterization of carbon 13 graphite oxide, they confirmed the presence of peaks in the NMR spectra attributed to sp^2 , hydroxyls and epoxides, which agrees with the Lerf and Klinowski's model.⁵³ In 2009, Gao *et al.* performed an

investigation into the synthesis of GO and restoration of the sp^2 structure for conductive purposes. Spectroscopic analysis of the synthesized GO proposed a structural model that is comprised of five and six-membered ring lactols as part of the main functional groups present in the structure of GO. It is important to note that during Dreyer *et al.* conclusive remarks on the structure of GO, they advised that the degree of oxidation of graphite and variation in the graphite used to synthesize GO may impart different structural features to GO.⁵⁴

- 2. Graphene Oxide- Reactivity and Solubility:** Graphene oxide, a chemically modified graphene, is synthesized from the chemical exfoliation of graphite following the most commonly used Hummers method, as stated earlier. Also as noted before, oxygen functionalities are introduced to the exfoliated graphene sheets during the oxidation of graphite. Even though graphene oxide loses the properties of pristine graphene, several modifications or treatments can be performed for the restoration of much of the graphene's properties. In addition, the oxygen-containing groups open up a whole new world of applications for graphene oxide.³

The solubility of graphene oxide in organic and inorganic solvents is of great interest to researchers. Graphene oxide possesses intrinsically hydrophilic properties due to its water loving ability. This was imparted due to the presence of the oxygen groups which increase the interlayer spacing of GO.^{27,55} As a result, water molecules are allowed to intercalate the sheets of GO rendering solubility and further increasing interlayer distance while sonicated in water.^{10,14,44,38} Also, according to Dreyer's group, hydrogen bonding between functional groups of GO and water imparts solubility to GO in water.^{3,27} Preparing a suspension of graphene oxide in an organic solvent was first performed by Stankovich' group. In their synthesis, they modified the hydroxyl and carboxyl functional groups of graphite oxide to form respective amide and carbamate groups with isocyanate, an organic compound. This modification resulted in the completely exfoliated graphite oxide product losing its solubility in water. However, this modified product formed stable suspension of graphene oxide with ~ 1 nm thickness in aprotic solvents such as: N-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO) and N,N- dimethylformamide (DMF). The resultant product was readily mixed with several organic polymers thus forming graphene oxide polymer composites.⁵⁶

Following a similar approach with the objective of solubilizing graphite oxide in different solvents, Xu *et al.* synthesized a graphite oxide following Hummers method. This was later coupled with bifunctional modifier which renders both hydrophobic and hydrophilic properties to the graphite oxide. During the grafting and coupling of bifunctional modifier, graphite oxide was mixed with excess toluene-2, 4diisocyanate (TDI), amphiphilic oligoester and 10 mL of DMF followed by stirring for 8 hours at 80 oC under nitrogen. Dry powder was obtained after purification and drying at 60 oC under vacuum. Powder of GO-TDI-AO was mixed with DMF and water with a final concentration of 1 mg/mL. GO-TDI-AO dispersion was stable in both water and DMF for minimum seven days with well exfoliated graphene oxide sheets of thickness 1.2 nm. They found that TDI grafted on the carboxyl and hydroxyl groups of graphite oxide forming carbamate and amide esters respectively. In addition, the oligoester attached to the isocyanate coupled to the carboxyl and hydroxyl groups, which in turn, enhances the solubility of graphene oxide in both DMF and water.⁵⁷

In other attempts to solubilize GO, Williams and co-workers synthesized suspension of graphene oxide coated with titanium oxide in polar solvent (ethanol). As stated earlier, exfoliated graphene oxide possesses carboxyl, hydroxyl and epoxy functional groups which make the material soluble in polar solvents. As a result of these properties, in this experiment, GO was synthesized following Hummers method to obtain a dark powder. Powder was mixed with TiO₂ colloid suspension and sonicated for 30 minutes before it was subjected to 2 hours of UV-irradiation resulting in TiO₂ grafted graphene composite consisting of reduced graphene oxide. Despite the reduction of graphene oxide in this experiment, TiO₂ grafted graphene maintained its solubility in ethanol and did not agglomerate or precipitate.⁵⁸

Paredes and co-workers in 2008 performed an in-depth investigation into the dispersive behavior of graphene oxide in organic solvents. Prior to Paredes' investigation, graphene oxide's solubility had been accomplished in organic media only through molecules and polymers covalently functionalizing graphene oxide. Even though this was a positive direction in obtaining GO soluble in organic solvents which increases the application potential of GO, these molecules and polymers were unsuitable for some applications. In Paredes' experiment, graphite oxide was synthesized using the Hummers method from graphite and NaNO₃, H₂SO₄ and KMnO₄. HCl was used to purify the oxidative product yielding graphite oxide followed by drying under vacuum at 80 °C. Dispersions of graphite oxide in different solvents were prepared by adding 5 mg of dried graphite oxide to 10 mL of acetone, methanol, ethanol, 1-propanol, ethylene glycol, DMF, pyridine, N-methyl-2-pyrrolidone, tetrahydrofuran, dichloromethane, o-xylene and n-hexane. Samples were sonicated for one hour yielding completely exfoliated single and few sheets of graphene oxide stable in ethylene glycol, tetrahydrofuran, N,N-dimethylformamide and N-methyl-2 pyrrolidone for weeks. These results further widen the potential for the practical applications of graphene oxide and highlighted its processability in various organic solvents.^{59,60}

III. REDUCTION OF GRAPHENE OXIDE

As stated earlier, the oxidation of graphite to obtain single and few-layers of graphene oxide (GO) introduces oxygen functionalities to the surface of graphene. This results in the disruption of the sp² network of graphene while introducing sp³ bonding to the product, graphene oxide. Even though the functionalization of graphene oxide imparts solubility and process ability, this significantly decreases the electrical conductivity of graphene oxide. As a result, there have been significant research interests in restoring the sp² hybridization by reduction of graphene oxide to produce reduced graphene oxide (r-GO). According to Dreyer and co-workers, reduction of graphene oxide is one of the most vital changes which graphene oxide can be exposed to. This is because reduction results in reduced graphene oxide having similar properties to pristine graphene and graphite. There have been three significant methods of reduction to date, namely; chemical, thermal, and electrochemical techniques.²⁷ The following sections of the literature review will discuss these techniques below.

1. Chemical Reduction of Graphene Oxide: Despite the many techniques available for the reduction of graphene oxide, chemical reduction is most widely used since significant amounts of reduced graphene oxide can be synthesized by this method.⁶¹⁻⁷² The chemical reduction of graphene oxide using hydrazine monohydrate was one of the first methods to be introduced. Stankovich *et al.* reportedly synthesized graphite oxide using Hummers

method. Upon producing graphite oxide, this was sonicated in 100 mL of water to obtain suspension of exfoliated sheets of graphene oxide. 1 mL of Hydrazine was added and mixture was heated at 100 oC for a day during which a black precipitate of graphene oxide was obtained. This material had characteristics of graphite and thin graphene-like sheets with surface area of 466 m²/g. Elemental analysis revealed a carbon-to- oxygen ratio of 10:1 which is a significant reduction from 3:1 for grahene oxide. XPS analysis further revealed the restoration of the C=C (sp² hybridization) and C-C bonds in reduced graphene oxide while the signals associated with oxygen functionalities carboxyl, epoxy and hydroxyl decrease significantly.⁶¹ While hydrazine proves to be reducing oxygen functionalities from GO, it has its disadvantages. Hydrazine contains nitrogen which bonds to GO in the form of aziridines, amines and hydrazones commonly referred to as heteroatomic impurities.⁶² The downside to this and other chemical methods is the aggregation of graphene sheets due to Van der Waals attraction after the oxygen functional groups have been removed.⁷⁰

Sodium borohydride use as a chemical reductant for graphene oxide was reported by Shin *et al* 2009. In their experiment, they compared reduced graphene oxide (RGO) made from hydrazine and sodium borohydride. Graphite oxide was synthesized using the modified Brodie method. After synthesis using modified Brodie's method, 10 mg of GO was sonicated for one hour in sodium hydroxide solution. This was followed by centrifugation to obtain supernatant rich in GO. Thin films of GO was made and place in different concentrations of sodium borohydride and hydrazine for two hours. Sheet resistance analysis performed revealed that reduced graphene oxide made of hydrazine was much higher than that of reduced graphene oxide made of sodium borohydride even though both products contain the same carbon to oxygen ratio. Higher sheet resistance exhibited by RGO was due to the addition of nitrogen from hydrazine to the surface of graphene oxide during the reduction process, which compensate p-type hole carriers by playing the role of dopants. Overall, the qualities of reduced graphene oxide made from sodium borohydride make it very promising for electrical and other practical applications due to its low sheet resistance.⁶²

A facile synthesis procedure for graphene nanosheets was reported by Wang and co- workers by using hydroquinone to reduce graphene oxide. In their experiment, graphite oxide was synthesized by modified Hummers and Offeman's method. Graphite oxide powder was exfoliated into ethanol and water through sonication for one hour to form graphene oxide. Hydroquinone was added to the graphene oxide suspension and heated under reflux for 20 hours at constant temperature forming graphene nanosheets indicated by a color change from brown or yellow solution to a black precipitate.⁶³ XRD analysis of exfoliated graphite oxide confirmed the presence of carbon (002) diffraction peak at 11.80. However, after reduction with hydroquinone this peak disappeared and a new peak representing carbon (002) diffraction peak appeared at 26°, which is attributed to the restoration of the ordered crystal structure of graphene sheets of graphite.⁶³ In addition, graphene nanosheets were sonicated in water to prepare a suspension. However, it was unstable, and graphene nanosheets fell out of solution and agglomerate which indicated this material is hydrophobic. This occurs due to the reduction of GO during which the hydrophilic epoxy, hydroxyl, carboxyl, lactone or ether groups were removed. Even though the exact manner of GO reduction is still under discussion, It is believed that hydroquinone reduces GO by either giving up one or both of its H⁺ ions to GO thus forming quinone.^{63,64}

Due to the toxicity and explosive properties of some of the chemical reductants explored earlier, nontoxic and friendlier reductants are of interest to the scientific community. As a result, graphene oxide reduction using L-ascorbic acid was most recently reported by Zhang *et al.*⁶⁵ L-ascorbic acid (L-AA) is a mild reducing agent commonly used in living organisms and as principal reductant in experiments.⁶⁰⁻⁶⁹ Graphene oxide was synthesized following the Hummers and Stankovich's procedures.^{26,44} Sheet thickness of graphene oxide obtained was ~1.2 nm which matched previous reported results.¹³ The reduction of graphene oxide at room temperature was performed as follows. 50 mg of L-AA was added to 50 mL of GO suspension in water having containing a concentration of 0.1mg/mL. Mixture was stirred violently. Ultraviolet-vis spectroscopic analysis confirmed formation of reduced graphene oxide by the total disappearance of bands related to GO at 230 and 300 nm respectively after twenty-four hours. On the other hand, a band representative of the restoration of the aromatic structure of GO, appeared around 300 nm. FTIR analysis also confirmed the formation of reduced graphene oxide as the peaks related to the oxygen functionalities of GO either decreased significantly or totally disappeared after 48 hours exposure to L-AA. Unlike other reduced graphene oxides discussed previously that agglomerate and lose stability in water, this reduced graphene oxide suspension was stable for several days in water without use of any stabilizing agents.⁶⁵

- 2. Thermal Reduction of Graphene Oxide:** Graphene oxide offers a nonchemical approach to obtain reduced graphite oxide by thermal and hydrothermal reduction, which may reduce or no toxic property than chemical approach.⁷³⁻⁷⁸ The earliest form of thermal reduction of graphene oxide was performed by Boehm and co-workers. Instead of using chemicals to reduce graphene oxide, they thermally heated graphene oxide in a furnace, stripping the oxygen groups (hydroxyl, epoxy, carboxyl) from its surface.⁷³ Since then, other researchers have investigated the thermal reduction as a means of obtaining graphene sheets.⁷⁴⁻⁷⁸

Schnieppet *al.* reported the thermal splitting of graphene oxide into functionalized graphene sheets. In a typical synthesis, graphene oxide was synthesized following the Staudenmaier procedure which results in the complete oxidation of graphite flakes. To obtain single exfoliated sheets of graphene rapid heating of oxidized graphene oxide was performed. NMR analysis revealed the presence of epoxy, hydroxyl and carboxyl groups attached to oxidized aliphatic six-membered rings of carbon. Also, XRD analysis revealed an interplanar spacing of 0.75 nm for GO compared with 0.34 nm of graphite flakes. GO was heated to 1050 °C at a heating rate greater than 2000 °C/min. During this process, carbon dioxide evolved due to the decomposition of functional groups attached to the surface of graphite oxide expands thus further exfoliating GO into single sheets of graphene. It is important to note that after rapid heating, residual functional groups remain in the nanoplates of graphene layers. Atomic force microscopy analysis indicated formation of single sheet of graphene which corresponded with first-principle atomistic modelling. Compacts with density of 0.3 g/cm³ made from single sheets of graphene possessing residual oxygen functionalities and defect sites reported direct current conductivities of 1×10^3 to 2.3×10^3 s/m. As a result of the above properties these graphene nanosheets have potential in composites and conductive materials.⁷⁴

Later McAllister and co-workers also reported the oxidation of graphite and its thermal reduction. Oxidation of graphite was performed like the Staudenmaier method.

The oxidation of graphite was studied from zero to 120 hours by XRD analysis. GO formation was confirmed by the 0.7 nm interlayer spacing corresponding to the diffraction peak at 12θ from XRD analysis and the disappearance of the graphitic peak between 25° and 30° . 200 mg of GO sample was flushed with argon and then heated for 30 seconds at 1050°C in an oven. During this time, carbon dioxide generated between the layers of GO were of pressures 40-130 MPa (when heated from 300 - 1000°C) which resulted in the exfoliation of the sheets of GO. AFM analysis revealed an average sheet thickness of 1.75 nm of 140 sheets of thermally reduced graphite oxide studied. In addition, 80 % of these sheets were single sheets. Furthermore, surface area analysis revealed a BET surface area of 600 - $900\text{ m}^2/\text{g}$ while surface area using the methylene blue absorption method yielded $1850\text{ m}^2/\text{g}$.⁷⁵

- 3. Electrochemical Reduction of Graphene Oxide:** Previous reduction methods revealed that nanosheets of reduced graphene oxide can be obtained chemically or thermally. However, there may be defects among other unfavourable constituents which limit graphene nanosheets applications. Hence, other method such as electrochemical reduction of graphene oxide has been explored by the scientific community.⁷⁹⁻⁸³ Zhou *et al.* were the first to report the green, cheap and efficient method to electrochemically synthesize reduced graphene oxide films.⁷⁹ A slurry of graphene oxide was synthesized using modified Hummer's method which was later used to synthesize various concentrations of GO suspension. Spray coating was performed to deposit films of GO on quartz substrate followed by drying for twenty seconds with infrared lamp. Film thickness ranging from ~ 1 - 2 nanometers to ~ 7 micrometer was determined by scanning electron microscopy (SEM) and atomic force microscopy analysis. Films deposited on conductive/nonconductive materials were electro-reduced when glassy carbon electrode contacted GO film in buffer solution of sodium phosphate started at -0.68 V and stopped at -0.87 V over 5000 seconds. This reduction proved that the potentiostatic method could be utilized to reduce GO. During reduction a color change from yellow to black occurred around the tip of the electrode which could be attributed to the restoration of the sp^2 hybridization (π network) of reduced GO. Further SEM analysis revealed that the morphology of the films of GO and electrochemically reduced GO showed no difference. However, reduced GO films exhibited a decrease in thickness from $\sim 7\text{ }\mu\text{m}$ to $\sim 5\text{ }\mu\text{m}$, while elemental and XPS analysis indicated oxygen to carbon content of only 4.19% and 4.23% respectively, when compared with GO films which have oxygen-to-carbon content of 68.6% and 69.2%. In addition, electrical conductivity of reduced GO increased approximately eight times to $8.50 \times 10^3\text{ S/m}$ compared with $2.0 \times 10^3\text{ S/m}$ of original GO. The mechanism by which reduction of GO occurs is not fully studied, however, it is believed to be brought about by the hydrogen ions present in the sodiumphosphate buffer solution. Despite the positives results of this method, it does not offer a scalable approach to graphene nanosheets production.⁷⁹

IV. CONCLUSION

Overall, in the above chapter, graphene, its synthesis, and some reduction techniques for hefty extent production of graphene were discussed.

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