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Facile Synthesis of Graphene Via Chemical and Biological Methods- A Review

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Abstract
Graphene, a single atom thick planar layer of sp^2 hybridized carbon atoms densely packed in a honey comb crystal lattice, has fascinated much attention in recent years owing to its exceptional electronic, optical, magnetic, thermal, mechanical properties and high specific surface area. The reported properties and applications of this two-dimensional form of carbon structure have opened up new opportunities for the future devices and systems. Although graphene is known to possess excellent properties, synthesizing single sheet of graphene has been less explored. Generally large-scale graphene nanosheets are reliably synthesized utilizing other forms of graphene-based novel materials including graphene oxide (GO), exfoliated graphite oxide and reduced graphene oxide (RGO). In this review article some selected synthesis of graphene such as mechanical exfoliation, chemical exfoliation, oxidation of graphite, chemical vapour deposition, flame synthesis and epitaxial growth on SiC and methods of reduction of graphene oxide are also presented which includes chemical reduction methods, bio-molecules employed graphene oxide reduction, microbial reduction of graphene oxide, phytoextracts mediated graphene oxide reduction, solvothermal/hydrothermal reduction, photoreduction, microwave assisted technique and thermal reduction. This review also covers the advantages and disadvantages of various methods of synthesis.

Keywords
Graphite, graphene nanosheets, graphene oxide and reduced graphene oxide.

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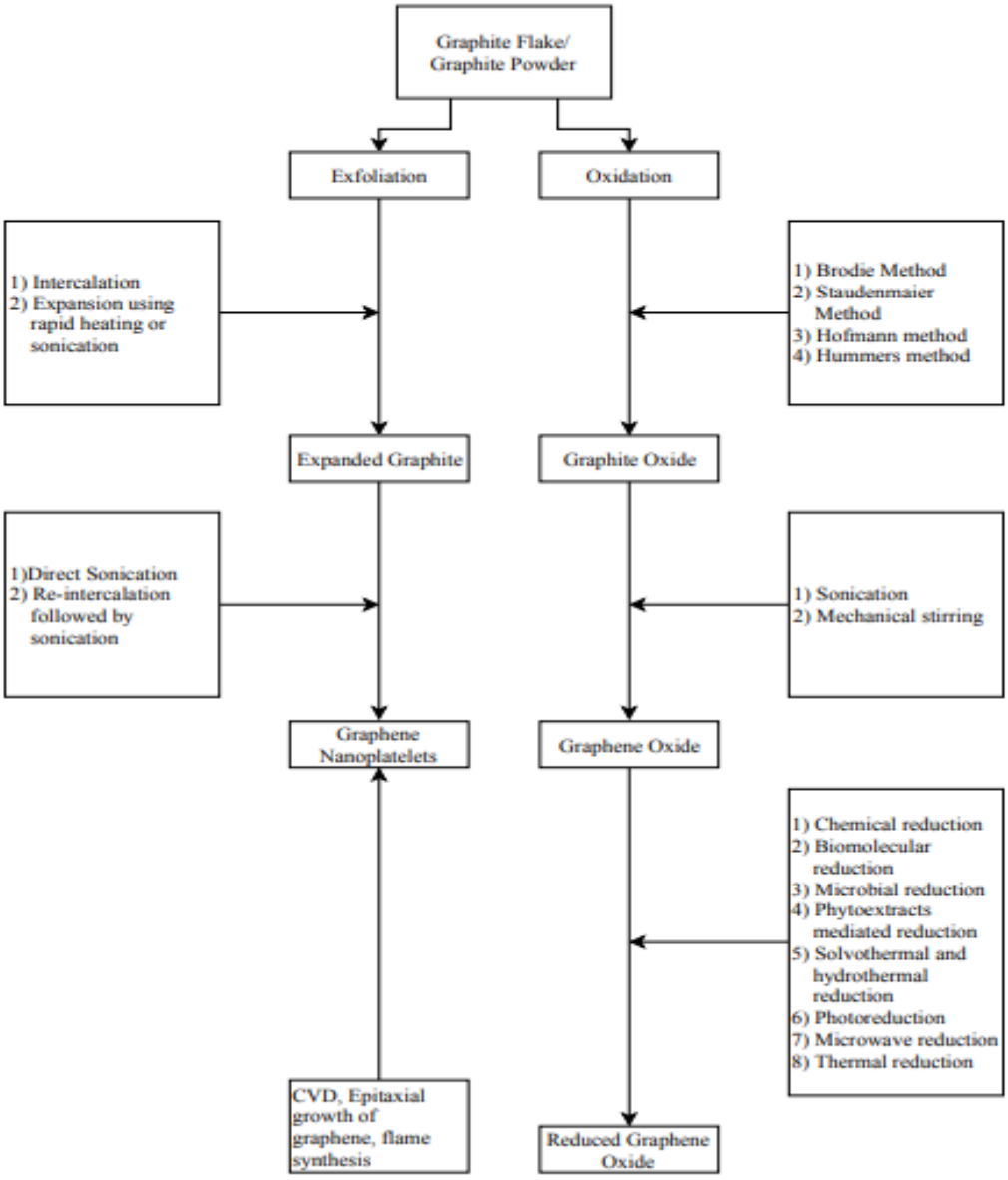
Graphical abstract



1 Introduction

Graphene promises to be the most exciting material of the decade. It is a plane sheet of sp^2 hybridized carbon atoms tightly confined into a honeycomb lattice. In 2004, the first discovery of graphene using a scotch tape peeling method brought a dramatic revolution, especially in the world of materials science [1]. Recently, this single sheet of carbon has attracted huge interest among the scientific community owing to the two-dimensional structure [2]. It is proved that an ideal graphene sheet is highly ordered and shows several extraordinary behaviors including outstanding surface areas (2630 $m^2 g^{-1}$), high Young's modulus (1.0 TPa), high thermal conductivity (~5000 W $m^{-1} K^{-1}$) and strong chemical durability and high electron mobility (2.5 x 10^5 cm^2 V^{-1} s^{-1}) [3]. It also exhibits single-molecule gas detection sensitivity [4], quantum confinement in nano scale ribbon [5], long range ballistic transport at room temperature [6] and high optical transmittance (~97.7%) [7]. These unique characteristics of graphene opened a new way for its wide range of application at different branches of technology such as: lithium-ion batteries [8], catalyst engineering [9], chemically derived sensor[10], biosensor [11], anti-bacterial activities [12], flexible thin film transistor [13], drug delivery [14], solar cells [15], photovoltaic devices [16], intracellular imaging [17], p–n junction materials [18], super capacitor [19], touch panel [20], water purification [21], absorption of different non aqueous liquid e.g., oils, dyes and organic solvents [22].

Large quantities of graphene materials are required to fulfill the huge demand of the aforementioned applications. Production of the best quality graphene in an inexpensive manner and on the desired scale is a big challenge of the time.

Graphene oxides (GO) are another important member in the graphene-graphite family, which are considered as derivatives of graphene. Different from graphene, which is almost not soluble and cannot be dispersed in water or any organic solvent [23], graphene oxide contains high-density oxygen functional groups, like hydroxyl and epoxy group on its basal plane, and carboxyl at its edge [24]. They afford graphene oxide with excellent water solubility, ease of functionalization and convenience in processing etc., [25], making it the most popular precursor of graphene. Graphene oxide reduction is considered a promising approach for the mass production of graphene. The product obtained by this method is commonly termed as reduced graphene oxide (RGO) or graphene nano sheet (GNS). However, graphene oxide acts as a precursor to synthesis reduced graphene oxide or graphene nano sheet [26]. It is produced from graphite flakes by oxidative reaction, which heavily decorates the sheets with different oxygen moieties.

A variety of attempts have been made for the synthesis of graphene such as micromechanical cleavage [27], chemical vapor deposition [28], epitaxial growth on silicon carbide [29], arc discharge [30], unzipping of carbon nanotubes [31], electrochemical synthesis [32] and chemical reduction of graphene oxides [33]. All these methods will be discussed in detail in the following sections. However, the above-mentioned methods employ hazardous chemicals and trace amounts of these in final product could pose harmful effects, particularly in case of bio-related applications such as catalysis and drug delivery. Handling of hazardous waste generated out of these processes could counter the environment protection and add up to the production cost. In this context, employment of green nanotechnology which reports on the reduction of graphene oxide to overcome the above problems using reducing agents such as biomolecules, microbes and phytoextracts reduction have also been summarized in this review.

2 Graphite, Graphite Oxides and Graphene

2.1. Graphite

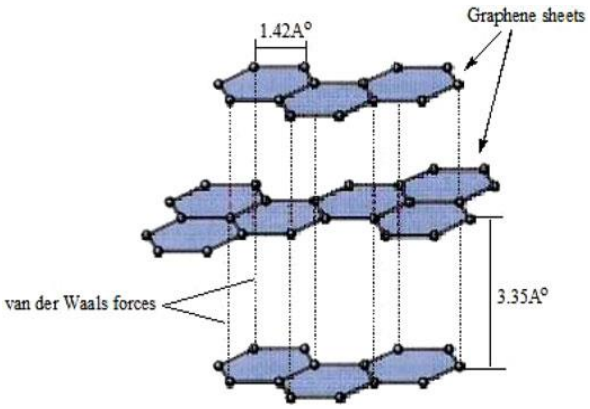


Fig. 1. Structure of Graphite

Naturally graphite is found in the form of graphite powder or flake with a range of different particle sizes. Graphite occurs in different structural forms such as flat, fibrous and spherical. On the basis of color, size, cleavage, habit and luster, they are divided into many groups. The flake graphite consists of thin layers having thickness smaller than 100 nm [34]. In graphite the carbon atoms are held together by covalent bonds to form a layered structure and held together by van der Waals forces (Fig. 1) [35]. In layers, carbon atoms are arranged in such a way to form hexagonal sheets. The distance between two carbon atoms in hexagonal sheets is being 1.42A° and there is distance of 3.35Å between the graphite sheets. Each hexagonal sheet of carbon atoms is called graphene layers or graphene sheets in which the carbon atom are sp^2-bonded, and their bond angle is 120° with respect to each other [36]. Due to the small distance between the graphite sheets, the intercalation of compound between sheets is very difficult. Therefore, the graphite flakes were processed for modification through physical or chemical methods. The chemical treatment involves intercalating different chemical species known as intercalating agents [37]. Chemical oxidation is shown by many methods, using different chemical species in which the van der Waals forces disrupt by the intercalation of atoms, ions and molecules into the graphite layers. This process results in the formation of the graphite intercalation compounds (GIC) (Fig.2), also known as graphite oxide. Graphite shows lubricants properties that are due to their sheets structure and van der Waals forces between the sheets; and, these sheets can easily slide with respect to each other. Graphite is a good thermal and electrical

conductor in the plane directions due to the presence of σ bonds and delocalized π bond. On the other hand, they have poor thermal and electrical conductivity in the stacking direction, due to van der Waals forces between the sheets [38].

Fig. 2. Graphite Intercalation Compound

Parent graphite is the source for graphite oxide production, which is exfoliated and later reduced to synthesize functional graphene sheets. Different types of graphite powder can be used as a starting material such as natural flaky graphite, artificial graphite, kish graphite and highly oriented pyrolytic graphite (HOPG). This selection of starting graphite is an important factor to pre-determine the number of layers in functional graphene produced upon the reduction of GO. Table 1 discusses the possible layer number of functional graphene obtained from different types of parent graphite. Significantly, graphite with low crystallinity and small lateral size is suitable to produce high quality single layer graphene with good electron conductivity ~ 1 x 10^3 S cm^{-1}. On the other hand, the highly oriented pyrolytic graphite (HOPG) is appropriate to produce thick or multiple layer graphene (>10 sheets) [39,40].

Table 1: The relationship between parent graphite and number of layers in graphene [39, 40]

Type of Parent Graphite	No. of Layers in Graphene
Artificial graphite	Single layer
Flake graphite	Single and double layer
Kish graphite	Double and triple layer
Natural flakes	Few layers (4-10)
Highly oriented pyrolytic graphite	Thick graphene (>10)

2.2. Graphite Oxide and Graphene Oxide (GO)

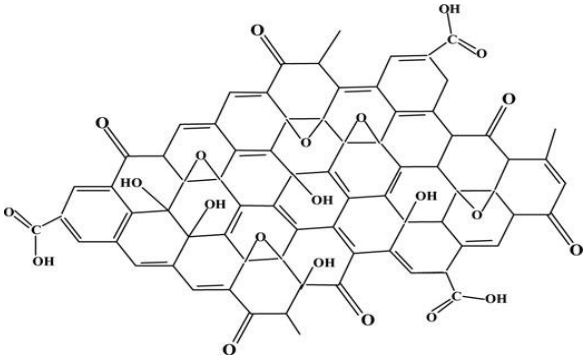


Fig. 3. Structure of Graphite oxide

Graphite oxide typically consists of layer of pseudo–two-dimensional lamellae, usually prepared by the oxidation of natural graphite flakes. It has mostly been prepared using Brodie, Staudenmaier and Hummer's methods. In all three methods, the oxidation of graphite occurs by oxidants and strong acid. The oxidation levels of graphite oxide are varied on the basis of method of preparation, graphite precursor and reaction conditions [41]. In oxidation results each layer has been attached with polar groups such as epoxide, hydroxyl and carboxylate groups in the six-member aliphatic regions. The hydroxyl and epoxy groups lie above and below on each graphene layer, and near edges carbonyl groups are located as shown in Fig.3. [42].

Due to the presence of these functional groups graphite oxide shows strong hydrophilic nature and can be easily dispersed in water. The graphite oxide may be exfoliated via ultrasonic vibration or thermal shock into two-dimensional graphene oxide nanosheets [43]. Nowadays the most common methods used for the preparation of graphene oxide

(GO) and/or graphite oxide are Hummers and Brodie method [44] which will be discussed in the following sections.

Graphene oxide contains abundant amounts of oxygen functional groups over the carbon basal plane not only makes it electrically insulating but also provokes thermal instability [45]. Therefore, reduction of oxygen molecules is the only key to resettle the π - lattice. It helps to produce thermally stable graphene and regain electronic conductivity. Graphene oxides can be readily converted into graphene by different reduction processes [46, 47]. As a precursor for graphene, graphene oxide can be easily derived from the oxidation of natural graphite at a large scale and low costs. The reduction of graphene oxide is a low-cost technique for producing graphene. The atomic layer of graphene oxide generally comprises phenol epoxy and epoxide groups on the basal plane and ionizable carboxylic acid groups around the edges [48]. The acid groups on the ionized edge enable the stabilization of graphene oxide in aqueous dispersion in the form of a single-sheet layer through weak dipole and quadrupole van der Waals interaction in the surrounding environment. This makes graphene oxide a high degree of processing and dispersion ability in solution and offers the desired convenient method for producing graphene-based materials in a large scale.

2.3. Graphene

Graphene is the monolayer of graphite, which can be prepared by several techniques. Geim et al. prepared graphene from graphite and demonstrated an experimental method to prepare a single layer of graphite with thickness in atomic scale, named as graphene as shown in Fig. 4 [2]. Since then graphene has become popular in various application aspects due to its inherently superior electrical/electronic and optical properties (i.e., tunable bandgap, extraordinary electronic transport behavior, excellent thermal conductivity, high mechanical strength and largely tunable surface area) [49].

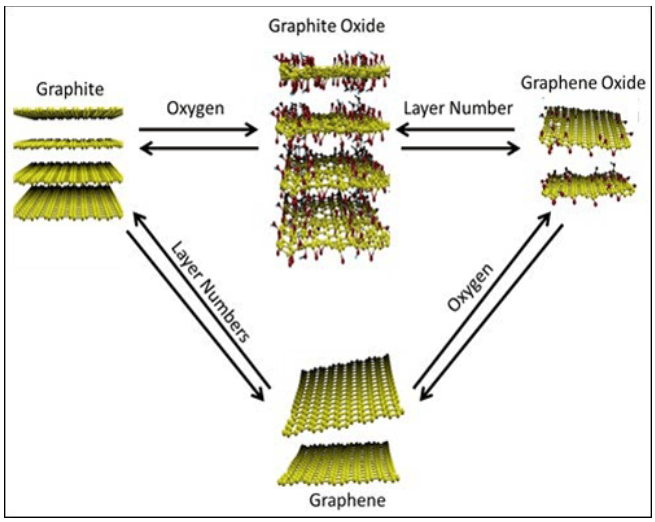


Fig.4. Structure of Graphene and its derivatives

3 Synthesis of Graphene and its derivatives

For the production of graphene various methods have been devised and categorized into top-down and bottom-up processes as shown in Fig.5 [50]. The bottom-up approaches involve the direct synthesis of graphene from carbon sources, such as the CVD, which is a typical method used to grow large-area, single and few-layer graphene sheets on metal foil substrates. For example, large area monolayer graphene has been achieved on Cu films [51, 52]. Another typical bottom-up approach is epitaxial growth on single-crystal SiC. Large-area growth on SiC wafer surfaces by high temperature evaporation of Si in either ultrahigh vacuum [29] or atmospheric pressure [53], has been developed to prepare wafer-size graphene. However, these methods are not widely used because of their complexity, limited scaling-up and high cost of the precious metal substrates. Different from the bottom-up approaches, the top-down approaches are advantageous in terms of high yield, solution based processability, and ease of implementation, which have been demonstrated by means of chemical

exfoliation of graphite [54], thermal exfoliation [55], and electrostatic deposition [56].

The bottom-up approach to graphene synthesis presents less defects compared to the top-down approach, the operation and procedures are much harder, making it difficult to realize mass production for practical applications, and it is an expensive affair. Still, the most commonly chosen route of graphene synthesis is a bottom-up strategy because it offers incredible possibilities to tailor the atomic size, composition, shape, stability and edge structure in graphenes [57].

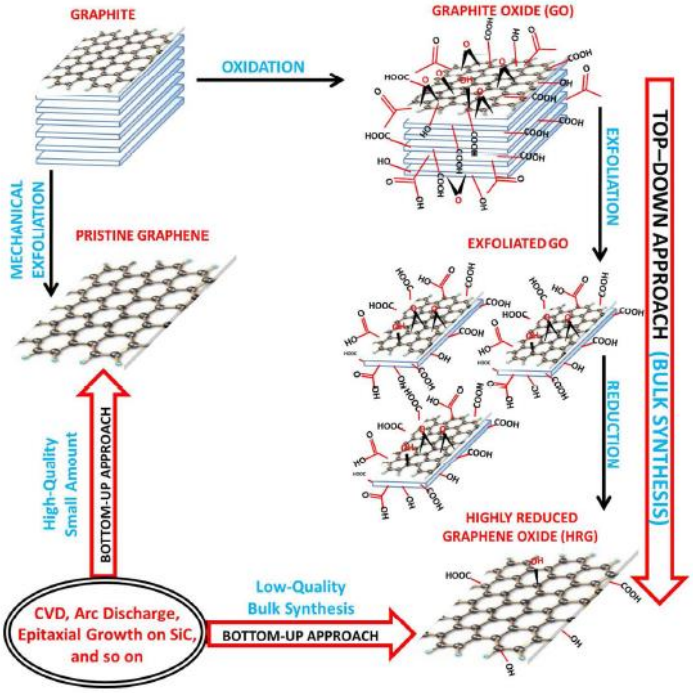


Fig.5. Schematic representation of the methods used for the synthesis of graphene, which is classified into top-down and bottom-up approaches [Ref.50]

3.1 Mechanical Exfoliation

Graphite is stacked layers of many graphene sheets, bonded together by week van der Waals force. Thus, in this principle, it is possible to produce graphene from high purity graphite sheet, if these bonds can be broken. The interlayer distance and interlayer bond energy is 3.34 A ° and 2 eV/nm^2, respectively. Exfoliation and cleavage use mechanical or chemical energy to break these week bonds and separate out individual graphene sheets. For mechanical cleaving, ~300 nN/µm^2 external force is required to separate one mono-atomic layer from graphite [58]. Graphene sheets of different thickness can indeed be obtained through mechanical exfoliation or by peeling off layers from graphitic materials such as highly ordered pyrolytic graphite, single-crystal graphite, or natural graphite. This peeling/exfoliation can be done using a variety of agents like scotch tape, ultrasonication, electric field and transfer printing technique etc. In certain studies, highly oriented pyrolytic graphite has also been bonded to the substrate either by regular adhesives like epoxy resin to improve the yield of single and few layer graphene flakes. Graphene flakes obtained by mechanical exfoliation methods are usually characterized by optical microscopy, Raman spectroscopy and Atomic Force Microscope (AFM) [59-62].

In the study of Novoselov et al., a commercially available highly oriented pyrolytic graphite sheet of 1 mm thickness was subjected to dry etching in oxygen plasma to make 5 µm deep mesas (area 0.4 to 4 mm^2). This was then put on a photoresist and baked, to stick the mesas to the photoresist. Then, a scotch tape was used to peel off layers from the graphite sheet. Thin flakes, attached to the photoresist, released in acetone and transferred to a Si substrate, were found to have single to few layer graphene sheets. This process of producing graphene sheets was found to be very reliable and easy and thus, attracted the immediate attention of the scientific community [63]. In slight

variation of the original process, it was shown that large (~10 µm) and flat graphene flakes can be produced by manipulating the substrate bonding of highly oriented pyrolytic graphite on Si substrate and controlled exfoliation [64]. In another approach, mm-sized single to few layer graphene was produced by bonding bulk graphite to borosilicate glass followed by exfoliation, to leave single or few layer of graphene on the substrate [65]. Both of these advancements stressed on modifying the bonding with the substrate to generate large-area graphene sheets. These methods show good promise to be scaled up to industrial level production for large size graphene based electronic devices.

3.2. Chemical Exfoliation

Chemical exfoliation is a two-step process. At first reduces the interlayer van der Waals forces to increase the interlayer spacing. Thus, it forms graphite intercalated compounds (GICs) Fig.2. Then it exfoliates graphene with single to few layers by rapid heating or sonication. For single-layer graphene oxide ultrasonication is done Fig. 6 [66] and various layer thickness Density Gradient Ultracentrifugation is performed [67]. The first attempt in this direction is done by Viculis et al. who used potassium metal to intercalate a pure graphite sheet and then exfoliated it with ethanol to form dispersion of carbon sheets [68]. Graphene oxide (GO) is readily prepared by the oxidation of graphite by Brodie method [69], Staudenmaier method [70], Hofmann method [71, 72] and Hummers method [73]. The oxidation reaction helps to penetrate oxygen functionalities on both sides of the sheets. It widens the inter sheet distance and disbands the tightly packed sp^2 hybridized atoms of carbon [74, 75].

Botas etal. pointed out a probable mechanism for the invasion of oxygen into the graphite flakes [76]. In the case of graphites with smaller crystal size, the invasion of oxygen occurs predominantly at the boundaries of the sheets, yielding small size graphene oxide sheets. In contrast, the more ordered graphites are predominantly attacked in the basal plane where the epoxy groups are developed. It yields large size graphene oxide sheets. This study also revealed that graphene oxide derived from lower crystalline graphite contains a large number of carboxyl and hydroxyl groups and graphene oxide obtained from higher crystalline graphite contains abundant epoxy groups. As a result of the above mechanism, the material becomes hydrophilic facilitating the separation of individual graphene oxide sheet using sonication [75] or magnetic stirring [77, 78]. This phenomenon is called exfoliation of graphene oxide. Water is the widely used solvent to disperse graphene oxide. Samulski et al. claimed, water soluble graphene is similar to single graphene sheets peeled from pyrolytic graphite (0.9 nm thick) [79]. Besides water, the dispersion of graphene oxide is also possible in several organic solvents such as N-methyl pyrrolidine (NMP), ethylene glycol and N, N-dimethyl formamide (DMF) [80]. It has been observed that graphite could utilize the surface energy of NMP to exfoliate and produce single layer graphene oxide sheets [81, 82]. But solvents are expensive, and their high boiling point limited their applications. Graphene exfoliation is possible in a surfactant–water solution (sodium dodecyl benzene sulfonate). The major benefit of surfactant is the prevention of sheet aggregation [83]. In another study, Green and Hersam used sodium cholate to simultaneously extract single graphene sheets from the bulk graphite with the help of a density gradient centrifuge machine at different buoyant density [67]. Both ultrasonication and magnetic stirring can be used in graphene exfoliation. However, excessive sonication can reduce the sheet quality. Chhowalla et al. found that graphene oxide dispersed in DMF solution could laterally degrade after 10 hours of sonication. Over sonication may increase the number of sheets to sheet junctions which limits electron mobility [84]. These types of sheets are not suitable for device applications. A higher amount of oxygen functionalities (epoxy and hydroxyl) can generate areas of weakness mainly consisting of cracks and fault lines. This defective zone leads to sheet breaking when ultrasonicated for a longer duration. A recent investigation by Qi et al. showed that the first hour of sonication is the critical point [85]. Because the exfoliation and sheet break up mainly occur in the very first hour, while later sonication facilitates sheet restacking. This suggests that when graphene oxide sheets are degraded in size, they would tend to intercalate or restack together. Therefore, in order to address poor quality or hole defects of graphene higher sonication time should be avoided. It is better to continue until the whole solution becomes clear with no visible particulate matter [67].

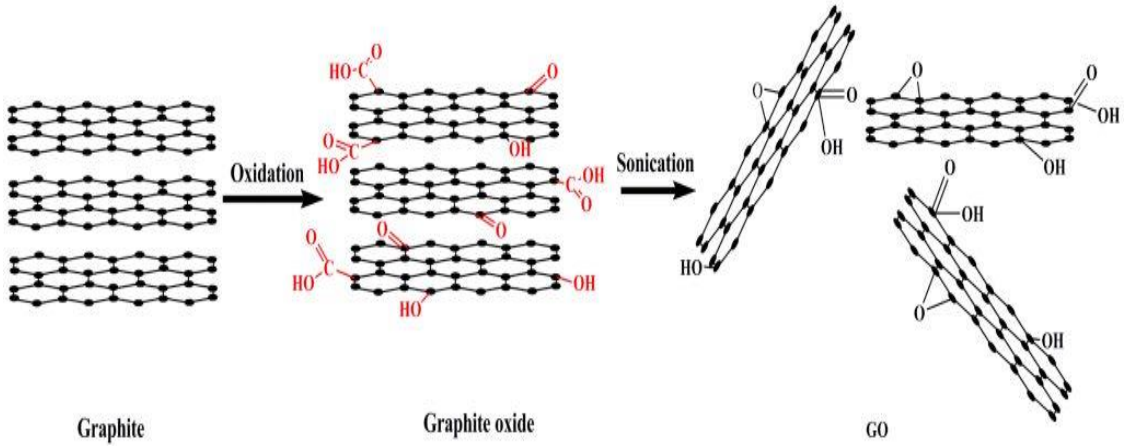


Fig.6. Synthesis of Graphene oxide [Ref.66]

3.3. Oxidation of Graphite

The Graphene Oxide is currently the most common precursor used for the synthesis of graphene materials. It can be prepared by the intercalation and oxidation of graphite powder. For synthesis of graphene oxide in bulk amount, we need to synthesize graphite oxide applying any of the methods discussed below Fig.7. The first report on the synthesis of graphene oxide by the intercalation of graphite sheets was given by a Schafacutl in 1840. He attempted to exfoliate graphite, when he tried to purify the impure graphite "kish" from iron smelters [86-88].

The well-known methods used for the synthesis of graphite oxide are Brodie method [69], Staudenmaier method [70], Hofmann method [71, 72] and Hummers method [73] and also their modified and improved forms. In these methods, initially graphite powder is chemically reacted with acids (HCl, H_2SO_4 and HNO_3 etc.) followed by the intercalation of alkali metals (alkali metal compounds $KClO_3$, $KMnO_4$, $NaNO_3$ etc.) into the graphitic layers which further helps in the breaking of graphitic layers into small pieces.

Brodie in 1859 first synthesized graphite oxide by adding potassium chlorate to the slurry of graphite in fuming nitric acid. After about 40 years, Staudenmaier improved this method by replacing about two thirds of fuming HNO_3 with concentrated H_2SO_4 and feeding the chlorate in batches. Based on these work, Hummers and Hofmann developed an alternate oxidation method in 1958, often called Hummers method, in which $NaNO_3$ and $KMnO_4$ dissolved in concentrated H_2SO_4 was used to oxidize graphite into graphite oxide within a few hours. Hummers' method was widely adopted to afford graphene oxide [89-91], but it still suffers from several flaws [92-97], including toxic gas generation (NO_2, N_2O_4), residual nitrate and low yield etc. To address these problems, various modification on Hummers' method have been made in the past 20 years, and the main strategies can be summarized as follows: first [92, 93], removing $NaNO_3$ directly from Hummers method with an improved workup; second [94, 95], adding a step of preoxidation before $KMnO_4$ oxidation (in the absence of $NaNO_3$); third [66, 96, 97], increasing the amount of $KMnO_4$ instead of $NaNO_3$; fourth [98, 99], replacing $KMnO_4$ with K_2FeO_4 while $NaNO_3$ was removed. For example, in the report of Kovtyukhova et al. graphite was preoxidized by $K_2S_2O_8$ and P_2O_5 before Hummers' procedure was implemented [94]. This work resulted in highly oxidized GO, but the whole process which contains solution transfer and material drying is rather time-consuming. By increasing the amount of both $KMnO_4$ and concentrated H_2SO_4 (containing 1/9 H_3PO_4) instead of $NaNO_3$, Marcano et al. found that the improved Hummers method leads to higher yield and the temperature can be easily controlled [66]. Recently, Peng et al. reported a K_2FeO_4-based oxidation approach instead of $KMnO_4$ and obtained single-layer graphene oxide at room temperature [98].

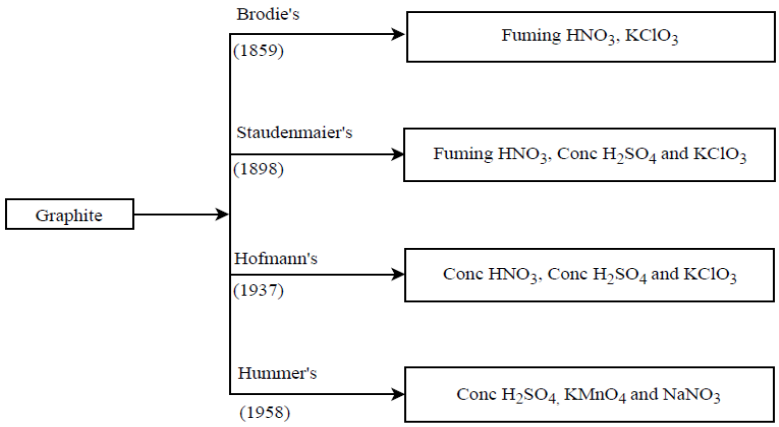


Fig.7. Methods of synthesis of Graphite oxide from Graphite

Despite the above progresses, two problems remain in various modified versions of Hummers method: (1) high consumption of the oxidants and intercalating agents was inevitable, (2) most of the synthesis routines proceed for a long time, both of which result in high cost and poor scalability in practical applications [93,100]. Therefore, there is a strong demand to develop an economical and efficient method for the synthesis of graphene oxide.

3.4. Chemical Vapour Deposition based synthesis

Chemical vapor deposition comprises chemical reaction on which process molecules are heated and changed to a gaseous state and that is called precursor. In this CVD process a substrate is diffused on thermally disintegrated precursors in high temperature. It deposits on thin films, crystalline, solid, liquid or gaseous precursors on the surface of the substrate. The deposition of high-quality graphene from CVD process is usually done onto various transition metal substrates like as Ni [101], Pd [102], Ru [103], Ir [104] and Cu [52]. CVD growth of graphene has been mainly practiced on copper and nickel substrates. Nickel was the first substrate on which CVD growth of large area graphene was attempted. These efforts had begun right from 2008 [105].

Graphene growth based on CVD has shown exceptional device properties [106], with electron mobility of 7350 $cm^2 V^{-1}s^{-1}$ [1]. In addition, large scale production of 30" graphene films was demonstrated using roll to-roll CVD. The graphene obtained from this process was of high quality, with a sheet resistance of ~125 Ω/ square and 97.4% optical transmittance. Graphene growth using CVD is fairly straightforward, where a copper or nickel substrate is placed in a reactor at temperatures normally around 1000°C. The initial step in the process is to introduce hydrogen in the reactor. This step is critical to eliminate any oxide layer present in the metal, for the case of Cu this will reduce any native layers of CuO and Cu_2O. The hydrogen atmosphere also enables the growth of grain boundaries, which is necessary for the growth of high-quality graphene [107]. Afterwards, a hydrocarbon gas (typically methane) is added to the reactor. The hydrocarbon gas provides the necessary carbon species used in the growth of graphene. The hydrocarbon gas to hydrogen ratio plays an important role in the growth of graphene. If insufficient hydrogen is present, this could result in oxidized metal layers being present, which can lead to a disordered graphene structure. By contrast, excess hydrogen has shown to etch away graphene. On polycrystalline substrates, the graphene flakes tend to have different lattice orientations. Using CVD, graphene is grown onto transition metals, which enables a low-energy pathway by forming intermediate com-pounds for the growth of graphene. The first row of transition metals Fe, Co, Ni, and Cu is of great interest due to their low cost and high availability. The difference in the carbon solubility between these metals impacts the growth quality, where Fe has the highest and Cu has the lowest carbon solubility. For this reason, Cu is an ideal metal for growing single layer graphene. When using Ni and Co it is common to get up to 10 layers of graphene. Similarly, on Fe it is common to have Few Layer Graphene (FLG). Most practical applications of graphene require that the underlying surface be insulating. For this reason, graphene must be transferred to an insulating surface, such as SiO_2 [108].

Additionally, this transfer is required to measure the optoelectronic properties of the synthesized graphene. The commonly used process to transfer graphene is to first deposit and cure poly (methylmethacrylate) (PMMA) on the metal sheet. Afterwards, etch the Cu metal sheet using iron chloride. This gives a floating sheet of PMMA and graphene, which is rinsed in deionized water. Subsequently, transfer this layer to an insulating surface and use acetone to remove the PMMA layer.

3.5. Plasma enhanced Chemical vapor Deposition Synthesis

Plasma enhanced chemical vapor deposition (PECVD) is another method used for the synthesis of graphene that is comparable to the thermal CVD process [109]. PECVD is based on a number of plasma sources, such as microwave (MW), radio frequency (RF), and direct current (dc) arc discharge have been utilized in the growth of graphene. Copper and nickel are typically used as the substrate for PECVD graphene growth; however, a number of additional substrates have also been used [110]. A particularly exciting technique is a substrate free method based on the decomposition of ethanol in MW-based PECVD reactor [111]. Such methods provide can be used for scalable production of graphene powder. Typical growth conditions of PECVD graphene on a substrate are 5–100% CH_4 in H_2 with a substrate temperature of 500–800°C. The power of the plasma is 900 W. Such processes can enable the growth of graphene at lower temperatures and shorter duration (<5 min). However, the quality of the graphene film is typically lower when compared to thermal CVD. The growth of graphene films at low temperature is important for a number of applications. For instance, fabrication of graphene for high-performance display glass has to be at a temperature lower than 660°C [110]. Furthermore, production at lower temperature can provide new manufacturing opportunities in the area of flexible electronics based on plastics [112]. Critical challenges still need to be overcome, as at lower temperatures the graphene film tends to have a higher disorder.

3.6. Flame Synthesis

Flame synthesis is extensively used to produce commercial quantities of nanoparticles. A key advantage of flames is that it readily provides the high temperature necessary for gas phase synthesis along with a carbonizing or oxidizing environment. With respect to graphene, flame synthesis is not as commonly studied when compared to CVD, but it offers several important advantages, such as scalability and cost effectiveness. The most commonly used flame types include premixed, normal diffusion, inverse diffusion, and co-flow. Since early 2000s, a number of researchers have focused on the use of flames for CNT synthesis [113]. However, the development of flame synthesis for graphene is still in its early stage. In addition to flame type, other parameters including temperature, species concentration, and velocity impact of the growth process. Graphene being a two-dimensional material requires large-scale production across a substrate. Due to the temperature and species gradients that occur in most flames it is difficult to scale the growth of graphene across an entire substrate. Moreover, a reduced environment with carbon rich species, which is necessary for graphene growth, is difficult to achieve in most flames. Nevertheless, flame synthesis has the potential to economically enable the mass production of graphene. Similar to earlier CNT flame synthesis papers, where the growth of CNTs was observed near the soot region of a premixed flame, carbon particles containing graphene were observed in Bunsen (propane) flame [114]. These particles were collected by placing a transmission electron microscopy grid 2 cm above the tip of the burner. The grid was held within the flame for 10–50 ms. The graphene films were several hundreds of nanometers in size. In an attempt to grow graphene on copper, Li et al. investigated the growth of graphene using an ethanol burner. The substrate was placed within the flame at a temperature of 550–700°C and the flame was extinguished using a cap to prevent the oxidation of the copper foil. The growth of an amorphous carbon film was observed on the substrate and XPS confirmed the formation of sp^2, sp^3 and C–O bonded atoms. Graphene was not observed due to the low temperature and the presence of oxygen within the flame. In a different experiment, Li et al. were able to synthesis graphene successfully on nickel [115]. The process utilized two different burners (burner 1 and burner 2), with the substrate situated within the interior region of the flame structure itself. Burner 1 (alcohol burner) surrounded the substrate for the entire time, where it prevented air oxidation and served as the carbon source. Burner 2 (butane fueled

Bunsen burner) provided the additional heating of the substrate and served as the carbon source for graphene growth. The flame was extinguished using a cap. There are still numerous challenges in using flame synthesis for the growth of graphene, specifically in developing methods that result in higher quality graphene.

3.7. Epitaxial growth of graphene

Epitaxial thermal growth on a single crystalline silicon carbide (SiC) surface is one of the most praised methods of graphene synthesis. When the deposition of a single crystalline film on a single crystalline substrate produces epitaxial film and the process is known as epitaxial growth. It fabricates high-crystalline graphene onto single-crystalline SiC substrates. There are two general epitaxial growth processes depending on the substrate, homo-epitaxial and hetero-epitaxial growth. When the film deposited on a substrate is of the same material it is known as a homo-epitaxial layer, and if the film and substrate are different materials it is called a hetero-epitaxial layer. SiC first used as on electrical measurements on patterned epitaxial graphene on electrical measurements on patterned epitaxial graphene. In 2004, SiC is a wide band gap semiconductor (3 eV) and thus electrical measurements can be carried out using it as the substrate [116]. In 1975, Bommel et al. first reported graphite formation on both the 6H–SiC (0001) surfaces [117]. The heat treatment in the range of 1000–1500 °C in an ultrahigh vacuum (~10–10 m bar) manufactured graphite on both of the SiC polar planes (0001). In 2004, de Heer's group reported the fabrication of ultrathin graphite consisting of 1–3 monoatomic graphene layers on the Si completed (0001) face of single-crystal 6H-SiC and explored its electronic properties. The growth rate of graphene on SiC depends on the specific polar SiC crystal face. Graphene forms much faster on the C- than on the Si-face. On the C-face, larger domains (~200 nm) of multilayered, rotationally disordered graphene are produced. On the Si-face, ultra-high vacuum (UHV) annealing leads to small domains, ~30–100 nm [118, 119]. (Si (0001)- and C (000-1)-terminated) annealed at high T (>1000 °C) UHV graphitize due to the evaporation of Si [109, 110]. Epitaxial graphene growth on SiC has been visualized as a very promising method for large scale production and commercialization of graphene for applications into electronics. Graphene on SiC produces high-frequency electronics, light emitting devices, and radiation hard devices. Graphene on SiC has been established as a novel resistance standard based on the quantum Hall effect (QHE) [1].

3.8. Reduction of Graphene Oxide

3.8.1. Chemical Reduction

Chemical reduction of graphite oxide is one of the excellent procedures to synthesized reduced graphene oxide and graphene in large quantities Fig.8 [73]. It includes ultrasonication of graphite oxide in water forming a homogeneous dispersion of predominantly soluble graphene oxide in water. The graphene oxide is reduced by a suitable chemical process; the reduced graphene oxide formed resembles graphene but contains residual oxygen and other hetero atoms, as well as structural defects. During the reduction processes, most oxygen containing functional groups of graphene oxide are eliminated and the π-electron conjugation within the aromatic system of graphite is partially restored. Finally, the graphene oxide gets precipitated from the reaction medium because of the recovered graphite domains of chemically converted graphene sheets with increased hydrophobicity and π-stacking interaction. The properties of reduced graphene oxide are nearly similar to that of graphene prepared through different chemical, thermal, photo, electrochemical or microwave reduction pathways [75]. The most widely applied technique used for preparing chemically converted reduced graphene oxide is the chemical reduction of graphene oxide. Shin et al. used $NaBH_4$ for the reduction of graphite oxide [120]. It shows enhanced electrical properties after reduction. Fan et al. reported that the exfoliated graphite oxide can undergo quick deoxygenation in strong alkali solutions like NaOH and KOH at moderate temperatures (50–90°C) resulting in stable aqueous graphene suspensions [121].

Various inorganic reducing agents such as phenyl hydrazine, hydrazine hydrate and sodium borohydride have been explored for the chemical reduction of graphene oxide.

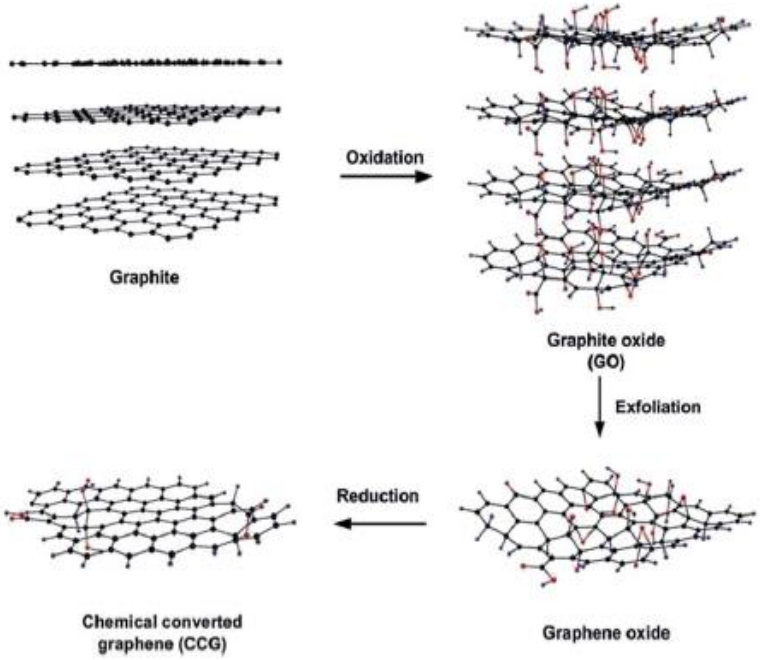


Fig.8. Preparation of chemically converted graphene (CCG) by reduction of graphene oxide [Ref.73]

3.8.2 Biomolecules in Graphene Oxide reduction

A number of biomolecules such as ascorbic acid [122], glucose [123], fructose [124], sucrose [124], melatonin [125], L-cysteine [126], L-glutamine [127], L-Lysine [128], L-Valine [129], oxalic acid [130], Thiourea dioxide [131] and glucose oxidase [132] have been used in the reduction of graphene oxide to graphene (Table 2). Most of these biomolecules are commercially available in large quantity, pure form and are known to be eco-friendly. For instance, a novel environmentally friendly strategy was developed toward one-pot synthesis of CuS nanoparticle-decorated reduced graphene oxide nanocomposites with the use of L-cysteine, an amino acid. L-cysteine was intelligently used not only as a reducing agent but also as a source or donor of sulfur, and also as a linker to anchor CuS nanoparticles onto the surface of RGO sheets. In another report, L-glutamine was used as a reducing agent in the synthesis of graphene oxide and the reduction was achieved in a single step, in aqueous solution under mild condition. Vitamin C was found to be an innocuous and safe reductant for the preparation of graphene suspensions by de-oxygenation of graphite oxide. In this endeavor, the yield of highly reduced graphene suspension was found to be comparable to that of hydrazine and safer thereby eliminating all the toxic effects of hydrazine. It was further observed that vitamin C mediated reduction of graphene oxide can also be carried out in organic solvents such as N,N,N-dimethyleformamide (DMF), or N-methyle- 2-pyrrolidone (NMP), thus projecting vitamin C as a potent alternative to powerful yet toxic reducing agents such as hydrazine. The reduction and functionalization of graphene oxide in presence of Fe catalyst has also been demonstrated, while Zhu et al. pointed out that reducing sugars such as glucose, fructose and sucrose not only act as mild reducing agents towards graphene oxide but also behave as excellent capping agents in stabilizing synthesized graphene nanosheets [124]. The important point about glucose reduction method was that authors have also proved the biocompatibility of the synthesized graphene nanosheet and their remarkable stability in water. Researchers have successfully demonstrated reduction graphene oxide using Melatonin, another biomolecule which has also shown potential to reduce graphene oxide [125]. Melatonin was found to be safe, biocompatible and efficient especially for large production of graphene and its bio-applications.

Table 2: Representative list of biomolecules used in the synthesis of graphene

S.No.	Biomolecules	Reference
1	Vitamin C	122
2	Glucose	123
3	Fructose	124
4	Sucrose	124
5	Melatonin	125
6	L-cysteine	126
7	L-glutamine	127
8	L-Lysine	128
9	L-Valine	129
10	Oxalic acid	130
11	Thiourea dioxide	131
12	Glucose oxidase	132

3.8.3. Microbial reduction

Bacteria have various capacities to manipulate atoms and chemical molecules in order to survive. There are natural paths used by bacteria depending on which kind of final form of a molecule is required for its life. Bacteria also use uncommon organic and inorganic molecules around them to substitute an essential molecule urgently needed as respiratory substrate through an adaptive oxidation and/or reduction mechanism to serve as possible sources of energy. This power of electronic manipulation of various compounds opened avenues for scientist to inspire from a biological process various methodology for synthesis a new materials at different scales. There have been various reports on synthesis of nanoparticles through exploitation of the capacity of bacteria cells to reduce metallic salts. Graphene oxide is one of such nanomaterials that bacteria have enduring capacity and mechanism for its reduction (Table 3). The mechanism of reaction involved depend on bacterial cells that have such capacity directly or indirectly for hydrolyzing acid groups associated with nanosheets of carbon especially oxygen atoms. Like a final acceptor of electron in respiration process of bacteria, grapene oxide can capture the electron coming from the respiration process.

For instance, Wang et al. used *Shewanella* for reducing graphene oxide via external electron transfer mediated by the outer membrane c-type cytochromes included heme group, and by self-secreted electron mediators [133]. *Bacillus subtilis* was also used for reduction of graphene oxide and development of an advanced supercapacitor in this same way, while Zhang et al. showed that graphene oxide reducing bacteria participate not only in the reduction step but also in the final composite by being entrapped inside the reduced graphene. This work shows that a chosen methodology for reduction of graphene oxide can define the application of a final nanomaterial [134]. It seems that different types of bacteria can participate in the reduction and in the orientation of a final material obtained with micro-organism assistance.

Raveendran et al. used extremophiles bacteria for reducing graphene oxide to get a highly conductive graphene that can be used in microelectronics [135]. Here, the reduction of graphene oxide comes from the potential of extremophiles with adequate mechanisms for degradation of a toxic element in order to survive under harsh environmental condition. *Escherichia coli* in mixed acid fermentation with an anaerobic condition were used to reduce chemically exfoliated graphene oxide nanosheets with attendant bactericidal property attributed to the surfaces of reduced graphene oxide nanosheets formed [136], while this same bacteria biomass have been employed in the reduction of graphene oxide to graphene sheets that are dispensable in water [137].

Wang et al. opined on the possibility of bacterial reduction of graphene oxide being associated with a catalytic reaction assisted by enzymes like *glycose oxidase* [132]. Huge amount of various enzymes are produced inside bacterial cells. In the case of using a whole cell of bacteria for reduction of graphene oxide, these enzymes are not readily available unless they are localized in the membrane. In addition, such reactions require some part of the external group in the nano-

sheets and/or a final product of a catalytic reaction that can react with graphene oxide and achieve its reduction. Nevertheless, reducing graphene oxide by bacteria has made in situ manipulation of graphene oxide possible and bacteria have become a natural factory capable of recycling and synthesizing a desired graphene from the pre-existent precursor. However, in another investigation by Avinav et al. graphene oxide was obtained from a cellulose precursor and reduced in situ using *Gluconacetobacter xylinus* [138]. Yeast is also used to reduce graphene oxide. Lee and co-workers have made use of baker's yeast containing nicotinamide adenine dinucleotide phosphate (NADPH) as the reducing agent for GO reduction [139]. Capability of baker's yeast in reducing prochiral ketones and α, β-epoxy ketones, as well as the reducing ability of NADPH towards organic ketones have inspired the group. The resultant RGO possesses good electrical conductivity.

Table 3: Representative list of microbes used in the reduction of graphene oxide

S.No.	Microbes	Reference
1	Shewanella	133
2	Bacillus subtilis	134
3	Extremophiles bacteria	135
4	Escherichia coli	136, 137
5	Gluconacetobacter xylinus	138
6	Yeast	139

3.8.4. Phytoextracts mediated reduction

It has been discovered that various phytochemicals obtained from different parts of plants like leaves, peel, root etc. which mostly contains biomolecules including proteins, vitamins, amino acids, saccharides, alkaloids, pectins, alcoholic compounds, flavonoids and enzymes [140] have the potential to serve as reducing and capping agents in the bio-reduction and formation of functional graphene from graphene oxide.

Green tea solution was successfully used for reduction of graphene oxide [141]. This reduction was attributed to the antioxidant chemicals present in green tea extract mainly polyphenols which are readily oxidizable and get converted to the corresponding quinine forms. Some researchers have also observed that reducing ability of polyphenols is enhanced greatly in the presence of Fe [142]. Kulia et al. showed the potential of wild carrot roots in the bioreduction of graphene oxide [143]. Interestingly the reduction took place not because of the phytochemicals but due to endophytic microorganism that are always present in wild carrot root and it was achieved at room temperature in aqueous medium. Firdhouse and Lalitha reported simple and eco-friendly biosynthesis of graphene using aqueous extract of *Amaranthus dubius* as a reducing agent under reflux and the size of the synthesized nanographene was around 5 nm in size, which underscore the performance of *Amaranthus dubius* extract as a capping agent [144]. Furthermore, Thakur and Karak also synthesized graphene by employing an aqueous peal extract of *Citrus sinensis* (orange) and aqueous leaf extracts of *Colocasia esculenta* and *Mesua ferrea Linn* [140]. The common phytochemicals present in these leaves and peels are pectins, flavonoids, ascorbic acid, apigenin, luteolin and various flavones.

Barau et al. investigated simultaneous reduction of graphene oxide with silver ions by aqueous leaf extract of *Colocasia esculenta* and it was discovered that the graphene material produced exhibited improved antimicrobial activities and admirable cyto compatibilty for peripheral blood mononuclear cells (PBMCs) and mammalian red blood cells (RBCs) [145]. Reduction of GO has been brought out at room temperature as well as under refluxed condition. In case of *Colocasia esculenta* leaf extract, reduction has been observed faster than the other stated phytoextracts like *Mesua ferrea Linn* and *Citrus sinensis*. It has also been monitored that under reflux condition, reduction has been perceived much faster than that at room temperature.

In another report, graphene was synthesized using *Gingko biloba* extract as a reducing and stabilizing agent and the synthesized graphene was found to be cytocompatible, suggesting its applicability in

biomedical application especially in the area of tissue engineering, bioimaging and drug delivery [146]. Deoxygenation of graphene oxide to graphene using extract of aquatic macrophytes namely, *Potamogeton pectinatus L., Ceratophyllum demersum L., Lemna gibba*, and weed in rice field *Cyperus difformis* has been reported by Mhamane et al. [147], it is important to note that this is the only report where extracts of aqueous plants have been used for graphene oxide reduction. Furthermore, Kartick et al. established green reduction of graphene oxide using *Cocos nucifera L.* (coconut water) [148], while Haghighi and Tabrizi synthesized monolayered reduced graphene oxide nanosheets by reducing and stabilizing exfoliated graphene oxide using rose water. It was also experimentally demonstrated that this material has an excellent potential in sensors and biosensors applications [149]. Lee and Kim found that *Prunus serrulata* (Cherry) leaf extract stood out among seven plant leaf extracts (Cherry, Magnolia, Platanus, Persimmon, Pine, Maple, and Ginkgo) employed for reduction of graphene oxide [150].

Tannin substances constitute the third largest class of plant components after cellulose and lignin. The abundant units of catechol and pyrogallol in tannin molecules provide unique reducing characteristic. Tannic acid, one of the typical hydrolysable tannins, has been mainly

extracted from oak apple. Guo and co-workers introduced tannin for the reduction of GO [151].

GO suspension has been stirred with tannin solution for 10 h at 80 °C to obtain RGO. The obtained RGO has been found dispersible in ethanol, acetone, DMF and DMSO. But it cannot be

dispersed in water, acetone, tetrahydrofuran and chloroform. Also RGO shows high electrical

conductivity. Chen and co-workers exemplified caffeic acid for the reduction of GO. The obtained RGO provides a high C/O ratio [152]. Bud of *Syzygium aromaticum* (Cloves) have also been demonstrated as an effective reducing agent towards GO [153]. *Hibiscus sabdariffa* L. extract further been utilized to reduce GO by Tai and co-workers. The obtained RGO presented a good specific capacitance [154]. Spinach leaf extract has yet again been used to reduce GO and the ensuing RGO enclosed high potential antioxidant activity [155]. Jana et al. used *Phaseolus aureus* L. (Mung beans) soaked water for the reduction of GO [156].

Although, different types of plant extracts have been explored as reducing agents, but their basic reduction mechanisms are the same. Plant extract contains plentiful polyphenols which have a high tendency to oxidize. GO has mainly three types of reactive species namely epoxide, hydroxyl and carbonyl. Polyphenol reacts with the epoxide moiety through an SN2 mechanism resulting in the opening of the oxirane ring. The carbonyl and hydroxyl groups experience similar nucleophilic attack by polyphenol with elimination of a water molecule. This results in the successful conversion of GO to RGO [140].

3.8.5. Solvothermal and Hydrothermal reduction

The reduction of GO through solvothermal or hydrothermal route generally occurs at low temperature and high pressure is also an important series in the field of graphene synthesis and reduction [157,158]. Solvothermal processes can be defined as chemical reactions or transformations in a solvent under supercritical conditions or nearby pressure–temperature domain resulting from heating [159]. Inside the sealed container, the reduction occurs through processes involving surface chemistry, the reactivity being increased under high pressure conditions and at moderate temperatures. The hydrothermal method has been applied for the transformation of carbohydrate molecules to form homogeneous carbon nano-spheres [160] and nanotubes [161].

Fan et al. discovered that strongly alkaline GO suspension significantly gets reduced just by heating at temperatures of 50–90 °C [162]. This investigation confirmed the reduction of graphene oxide by different spectroscopic and analytical studies. Although this facile method is in principle very attractive, but recent studies demonstrated that strong alkaline conditions have some inefficiencies. These include limited reduction ability, yielding of a relatively low C/O atomic ratio and low electrical conductivity compare to Hyd-RGO. To overcome such limitations, solvothermal approach has been implemented in high boiling solvents such as DMF where moderate temperatures (125–160 °C) can be used to deoxygenate organic graphene oxide dispersions [163].

In this context, hydrothermal reduction of graphene oxide dispersions is also possible to carry out at various temperatures, up to 180°C [164]. Water acts as a

strong electrolyte with high diffusion coefficient and dielectric constant under hydrothermal conditions. Such properties permit in a variety of reactions that involve heterolytic bond cleavage facilitating the removal of oxygen groups via dehydration. This reduction method is undoubtedly greener and does not introduce any impurities to the final product. Along with these advantages, hydrothermal reduction has potential merits over the conventional chemical reduction methods. First of all, the process has easily been implemented in industry requiring only a very simple set-up (an autoclave). Second, the degree of reduction and the properties of RGO have been readily controlled by adjusting the pressure and temperature. Such possibilities allow the tuning of the optical transmittance and properties of RGO as the nonlinear optical properties of RGO are the function of the amount of oxygen-containing functional groups and structural defects [157].

3.8.6. Photoreduction

Photoreduction can be achieved by two means—a photothermal process or a photochemical process. In a photothermal process, the generation of heat on exposure to high intensity light causes deoxidation of graphene oxide. In a photochemical process, a sacrificial compound is used for the reduction of graphene oxide. The UV-Vis absorption spectra show high absorption at UV and low visible wavelengths [165]. Hence, a lot of photoreduction methods developed have used lasers with wavelengths in the 200 - 550 nm regimes.

A variety of photochemical methods for the reduction of graphene oxide have been developed using UV-irradiation in the presence of various gases and catalysts. One of the first reports on photochemical reduction of graphene oxide was reported in 2011 by Kamat and group at the University of Notre Dame [166]. A suspension of graphene oxide and TiO_2 nanoparticles was irradiated with a xenon lamp. They observed over an order of magnitude increase in conductivity after the reduction of graphene oxide TiO_2 suspension. Another facile method was reported by Li et al. by using polyoxometalate as a catalyst [167]. This method was used by Zhang et al. for inkjet printing of multi-layer films, which were demonstrated to be excellent chemical sensors [168]. Other catalysts such as zinc oxide nanoparticles [169], silicon nanowires, and $BiVO_4$ nanoparticles [170] have also been shown to increase the efficiency of the photochemical reduction process.

In a photothermal reduction process, the energy of the photons is converted to thermal energy, which increases the local temperature of the sample, resulting in reduction. Reduction of graphene oxide was reported by Matsumoto et al. using UV radiation in H_2 or N_2 at room temperature, without the use of a photo catalyst [171]. They achieved increase in conductivity by over five orders of magnitude. A group in Russia achieved photoreduction of graphene oxide films and suspensions using a mercury lamp [172]. Sun's group at Jilin University in China recently reported on using a two-beam laser interference technique for patterning and reduction of graphene oxide [173]. Numerous groups have reported using pulsed lasers for reduction of graphene oxide in suspension [174,175].

In addition to lasers, novel light sources such as flash lamp and solar radiation have also been reported in the literature for graphene oxide reduction. Cote et al . reported using a xenon flash lamp to reduce graphene oxide at ambient conditions [176]. They also demonstrated patterning on graphene oxide and polymer composite films by using a photomask. Focused solar radiation, for one-pot synthesis of reduced graphene oxide and its composites, was shown to achieve conductivity values which are close to that of graphite [177]. Table 4 gives the advantages and the disadvantages of the methods of reduction of Graphene Oxide

Table 4: Advantages and disadvantages of the methods of reduction of Graphene Oxide

S.NO	Reduction Methods	Advantages	Disadvantages
1	Chemical	Very high yield	i. Reducing agents are highly toxic. ii. Less suitable for bio-related applications. iii. RGO tends to form irreversible aggregations resulting from strong Van der Waals attractive forces among the graphene planes which confines its processability. iv. Not environmental friendly.
2	Thermal	i. Good yield ii. Oxygen containing functional groups are removed easily. iii. High electrical conductivity.	i. Very high temperature is applied which generates out hazardous waste. ii. Not environmental friendly.
3	Microwave	i. Fast, high purity and good yield. ii. Minimal time for synthesis. iii. Conductivity of RGO prepared is about 10^4 times higher than that of GO.	
4	Electrochemical	i. Fast, controllable and green method. ii. No toxic solvent. iii. RGO is contamination free. iv. Efficient reduction.	i. Generally, yields a solid RGO film as the final product which is useful for few specific applications but less suitable for the cases where the manipulation and processing of well dispersed RGO are required.
5	Photothermal	i. Rapid, chemical free, energy efficient and versatile method. ii. The resulting RGO possess high electrical conductivity over GO. iii. This technique is more useful in patterning GO films in the device and composite applications.	
6	Solvothermal	i. Reduction carried out at lower temperature.	i. Limited reduction ability. ii. C/O ratio of RGO is very low. iii. Low electrical conductivity compared to hydrothermally prepared RGO.
7	Hydrothermal	i. Greener method ii. Does not introduce any impurity to final product. iii. Simple reaction set up (an autoclave) degree of reduction. iv. Properties of RGO are readily controlled by	

			adjusting the pressure and temperature.		
8	Biomolecules	i.	Aqueous and organo-dispersible RGO.	i.	Some bimolecular reagents are relatively expensive.
		ii.	Good reducing efficiency.	ii.	High reduction time.
				iii.	Poor electrical conductivity.
9	Microorganism	i.	Simple and cost effective.	i.	High reduction time.
10	Plant extract	i.	Cost effective	i.	Inconsistent performance.
		ii.	Readily available reducing agent.	ii.	Contaminated RGO.
		iii.	Good reducing efficiency.		
		iv.	Good electrical conductivity.		
		v.	Aqueous and organo-dispersible RGO.		

CONCLUSION

Graphene is a cheap and multifunctional material that improves electrical, thermal, mechanical, optical and gas barrier properties of polymer matrices. At very low filler contents most of these properties were better for graphene than those observed for other carbon – based reinforced nanocomposites.

In summary, we have provided an efficient, scalable, nontoxic approach for the environmentally friendly production of graphene. Various methods of reduction of Graphite oxide were discussed from which stable graphene aqueous dispersions can be readily produced.

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