Synthesis, characterization and qualification of graphene for electronic applications

Original Article

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Abstract

Nanomaterials have unique properties due to their nanoscale dimensions. They can be used to design new technologies or enhance the performance of existing processes. One of the most promising and remarkable materials that play a vital role in nanomaterial technology is graphene and its carbon family(Graphene/ Graphene Oxide (GO)/Reduced Graphene Oxide (RGO). Different techniques areused forthe synthesis and characterization of graphene.Top-down and Bottom-Up techniques are the main techniques for graphene production. Thesesynthesis methods play a dominant role in deciding the final properties of the produced graphene.Different characterization methods are used to identify the synthesized graphene.This work provides a comprehensive review of graphene preparation and characterization techniques. A new factor is proposed to describe the quality of the prepared graphene according to the Raman spectroscopy, Scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements.This graphene quality factor (GQF) is used to compare the graphene produced using several preparation techniques and prepared chemically RGO samples. High-quality factor values of (0.9) were achieved for Chemical vapor deposition (CVD) based graphene compared to lower quality factors for other techniques. Chemically synthesized RGO samples were prepared and had comparable quality factor values to other published works.

1. INTRODUCTION

One of the most important elements having great contributions in nanomaterial technology is carbon. Graphene is mainly a carbon allotrope having many outstanding mechanical properties in addition to astonishing electric and thermal properties. These striking properties make the graphene considered to be a candidate to replace many conventional materials for many applications.Graphene and its family (GO) and (RGO) received increasing attention from the scientific community since Andre Geim and Konstantin Novoselov wonthe 2010 Nobel Prize. Theoretically, graphite was a study case 6 decades agoand used for relating properties of various carbon-based materials[1,2]. A timeline of selected events in the history of Graphene is shown in Fig.1.

Nobel Prize in Physics 2010 was awarded for innovative experiments about the 2-D graphene material. After a literature survey in the graphene field and its applications, it is found that a considerable share of graphene produced is fabricated through exfoliation as shown in Fig. 2. This is because exfoliationmethods can be regarded as an inexpensive synthesis methodcompared to any synthesis method with high-quality products.
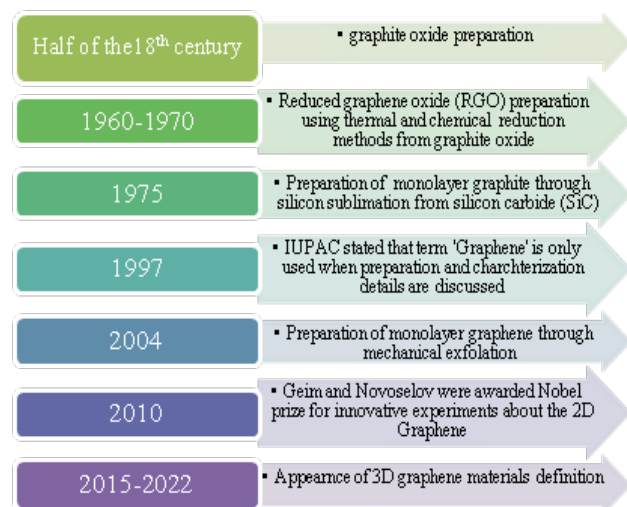

Fig. 1: Timeline of events concerning synthesis and characterization history of graphene

Carbon atomsgenerally can be found in 0-D fullerenes, rolled up into 1-D nanotubes,2-D graphene sheets and 3-D graphite[3]. Graphene is a 2-D single-layer sheet of sp2 hybridized carbon atoms arranged in a honeycomb (hexagonal) lattice.Many types of Graphene-based materials exist including monolayer and multilayer Graphene,Graphene quantum dots (GQDs), Graphene nanoribbons (GNRs), nanomesh, nanosheets, and Graphene oxide (GO)[4]. Graphene is described as "the thinnest, most flexible and strongest material ever known"[5]. Graphene is considered to be a great material since it can be functionalized to acquire great properties.Moreover, it has excellent optical properties, high mobility and the highest Young's modulus that facilitate it to be applied in many applications[6].
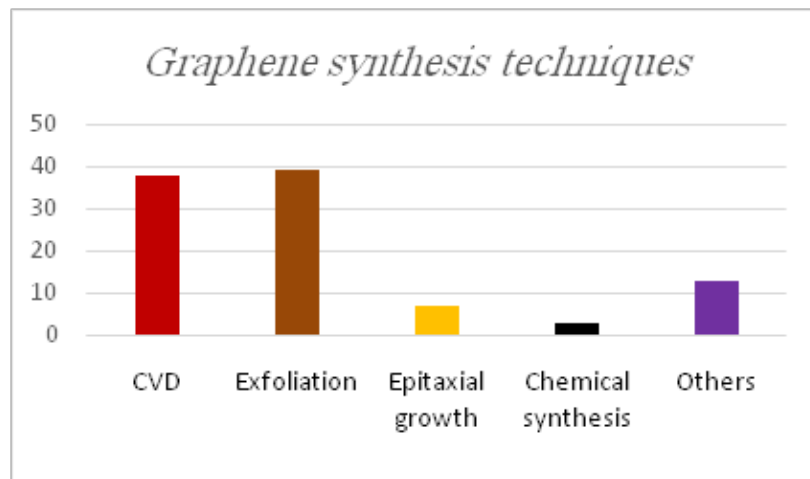

Fig. 2: Segmentation of graphene synthesis techniques

High-quality graphene (prepared by bottom-up methods) can be used in flexible photovoltaic devices as conductive electrodes due to its superior conductivity whereas RGOs (prepared by Top-down methods) which are relatively lower quality than graphene, are compatible with conducting polymers and metal oxides which enable themto be used as electrode interlayer material[7], as an active area for devices[8] or with nanocomposites for biomedical applications[9], electrochemical capacitors[10], supercapacitors[11] and sodium-ion batteries[12]. Recently, graphene nanocomposites have been used in many applications instead of using graphene only.

Graphene nanocomposites based on polymers[13-16], dopant atoms[17,18] or even metal oxides[10,11] show improved electrical and mechanical properties compared to individual graphene.Graphene-based materials canbe used as conductors due to their excellent conducting properties. Enoki *et al.*[6], showed the outstanding magnetic properties of graphene, such as magnetic switching and spin glass states for applications in electronic and magnetic devices[19]. Graphene is also a perfect conductorofheat and electricity. Compared to copper, its density is fourtimes lower than copper. In addition, its thermal conductivity is fivetimes that of copper. All these outstanding properties make graphene a famous material in nanotechnology researchanda possible substitution for silicon in electronic applications and many other advanced technologies.

This work describes the worldwide techniques used for graphene synthesis and the most usually utilized characterization techniques for characterizing the graphene produced. It was noticed that no common standard factor was used for qualifying the synthesized graphene. In accordance, a quality factor figure of merit is proposed based on characterization results that can be used for qualifying the synthesized graphene. This quality factor will be applied to literature published works for comparison of the different techniques of synthesis along with prepared graphene samples produced by chemical synthesis.

2. GRAPHENE SYNTHESIS METHODS

Pure graphene preparation is difficult and expensive so graphene nanocomposites, which contain inorganic elements or other organic elements (polymers) can be utilized to reduce the synthesis cost of pure graphene preparation.Graphene composites are made of graphene mixed withorganic/inorganic materials by melt blending method or mixing method that enhance the interaction between graphene and these inorganic/organic materials respectively[13,20]. They can be synthesized using either chemical reductionor deposition methods and sinter molding.

These organic/inorganic materials have many disadvantages as being bad thermal and electrical conductors, fragile materials, and showing low isolation behavior. However, with graphene addition to form graphene nanocomposites, the effect of these limitations can be reduced which makes it possible to be used in many electronic applications such as field effect transistors (FET)[21], capacitors[22,23], transparent electrodes[24,25], batteries[26-28] and sensors[15,20,29]. Graphene is generally synthesized by two common approaches, the top-down method and the bottom-up method as shown in Fig. 3.
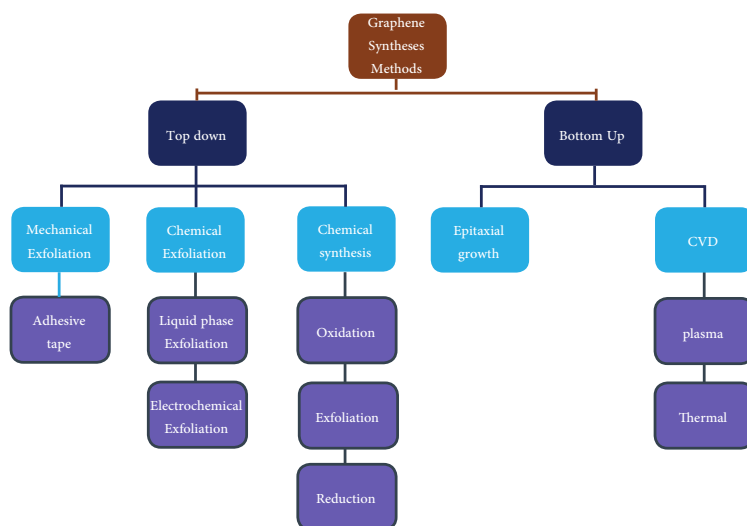
Fig. 3: Graphene synthesis approaches

2.1. Top-down synthesis

This synthesis method is based on reducing or breaking down larger-scale carbon material into nanoscale materials through various processes such as oxidation, exfoliation and reduction [30].It is preferred since it enables the mass production of graphene and its derivatives. This method has also many advantages such as low processing cost, suitable quality graphitic materials and high productivity.

2.1.1 Exfoliation

Exfoliation is considered to be one of the most important methods to produce a few layers of graphene or even mono-layer graphene. It mainly targets the separation of graphite layers into few/mono-layer graphene by exerting a force on the graphite to overcome Vander-Waals attraction forces between graphite layers.This force has two effects. The first is the exfoliation which is desirable to separate between graphite layers. The second one is the shattering effect in which large flakes of graphene are shattered /broken down into smaller flakes which are easier to exfoliate but not favorable as they limit the process of obtaining large graphene flakes which are needed in many electronic applications[31]. Generally, exfoliation can be divided into mechanical exfoliation and chemical exfoliation.

2.1.1.1. Mechanical exfoliation
2.1.1.1.1. Adhesive tape (mechanical cleavage)

It is one of the simplest methods to synthesize graphene from graphite. It's mainly dependent on longitudinal or transverse stress generated on the surface of the layered structure materials. The main challenge is to overcome the Vander Waal attraction forces between adjacent graphene layers. Therefore, the overall process of overcoming the attraction forces, peeling the layer, and obtaining the graphene is known as the mechanical exfoliation process. Andre Geim and Konstantin Novoselov, the winners of the Nobel Prize were the first to use this method in the exfoliation of graphite into micrometer-scale graphene sheets. They depend upon the normal tapping force to exfoliate graphite and obtain graphene sheets.

This tapping/peeling method involves the use of scotch tape to separate the graphene sheet from graphite flakes. It interferes with light showing different colors to indicate several layers of graphene[32]. This method is considered to be the cheapest method to produce high-quality graphene with almost no defects (used for FET applications). However, its main limitation is the difficulty of obtaining large amounts of graphene so it's not a mass production method.

2.1.1.2. Chemical Exfoliation
2.1.1.2.1. Liquid phase exfoliation (LPE)

LPE is an exfoliation method that can be accomplished in three main steps: dispersion, exfoliation and purification. Graphite is firstly dispersed in wet chemicals in the presence (assisted) or absence (non-assisted) of surfactants or chemicals. For the non-assisted LPE method, graphite flakes are dispersed in organic solvents. Then, ultrasonication is used to exfoliate graphite oxide flakes into graphene sheets by ultrasonic irradiation at a certain power, and frequency and for some time.

Sonication is a mechanical exfoliation method that is conducted after graphite powder is dispersed into organic solvents. The advantage of using this method is that it is a simple, mass-production, and low-cost method to obtain graphene. However, the graphene prepared by such a method has many defects in its structure in the form of oxygenated function groups such as ethers and carboxylic acids that can be limited by controlling the sonication time and/or power[33]. Bracamonte *et al.*[34] reported that the position of defects in graphene structure (basal plane/edges) mainly depends on the time of sonication and not its power. So, by controlling the sonication time, defects

can be reduced. Finally, the product is filtered and purified through a filter paper to give the final graphitic material. On the other hand, the assisted LPE method was developed to obtain graphene sheets with the aid of surfactants or chemicals.

Stirring in addition to the sonication process can be used together to enhance the exfoliation process. The advantages of the LPE method are being a time-saving method, less energy-consuming and a rapid processing method that can be used in graphene preparation to be used in many electronic applications. Recently green synthesis methods have been used for mass production of graphene with no need to use any chemicals.

The main concept of this method depends on the exfoliation of graphite flakes with the aid of vapor pretreatment to prepare edge hydroxylated graphene (Functionalized graphene). This paves the way towards high quality, less cost and more environmentally friendly methods for graphene production. Another method that depends on graphite dispersion was reported to produce defect-free mono/few layers of graphene with large producibility[35]. Graphite was dispersed with a water-soluble polymer followed by a sonication process to exfoliate graphite into graphene sheets directly. High-quality graphene sheets with a very small thickness were obtained. The enhancement of this method is considered to be a challenge that mainly depends on the enhancement of the sonication process parameters (time and/and power) to obtain graphene with minimum defects.

2.1.1.2.2. Electrochemical exfoliation

It's an exfoliation technique using graphite sources as electrodes in an aqueous or non-aqueous electrolyte solution and applying bias on them. The applied bias and electrolyte concentration control the graphene flakes' size and the level of exfoliation. Munuera *et al.*[36] reported a simple method for the synthesis of graphene with low oxygenated function groups material based on electrochemical exfoliation of graphite in aqueous solution using sodium halides as the electrolyte. The obtained graphene can be used as electrodes for supercapacitors or adsorbents for pollutants as a dye adsorbent with superior performance. Kumar *et al.*[37] reported the electrochemical exfoliation of graphite in the presence of sulphuric acid as an oxidizing agent to obtain GO and then obtain thermally reduced graphene oxide (TRGO).

From the two previous exfoliation methods (chemical and mechanical), we can conclude that the mechanical exfoliation method depends on applying a normal peeling force as a cheap method to produce high-quality graphene with almost no defects. The quality of the produced graphene can be enhanced by repeating the peeling process many times to obtain large-area graphene flakes. The disadvantage of this method is the difficulty of transferring graphene flakes on substrates which limits this method to being a mass production method. On the other hand, the chemical exfoliation method depends on the dispersion of graphite in organic/nonorganic solvents in the presence or absence of surfactants to assist the exfoliation process followed by sonication. Enhancement of the produced graphene can be obtained by controlling the sonication power and time to obtain the optimum quality graphene. The main disadvantage of this method is producing small-area graphene flakes with structural defects. However, transferring the process of graphene to many substrates is relatively easier which makes it a mass-production method.

2.1.2. Chemical Synthesis

Researchers were enabled to synthesize graphene/(RGO) from graphite precursor through chemical synthesis methods. Graphite or any other form of carbon materials is converted to graphene sheets using particular chemicals (Oxidizing/Reducing agents). The synthesis of the graphene/reduced graphene oxide (RGO) can be achieved in three main steps: oxidation, exfoliation and reduction.

2.1.2.1. Oxidation

Early in 1859, Brodie managed to prepare graphite oxide[38]. Graphite was added to a mixture of potassium chloride and nitric acid at 65°C for three days at 60C. The product was formed of carbon, hydrogen, and oxygen, with an increment to the overall mass. The heating effect was clear after heating that chemical structure to a temperature of 220°C to obtain an increase in the C:O ratio. The drawback of this mixture is that it wasn't dispersible in any acidic media (Graphitic acid) so it can't be exfoliated into mono/few layers to form the required graphene oxide (GO) mixture. In 1898, Staudenmaier[39] improved Brodie's method by adding chlorate (such as potassium or sodium chlorates) besides adding concentrated sulfuric acid to increase the acidity of the mixture. The oxidation result was nearly the same. However, Staudenmaier synthesis methods generate chlorine toxic gas that decomposes in the air and may produce explosions. In 1958, Hummers and Offeman[40] reported another oxidation method. Firstly, ultrapure graphite powder and sodium nitrates were mixed in concentrated sulfuric acid. Then potassium permanganate was used as a catalyst for the chemical reaction permanganate was used as a catalyst for the chemical reaction instead of potassium chlorate to avoid explosions during the oxidation process. Finally, the graphite was oxidized to give graphite oxide with the same oxidation level as the preceding two methods. Graphite oxide was diluted in water and hydrogen peroxide was added to minimize the effect of manganese dioxide and permanganate residuals in the mixture that acts as contaminations in the mixture. This method was assigned worldwide as "Hummer's method".

A yellow-brown graphite oxide residue was obtained indicating the formation of graphene oxide (GO). All of the above three methods are used to prepare graphite oxide from graphite in which graphite is oxidized. Fortunately, Hazardous chlorine gas produced in the Staudenmaier method can be eliminated by using Hummer's method,

which has a relatively shorter reaction time and no hazardous chlorine gas. Hummer's method has been widely used but still has drawbacks in which the graphite mixture is contaminated by surplus permanganate ions in addition to toxic gas production[41]. This drawback was solved by adding hydrogen peroxide to the mixture followed by washing to give graphene oxide[42].

Marcano *et al.*[43] investigated the improved and modified Hummers method. In the improved Hummer's method, potassium permanganate is mixed with sulphuric acid and orthophosphoric acid in which orthophosphoric acid is added as an oxidizing agent instead of sodium chlorates to avoid toxic ClO2 gas that may decompose in air and result in explosions[41]. In the modified Hummer's method compared to Hummer's method, the potassium permanganate ratio was doubled with the same ratio of sulphuric acid and sodium nitrate. It was noticed from Raman spectroscopy measurements that GO produced by improved Hummer's method has the least defects in its structure compared to the GO prepared by the other two methods. In addition, there are no toxic gases produced during GO synthesis prepared by the improved Hummers method.

2.1.2.2. Exfoliation:

Exfoliating graphite into graphene oxide GO can be done mechanically through sonication of graphite oxide in water or any polar organic media or chemically through the addition of oxidizing agents. This method can exfoliate the graphite oxide totally into graphene oxide GO[44]. Mechanical stirring of graphite in water is another applicable method that can be also used as an exfoliation method for graphite[45]. The two mechanical methods (sonication /stirring) can be merged instead of using one method to exfoliate graphite with a better quality than using each one individually. Sonication in water or polar organic media is more rapid than the stirring method, However, it causes great damage to the GO flakes formed during this process[44]. Thermal, chemical and mechanical exfoliation methods are also used to exfoliate graphite oxide into mono/few layers sheets. In 1962, Boehm *et al.* were the first to reveal graphite oxide thermal exfoliation, in which carbon thin films were synthesized by graphite oxide burning[46]. Later, the thermal exfoliation process progressively becomes a common method to obtain graphene from graphite[47].

2.1.2.3. Reduction:

The reduction process can be defined as the partial elimination of oxygen function groups from GO structures to obtain reduced graphene oxide (RGO). The reduction process can be established through various methods which will be discussed below. These different methods result in variations in the quality of the obtained (RGO). Although the reduction process is expensive and time-consuming, however, it is needed to reduce the structural defects in GO to be used in different applications knowing that few

of these reduction methods are capable of producing high-quality RGO.

2.1.2.3.1. Chemical Reduction:

The chemical reduction process is done by using chemical-reducing agents. Its main target is to remove the oxygen-containing groups increasing the C: O ratio. The existence of some function groups especially hydroxyl and epoxy groups can affect the electrical and thermal conductivity. So, the removal of these oxygenated function groups is a necessity. Graphene can be obtained through the reduction of GO. The reduction process of GO is very important as the product RGO has higher electrical/thermal conductivity and higher specific surface area than GO. Also, by controlling the reduction process parameters, the solubility of graphene in water can be controlled.

Dan Li *et al.*[48] prepared graphene sheets after sonication and reduction of graphite oxide using hydrazine as a reducing agent. The advantage of this method is being a simple low-cost method for graphene synthesis. However, hydrazine is a highly toxic reducing agent and the graphene sheets obtained tend to agglomerate again after being exfoliated which is undesirable. In addition, it can't be used for mass production processing methods. To overcome this problem, other green "non-toxic" reducing agents are used instead of hydrazine) which can be used in large-scale production. Ascorbic acid(AA)[49], sodium borohydride[50], hydroiodic acid with acetic acid[51]and sulphonic acid[52] were used as reducing agents to reduce (GO) into (RGO).

Gijare *et al.*[53] showed that GO can be reduced using Vitamin C (VC) as a green reductant of GO into RGO to be used in Glucose sensor applications. Joshi *et al.*[54] used also Vitamin C from lemon juice as a green reducing agent to reduce GO into RGO to be used for supercapacitor applications. Compared to hydrazine, VC is a nontoxic reducing agent and graphene sheets show no tendency to agglomerate after reduction. Xiaobin Fan et al. managed to reduce the GO into RGO using sodium borohydride as a green reducing agent[50]. Graphene prepared by this reductant showed a stable suspension in NaBH4 solution that can be easily separated from the suspension and a monolayer sheet of graphene was obtained with a thickness of 0.8 nm. Dongfeng Pei *et al.*[51] reported that GO was successfully reduced into RGO using hydroiodic acid as a reducing agent. Hydroiodic acid showed astonishing reduction properties. RGO obtained has a C/O ratio much higher than that obtained by the previous reducing agents.

Highly conductive and transparent films were also obtained which makes it one of the best reducing agents. However, the suspension stability of RGO in water obtained by NaBH4 is less than that of RGO obtained by AA which makes it difficult to collect it from the suspension.

The reduction process can be also progressed through an electrochemical reduction in which the reduction process can be executed in the electrochemical cell using an aqueous buffer solution at room temperature[55]. The

main advantage of this method is that it doesn't need any special chemical reducing agent and the reduction process is accomplished due to electron exchange between GO and electrodes. In addition, it's an inexpensive, time-saving method for mass production of RGO. Chemically synthesized RGO samples were produced at our labs using a modified Hummer's method. Process details will be published elsewhere. Fig. 4 shows reduced RGO powder by ascorbic acid.
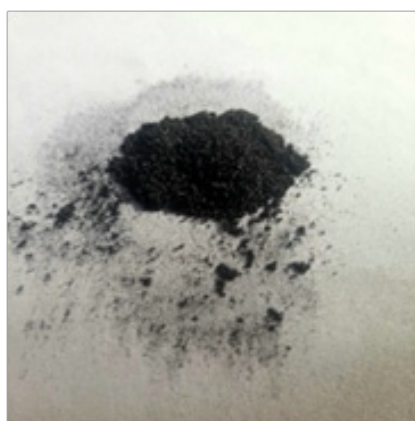

Fig. 4: RGO powder prepared using ascorbic acid as a reducing agent

2.1.3.3.2. Thermal reduction

Thermal reduction is a reduction method that uses heat treatment to heat GO in different atmospheric, and ambient conditions[56] or through using different heating sources such as laser[57], flashlight[58], microwave[59]. Due to heat treatment, the volume of heated GO is expanded. It was reported that with increasing the time of annealing, the C/O ratio is improved[60]. However, this creates defects in the carbon lattice plane which is undesirable matter. Wufeng Chen et al[56]managed to reduce GO into RGO at low temperatures at atmosphere pressure with the aid of nitrogen gas. GO was suspended in a mixture of N, N-dimethylacetamide and water. The stability of graphene suspension in the mixture (which is required) shows high dependence on the time of heating and the heating temperature.

Laura J. Cote *et al*[58] reported another thermal reduction method for GO into RGO using the flashlight. The advantage of this method is being a rapid, room temperature and clean method (no chemicals used) that may be also used in patterning and reduction of GO films into RGO at the same time. Denis *et al.*[57] reported that GO also was successfully reduced into multilayer graphene by using laser reduction. Laser reduction is a flexible green reduction method that can be used with solid substrates on the scale of micrometers to reduce GO into RGO. The laser was used as a patterning tool and a reducing agent at the same time with high patterning accuracy. Yanwu Zhu *et al.*[59] used microwave treatment as an exfoliation method of GO to obtain microwave-exfoliated GO

(MEGO). MEGO was then dispersed into a KOH aqueous solution to give activated MEGO and a chemical exfoliation method using KOH to activate microwaved exfoliated GO. Papari Das *et al.*[61] managed to prepare RGO from graphite powder by improving Hummer's method.

The reduction of GO into RGO was completed at a low temperature (50C). The activated graphene obtained by this method can be used in energy storage devices as supercapacitors. Currently, there is a great interest in determining the onset temperature for volume expansion during thermal reduction of GO and studying the effect of temperature for optimization of carbon content in weight. The advantage of this method is that it is a simple, safe and inexpensive method. The C/O ratio can indicate the quality of the reduced GO obtained. A better reduction process gives a higher C/O ratio.

2.1.2.3.3. Ultraviolet (UV) light reduction

GO can be reduced by the dispersion of GO powder in a suitable solvent. By exposing this GO solvent to UV light, UV light is absorbed by the bonds of GO which are followed by a chemical reaction associated with reactive oxygen species (ROS) production, and the reduction process is confirmed. Yudi Tu[62] managed to convert GO into RGO by UV irradiation. RGO lines with high resolution appeared on the GO micro sheet upon applying a photolithography process on the GO sheet using UV irradiation. This method is not a green method for reduction as UV rays can cause skin cancer risk. In addition, it is considered to be expensive and not a mass-production method. However, it seems to be a promising method for graphene-based micro-electronic devices.

From the above reduction results, we can conclude that chemical, thermal and light reduction methods have been used for GO reduction. The efficiency of these reducing agents can be generally determined according to some parameters such as a) toxicity level, b) efficiency of removing the oxygenated function groups from graphene structure and its capability of preventing restacking of graphene sheets again after reduction, c) C:O ratio in graphene after reduction, d) reduction method simplicity, e) productivity, and f) cost. All these parameters must be optimized upon selecting the reducing agent according to the needed final product quality and its application. In our point of view, thermal reduction methods are considered to be the best reduction methods being simple, inexpensive and nontoxic methods for graphene reduction. The chemical reduction method is relatively better than the UV reduction method being a mass production method, inexpensive and relatively simpler than the UV method. However, they share the same toxicity disadvantage in the case of using hydrazine for chemical reduction so, Ascorbic acid (AA) is used instead and green reduction methods can be further used to avoid using any chemical agent.

2.2. Bottom-up synthesis

In this method, graphene and its derivatives are

built from smaller carbon precursors such as carbon hydrocarbons through processes including epitaxial growth of graphene[63,64], sputtering methods[65], chemical vapor deposition (CVD) of hydrocarbons on Ni/Cu films forming graphene[66,67]. One of the main challenges in graphene synthesis is increasing reproducibility on a large scale with high-quality material and at low cost. Every synthesis method is chosen depending on the use and the required application.

2.2.1. Epitaxial growth:

Epitaxial growth of graphene on silicon carbide (SiC)/ nickel (Ni) layer structure using the thermal decomposition method is used to produce large-scale few-layer graphene (FLG) with high quality at low temperatures. When SiC/ Ni is heated at high temperatures, Si atoms are desorbed from the surface and leave C atoms behind as carbon has low solubility in Ni. Carbon atoms agglomerate on the Ni surface upon cooling forming a few layers of graphene. This method manages to produce a continuous graphene film in mm scale. This method was used to produce a continuous graphene film in mm scale thickness on a SiC substrate coated with Ni layer at a relatively low temperature (750 °C) with no need for graphene transferring[68]. Heating and cooling rates can control the thickness of the formed graphene layer. Jeonghyun Hwang et al.[69] managed to grow epitaxial graphene film by thermal decomposition of epitaxial SiC layer on sapphire substrate in the presence of a polymer thin layer as a buffer layer. The advantage of this method is that high-quality, large-area graphene can be produced to be used in many electronic applications. It can be considered as a graphene growth method with no need for metal growth or deposition before thermal decomposition. This method also introduces a continuous epitaxial graphene film over a complete SiC surface at lower temperatures compared to the normal CVD method. However, this method is not a mass production method for graphene as it is an expensive method for graphene production.

2.2.2. ThermalChemical Vapor Deposition Technique (TCVD)

The chemical vapor deposition (CVD) method is a suitable method to prepare high-quality graphene. Hydrocarbon vapor (CH4 for example) is distributed over transition metals such as Ni or copper (Cu) substrates or foils at high temperatures. It's called a thermal process due to its need for high temperatures to confirm the deposition process. During the cooling process, carbon atoms diffuse on the surface of the substrate and a few layers of graphene sheets are formed. The quality of the graphene formed using Cu as a transition metal gives the best quality graphene than using other transition metals such as nickel (Ni) or Platinum (pt)[70]. Copper is one of the most promising transition metals for graphene growth.

It is a simple, low-cost, easily etched transition metal in which carbon has low solubility in it. In addition, Cu has a weak catalytic activity upon methane gas exposure which helps in the formation of graphene directly on the copper surface with no chemical reaction interference at high temperatures in the presence of inert gases as argon and hydrogen gases at certain flow rates[71]. All these promising features of copper make it one of the most important transition metal candidates in the graphene growth process. Jincheng Fan et al.[67] studied the growth of graphene on Cu foil. At the end of the CVD process after graphene growth on Cu foil, a PMMA layer was spin-coated on the Copper/graphene structure. Etching to the Cu foil was performed in an aqueous solution leaving behind a graphene/PMMA structure. Finally, removal of the PMMA layer was done after transferring PMMA/graphene on target substrates such as Si/SiO2 and glass.Changsheng Shan et al.[72] investigated a simple mass production method for graphene synthesis by CVD method. Ni powder and PMMA as a carbon source were mixed and introduced to the CVD chamber at high temperatures in the presence of hydrogen/argon gas flow. Upon fast cooling, graphene precipitated on the Ni surface which was later removed by HCL etchant.

Na Liu et al.[73] investigated a direct graphene growth method on Si/SiO2 substrate to avoid graphene transferring problems that may affect its quality and performance. Ethanol gas was used instead of methane gas and Si/SiO2 substrate covered with Cu foil was inserted in the CVD chamber for 20 min annealing in the presence of Ar /H2 gas flow. A continuous high-quality graphene film was formed on Si/SiO2 substrate which was confirmed by Raman and TEM characterization. Jungtae Nam et al.[74] reported that graphene was successfully grown on sputtered platinum films at high temperatures and low-pressure systems to give multilayer high-quality graphene films that can be easily transferred onto Si/SiO2 substrates. Graphene formation was detected using Raman spectroscopy.

Wang et al.[67] managed to prepare graphene on Cu foil when methane gas (CH4) was introduced into the CVD chamber to give monolayer high-quality graphene with a smooth surface having almost no wrinkles. The prepared graphene was transferred to a glass sheet. Raman analysis and SEM imaging of the transferred graphene confirmed the formation of high-quality graphene film with almost no wrinkles compared to the multilayer graphene film prepared using platinum films as a transition metal. The main advantage of the TCVD method is the ability to produce high-quality graphene sheets with minimum structural defects which can be helpful in electronic applications. However, its disadvantage is the difficulty of controlling the graphene film thickness in addition to the high cost of materials including gases.

The need for very high degrees of temperature is another drawback that affects later on the thermal stability of the oxide layer on the silicon wafer during the deposition process. The transfer of the graphene layer on the required substrate is another drawback that may cause damage to the transferred graphene layer. All these disadvantages make this method limited to mass production. Finally, it can be concluded that (TCVD) technique is a high-quality

graphene synthesis method that requires high temperatures to achieve the deposition process. Pt, Cu, Ni, Co, and Fe are all transition metals that can be used as a catalyst for graphene growth in the CVD method. This catalytic activity has a great effect on reducing the operation temperatures during the deposition process. However, it makes it difficult to control the growing graphene film thickness.

By studying the above metals as foils and substrates in the CVD process, it was found that Cu (foil/substrate) is the most promising metal for graphene growth but not a mass production method. In case of mass production needs, Ni can be used with PMMA instead of Cu and methane gas. By controlling the Ar/H2 gas flow in addition to the hydrocarbon gas flow in each deposition process, high-quality graphene films can be obtained that may be used in many electronic applications.

2.2.3 Plasma-enhanced chemical vapor deposition technique (PECVD)

In this deposition method, plasma is used to provide the energy needed for the chemical reactions to take place and "enhance" the deposition of thin films on the surface of the substrates at low operating temperatures. Plasma and gas flow(H2/ methane/...etc.) can control the graphene film properties (e.g. Thickness, composition, density, etc.). This method also gives the advantage of using a variety of substrates such as (Zr, Si, and W) with no need for a surface catalyst and generating high-quality graphene films at low temperatures with excellent sensing properties. Its main disadvantage is being an expensive method with the high cost of the produced graphene sheets.

Munoz *et al.*[75] managed to grow monolayer and few-layer graphene directly on Si/SiO2 substrate at lower temperatures than that used in the TCVD method. Direct growth of the graphene layer was achieved with no need for graphene transferring at very low temperatures compared to the need for graphene transfer in the thermal CVD method and without affecting the thermal stability of the oxide layers upon which graphene is deposited. A defect-free bi/monolayer of graphene was directly grown on the required substrate. Vishwakarma *et al.*[76] managed to grow transfer-free graphene directly on insulating substrates such as quartz and glass with high transmittance(80%)at low temperatures (300C). The graphene grown directly on the insulating substrates had a large area, high specific capacitance and high conductivity that can be used in many electronic applications.

Based on our study and by comparing PECVD to TCVD, the PECVD method has many advantages. Firstly, plasma is used to provide the energy needed for the chemical reactions to take place and enhance the deposition rate at low operating temperatures. In addition, controlling the film thickness is a hard goal in TCVD. However, for PECVD, plasma energy can also control the synthesized film properties including its thickness, composition and density. Its main disadvantage is the higher cost of graphene deposition. In addition, graphene grown has a relatively smaller grain size compared to TCVD. On the other hand, high nucleation graphene densities appear on graphene prepared by PECVD. This nucleation may affect the electric properties of the prepared graphene which may lead to the undesirable performance of graphene-based applications[77].

3. CHARACTERIZATION METHODS

The structure of RGO and graphene is mysterious as the oxygen-containing groups and their arrangements in the carbon network vary according to the synthesis methods. Some data must be known about the functional groups that are present in the prepared sample, the relative portion of the functional groups, the distribution of these groups during reduction phases and the types of oxygenated functional groups. This can be determined through Spectroscopic and Microscopic characterization techniques. Spectroscopic techniques are used to evaluate specific chemical information about the composition and structure of various materials. It includes Raman spectroscopy, X-ray diffraction XRD and Fourier transform infrared spectroscopy (FTIR). Microscopic characterization methods depend on probing and mapping the surface. These techniques can use photons, electrons, ions or physical probes to collect data about a sample's structure and its morphology. Scanning electron microscope (SEM), Transmission electron microscope (TEM) and atomic force microscopy (AFM) are examples of microscopic characterization techniques.

3.1. Spectroscopic characterization techniques
3.1.1. X-Ray Diffraction (XRD)

XRD is an analytical spectroscopic characterization method for intercalated and exfoliated nanomaterials. It's used in the characterization of sp2 carbon nanomaterials structures. XRD is applied for phase determination and confirming the process of reduction of GO to RGO/graphene. The wavelength of the peaks characteristic of the target material. As the value of the interlayer spacing increases (d spacing), a decrease in 2θ occurred according to Bragg's law as in (1):

$$n\lambda = 2d\sin\Theta \qquad (1)$$

Where n is the refractive index, λ is the X-ray wavelength and d is the interlayer spacing between graphene sheets. Distinct peaks of graphite, graphite oxide and graphene can be used to differentiate between their structures. Fig. 5 illustrates XRD measurements of graphite, graphene oxide and reduced graphene oxide samples. Graphite appears to have a sharp and intense peak at a 2θ value of 26.9° indicating the crystal structure of pure graphite. For graphene oxide after graphite oxidation and exfoliation, the graphitic XRD peak shifts towards smaller angles and a wide range to give a peak at 2θ=10.1° as shown in fig 6. From Bragg's Law, a decrease in 2θ indicates an increase in the interlayer spacing between graphene layers. This is due to the insertion of oxygenated function groups after oxidation and exfoliation of graphite so, the interlayer

spacing increased. After the chemical

reduction of GO using ascorbic acid, the XRD peak appeared at a 2θ value of 26.1º with low intensity and a broad shape. This is due to the removal of oxygen function groups from the GO structure resulting in a remarkable decrease in the interlayer spacing between graphene sheets so, an increase in the XRD peak shifting occurs indicating restacking of RGO sheets and restoring the graphitic properties. This confirms the reduction of graphene oxide (GO) into RGO and the removal of most of the oxidizing functional groups.
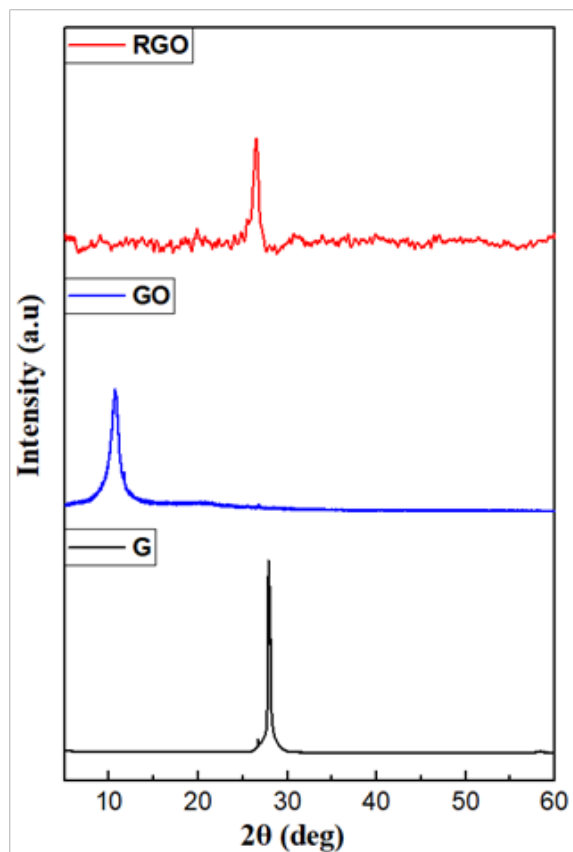

Fig. 5: XRD analysis for Graphite (G), graphene oxide (GO) and reduced graphene oxide (RGO)

3.1.2 Raman Spectroscopy

Raman spectroscopy is used to give information about the stacking order, the structural defects and phonon dispersion of graphene. Raman spectra give a molecular fingerprint as different molecules have different Raman spectra. Raman spectra are used for Qualitative and Quantitative analysis. In graphene, laser excitation creates three main peaks in the Raman spectrum: D peak at wavenumber range (1300 -1360 cm-1) referring to sp3 disorder and defects in the sp2 graphene lattice. G peak at the wavenumber range (1560-1620 cm-1) to refer the in-plane vibration due to sp2 hybridization of carbon atoms, which is responsible for the compression of graphene sheets. The 2D peak at the wavenumber range (2690 -2750

cm-1) indicates a second-order overtone of a different in-plane vibration[78]. 2D peak representing the second order of D peak that is due to the two-phonon lattice vibration process to detect the number of graphene layers[79, 80].

It's found that as the intensity ratio of D and G peaks (ID/IG) gets smaller, this indicates lower defects in the graphene structure and higher carbon content. In addition, the increase in the intensity ratio (I2D/IG indicates a decreased number of graphene layers. Fig (7) indicates the Raman spectroscopy results for our RGO samples prepared by improved Hummer's method from graphite precursor and reduced using ascorbic acid compared to graphite. Three main peaks were found at (1352 cm-1), (1620 cm-1) and (2720 cm-1), which correspond to D, G and 2D peaks respectively. It's observed that graphite G-peak has a sharp and high intensity compared to relatively broad G-peak for RGO indicating asymmetry of carbon honeycomb lattice for RGO. This asymmetry is attributed due the presence of residual oxygen functional groups even after the reduction processes are confirmed. D-peak was observed at high intensity for RGO due to defects during the chemical reaction of graphite with oxidizing agents as sulphuric and orthophosphoric acids which resulted in a change of hybridization of carbon from Sp2 to Sp3. However, the D-peak of graphite is observed with a very small intensity value indicating low defects and crystal symmetries in the graphite structure as it undergoes no chemical or physical treatment.
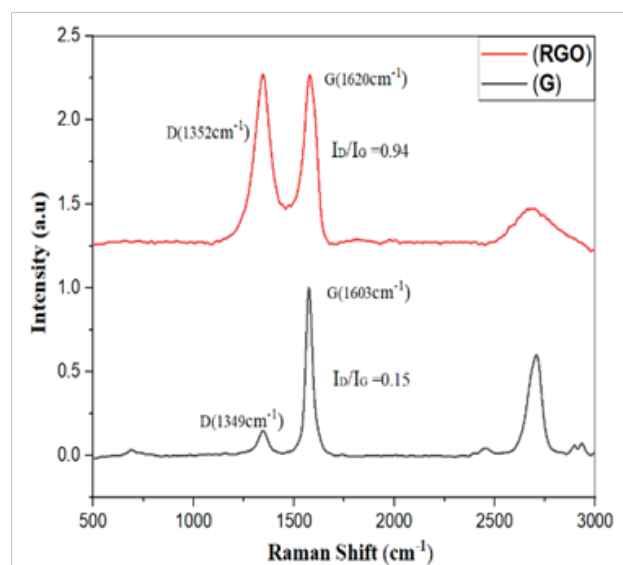

Fig.7: Raman spectra for G and prepared RGO powder.

3.1.3 FourierTransform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is considered to be an important characterization method to study different types of functional groups in graphite/GO/graphene and RGO at certain wavenumbers. The presence or absence of these functional groups can determine the type of graphitic material. Lee *et al.*[81] reported the presence of four main

peaks in the spectra of GO in FTIR. The first peak at (1,050 cm−1) arises from epoxide groups (C–O–C). Thesecond one centered at (1,680 cm−1) indicates the vibrational modeof the ketone groups (–C=O). The third peak at (1,380 cm−1)which is assigned to a (C–O)vibrational mode. Finally, the fourth peak at (3,470 cm−1) denotes(C-OH) stretching.So, by revealing the types of the functional groups and their position, material type can be determined and the reduction process can be verified. Generally, FTIR measurements for graphene/RGO can be divided into two regions. The region with wavenumber <1500 is called the fingerprint region while that of wavenumber >1500 is called the function groups region. O-H group (very broad) peak (acids group) and C=O peak appear at 3420 cm-1 and 1685 cm-1 respectively in the function group region. In the fingerprint region, two FTIR peaks appear around 1100 cm-1 and 1400 cm-1 referring to the C-O epoxide group and the C-OH group respectively. FTIR measurement of our RGO samples is shown in Figure (8). All previously mentioned peaks at the two regions appear in the measurement which confirms the presence of oxygen function groups.
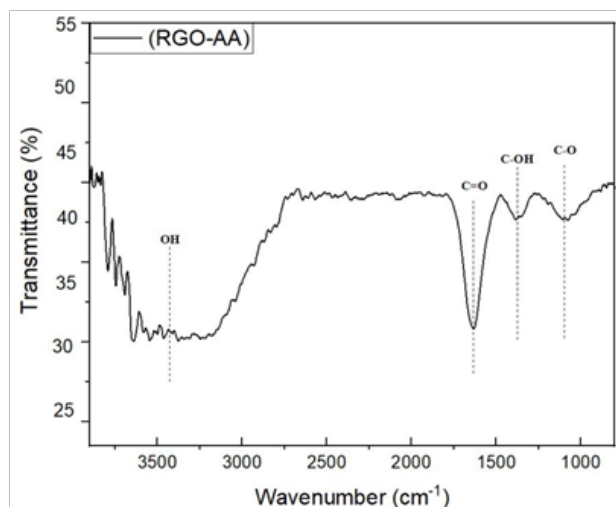

**Fig. 8:** FTIR for RGO reduced by AA

3.2 Microscopic characterization
3.2.1 Scanning Electron Microscopy (SEM)

SEM is a microscopic characterization technique for micro and nanostructured materials. It gives information about surface roughness, morphology, grain size, shape and chemical structure of materials, grain shapes and folding lines. SEM was used to characterize single-layer graphene and multi-layer regions[52,82]. Figure 9 illustrates an SEM image of our RGO samples which appears as a wrinkled paper sheet indicating that exfoliation and reduction of graphite oxide were successfully transferred into a few layers of RGO.
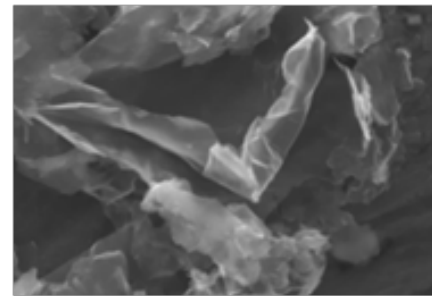
(a)
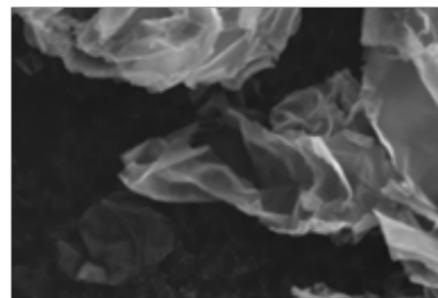
(b)

Fig. 9 (a, b): SEM images of reduced graphene oxide (RGO)

3.2.2 Transmission Electron Microscopy (TEM)

TEM is a microscopic characterization technique to analyze the atomic structure of nanomaterials. It was used to image the lattice structure, and morphological and topological defects in GO[83]. It depends on the transmission of electrons through an ultra-thin (<100 nm thick) specimen. In addition, TEM can reach a very high-resolution image up to the atomic level, so it indicates the number of graphene layers per flake. Increasing the oxidation level, GO samples become more transparent as the samples have high amounts of oxygenated functional groups that can be easily exfoliated into monolayers or a few layers of GO after ultrasonic treatment. Nakamura *et al.* used TEM for the analysis of graphite-like thin sheetsThey were synthesized by ablation of graphite using a laser with the aid of argon gas[84]. The produced Graphene-like thin sheets (GLSs) were freestanding high-quality sheets. Navik *et al.*[85] analyzed the exfoliation of graphite through the ultrasonic exfoliation method into graphene via TEM. Transparent graphene sheets with large surface area and a stack of 1–5 graphene layers thick were characterized. Al-Hagri[86] managed to synthesize a monolayer graphene nanosheet using the CVD deposition technique, which was then studied using TEM.

3.2.3. Atomic Force microscopy (AFM)

Atomic force microscopy (AFM) is a microscopic technique for studying samples with a very high resolution that can reach down to the atomic level. It is a scanning probe microscopy that is used to produce 3D topological

images of the surface and analyze the thickness histograms of specimens. Lu et al.[52] synthesized RGO through the reduction of graphene oxide with sulfonic acid in addition to adding platinum nanoparticles as an effective catalyst to prepare Pt/S-RGO electrocatalyst via a self-assembly route. Both GO and S-RGO were examined morphologically in detail by AFM. The AFM images assert that both GO and S-RGO have fully exfoliated dispersed GO sheets with nm thickness and mm lateral dimensions.

4. QUALIFICATION

To our knowledge, no general quality factor was universally considered to qualify the produced graphene/RGO/GO samples. In the following, we propose a graphene quality factor (GQF) to be considered for this purpose. This proposed factor can be extracted basically from both Raman spectroscopy and XRD measurements. The proposed quality factor (Q) is given by equation (2) as:

$$Q = \frac{I_{2D} \times d}{I_D} \qquad (2)$$

Where I2D/ID is the Raman spectrum intensity for the 2D and the D peaks respectively. Layer spacing (d) is the spacing between graphene/RGO/GO sheets obtained from XRD analysis calculations. From the previous discussion, it can be concluded that high-quality graphene requires the lowest layer stack and defects with the highest possible carbon content. This can be translated to achieving the highest possible (I2D/IG) ratio and lowest possible (ID/IG) ratio. In other words, achieving the highest possible ratio division which is (I2D/ID). As the intensity of the 2D peak increases and that of the D peak decreases with the increment of d spacing, the value of the quality factor increases indicating a better-quality product.

This factor was extrapolated from several published works in a comparison form along with that of our prepared samples as shown in table (1).

By comparing the extracted quality factor for the reported works in Table (1), we can conclude that the quality of the graphene produced by bottom-up techniques is relatively higher than that of RGO obtained by the top-down techniques. This is attributed to the presence of the oxygenated function group's residuals in the RGO structure after the oxidation process whatever the reduction method. In addition, the probability of obtaining a mono or few-layer graphene (less than 10 layers) by CVD techniques is higher than using chemical methods. This fact was confirmed by calculating the value of the I2D/ID ratio obtained from Raman analysis by extrapolation shown in table (1). From the table, the I2D/ID value is higher than 2 for CVD-prepared graphene while it is less than 2 for chemically prepared graphene. Accordingly, the quality factor for CVD-prepared graphene is almost higher by an order of magnitude than chemically prepared counterparts

Table 1: Calculated quality factor of prepared graphene/RGO published works including our prepared samples

Synthesis Technique	IG/ID	I2D/IG	I2D/ID	d	Q	Notes	Ref
	1.782	0.521	0.909	0.38	0.34542		[87]
	0.909	0.44	0.4167	0.36	0.15001		[9]
	0.909	0.3	0.2842	0.36	0.08935		[88]
	0.65	0.096	0.0625	0.36	0.0225		[89]
	0.847	0.23	0.195	0.384	0.0748		[90]
	0.829	0.0769	0.0638	0.384	0.0244		
	1.594	0.494	0.787	0.3459	0.272	Treated at 8500C	
Top- Down	2.136	0.436	0.9316	0.3375	0.31441	Treated at 9000C	
	2.33	0.4	0.932	0.3327	0.31	Treated at 9500C	[91]
	4.255	0.409	1.74	0.36118	0.6284	Treated at 10000C	
	1.095	0.09	0.099	0.339	0.0335	This work	
	0.8	0.44	0.352	0.34	0.1196		
	1.5	0.495	0.7425	0.34	0.2524		[92]
	1	0.1667	0.1667	0.35	0.0583		
	2.4	0.322	0.7728	0.34	0.262		
Bottom- UP	1.174	2.407	2.82	0.33	0.9306		[93]
	1.1	2.393	2.633	0.353	0.92944		

By comparing Q values, Graphene prepared by CVD methods has the highest Q values (<0.9) compared to chemically prepared graphene. For some chemically synthesized graphene, Q appears to have a relatively high Q value that can be compared to Q values of CVD-prepared graphene [95]. This is due to using the electrochemical method for graphite exfoliation instead of improved/modified Hummer's method in addition to using thermal reduction instead of chemical reduction. So, fewer defects appeared in the prepared RGO (highest IG/ID ratio) and consequently, high Q values are obtained. The reason behind this is that the electrochemical exfoliation method is relatively clean compared to improved Hummer's method in which chemical oxidizing agents are used to exfoliate graphite sheets resulting in structural defects in graphite so, D-peak increases in this case. Also, thermal reduction of GO was used at different temperatures instead of using ascorbic acid as a reducing agent that causes defects to the graphite structure of RGO. So, a total increase in I2D/ID in the case of electrochemical exfoliation compared to other samples prepared by improved Hummer's and reduced by (AA) leading to a higher quality factor.

5. CONCLUSION

Graphene is one of the most important carbon allotropes. It shows a unique hexagonal chemical structure and outstanding electronic, optical, thermal, and mechanical properties. Different synthesis methods have been recently used. Top-down methods include mechanical exfoliation, chemical exfoliation and chemical synthesis methods. The bottom-up method includes the epitaxial growth of graphene, thermal Chemical vapor deposition technique (CVD) and plasma-enhanced chemical vapor deposition technique (PECVD). The method to be chosen is determined according to the desired graphene size, cost, volume, and quality. Produced G/RGO is usually characterized by spectroscopic and microscopic characterization methods such as Raman, XRD, FTIR, and SEM to evaluate specific information about composition structure, and morphology. A new qualification factor was proposed based on Raman and XRD characterization to generally qualify produced G/RGO. RGO samples were prepared by improved Hummer's method and characterized by Raman, XRD, FTIR, and SEM techniques. Their quality factor was calculated and compared to reported works. The prepared samples showed comparable results to their chemically prepared counterparts. Generally, chemical methods for preparation show lower quality factor G/RGO which can be enhanced through processing steps compared to the higher quality CVD-based G/RGO products.

6. ACKNOWLEDGEMENTS

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