



Graphene's Structure, Synthesis and Characterization; A brief review



Samir Kamel¹, Mohamed El-Sakhawy^{1*}, Badawi Anis² and Hebat-Allah S. Tohamy¹

¹Cellulose and Paper Department, National Research Centre, 33, El-Bohouth Str., P.O. 12622, Dokki, Giza, Egypt

²Spectroscopy Department, Physics Division, National Research Centre, 33 El Bohouth Str., P.O. 12622, Dokki Giza, Egypt

IN 2004, Andrei Geim and Kostya Novoselov used a simple technique to separate graphene layer from graphite. They were awarded the Nobel Prize in Physics in 2010. After this, the publications of graphene have been increasing year after year and have emerged as the most popular topic in the research field which indicates the importance of graphene research. Due to unique properties of graphene, it can be considered as promising material for various applications in the fields of physics, chemistry, material science and engineering, and biology. Consequently, this review will focus on using of biomass and other wastes as precursor material for graphene preparation. We hope it could be of helpful to people who are interested in this field. The future outlook of graphene is also considered.

Keywords: Graphene, Graphite, Carbon allotropes.

Introduction

With an increasing global usage and a growing demand for agriculture products, agriculture wastes are considered as the most important resources urgent for humans. As agriculture is essential for the survival of the increasing population on earth, the effective management and recycling of agriculture wastes become critical to ensure the sustainable use of this resource into the future. These wastes attained due to crop production or from plant growth. For a long time, these wastes were either burnt or naturally converted into organic fertilizer. Recently, agricultural wastes are converted into wealth products. One of these materials is carbon which is categorized into non-graphitic (*i.e.* defects) and graphitic carbons. Graphitizable carbon is soft, non-porous, has high density, and carbons are arranged in preferential direction. So, it can be converted into graphitic carbon by the process of heat treatment. Meanwhile, non-

graphitizable carbon is hard, porous, has low density, and has very disordered microstructures. So, it cannot be transformed into graphitic carbon. Since activated carbon has a low density due to its porous structure so, it is categorized under non-graphitizable carbons [1, 2].

Graphene is a sheet of a single layer (two-dimensional (2D)) of carbon atoms, tightly bound in a hexagonal honeycomb lattice. In more complex terms, it is an allotrope of carbon in the form of a plane of sp²-bonded atoms [3]. Graphene can be wrapped up into fullerene (zero-dimensional (0D)), rolled up into carbon nanotube (one-dimensional (1D)) and stacked on top of each other to form graphite (three-dimensional (3D)), with an inter planar spacing of 0.335nm [4].

Figure 1 shows that graphene gives birth to all graphitic materials; graphite, carbon nanotubes,

*Corresponding author e-mail: elsakhawy@yahoo.com

Received 23/07/2019; Accepted 2/10/2019

DOI: 10.21608/ejchem.2019.15173.1919

©2019 National Information and Documentation Center (NIDOC)

carbon nanofibers and fullerenes [3].

In general; graphene materials vary in layer number, lateral dimension, surface chemistry, defect density or purity. This difference give rise to various related forms of graphenes, such as, few-layer-graphene (FLG), ultrathin graphite, graphene oxide (GO), graphene nanoplatelets (GNP), and reduced graphene oxide (RGO) ...,etc [5].

Graphene possesses extremely high intrinsic charge mobility ($250000\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$) [6], a high specific surface area ($2630\text{m}^2\text{ g}^{-1}$) [7], good thermal conductivity ($5000\text{Wm}^{-1}\text{ K}^{-1}$) [8], a great Young's modulus (1.0TPa) due to the strength of covalent bonds between carbon atoms [9], and high optical transmittance (97.7%) [10].

These unique properties and huge potential of graphene have encouraged the researchers to carry out more research on graphene. It can be extremely useful in various applications and to replace many current existing materials [11]. For instance; due to its brilliant remarkable properties, it can be used in batteries, flexible and transparent conductors, super capacitors, transistors, fuel cells, solar cells, hydrogen storage, electrochemical devices, catalysis, electrochemical resonators, sensors and wastewater purification. Also, it can be used in bio-medicinal engineering, such as drug delivery, gene transfection, tissue engineering, neural network regeneration, cancer cell imaging, targeting and therapy [3].

Structure

Graphene is thinnest two-dimensional carbonaceous nanomaterial with unique structure and physical, chemical, and thermal properties [12]. It consists of carbon atoms in a hexagonal lattice on a 2D plane. Three atomic orbitals, $2s$, $2p_x$ and $2p_y$, from carbon atoms are hybridized into sp^2 orbitals which form covalent bonds with the neighboring carbon atoms. These lead to a hexagonal planar structure (honey comb lattice) and toughness of the graphene lattice structure. The distance between carbon atoms is 1.42 \AA . $2p_z$ orbital is oriented perpendicular to the planar structure and forma π bond (Fig. 2). These π bonds are hybridized together to form the π -band which contributes to the miraculous electrical conductivity of graphene [13].

Graphite and graphene have the exactly similar

basic structural array of their constituent carbon atoms. Each structure begins with six atoms of carbon that are tightly bound chemically together to form a regular hexagon- like benzene ring. Figure 3 shows that; the graphene carbon atoms are bonded to only three other atoms, although they have the capability to bond to a fourth atom. This capability with high tensile strength and high surface area to volume ratio makes graphene very useful in composite materials.

The oxidized form of graphene is the graphene oxide (GO) [14]. The surface of GO is saturated with oxygen-containing functionalities such as hydroxyl and epoxy groups on sp^3 hybridized on the basal carbon plane, while carbonyl and carboxyl groups attached at the edge's sheets of sp^2 hybridization carbon, (Fig. 4) [15].

These oxygenated moieties on the surface giving highly hydrophilic advantage for GO. Accordingly, GO can be dispersed in a wide range of polar organic solvents using ultrasonication. This dispersion contains single layered sheets of GO and provides a better surface affinity during the fabrication of nanocomposites. So, it can be utilized as precursor or starting material for a wide range of applications [12]. For instance, mixing of dispersed GO with ceramic or polymer matrixes improves their electrical and mechanical properties. On reduction of GO most of the oxygen groups are removed and the reduced graphene oxide (RGO) can be obtained, which is more difficult to disperse due to its tendency to create aggregates [16].

Oxidation of graphene leads to increase the D spacing and changes the hybridization of the oxidized carbon atoms from planar sp^2 to tetrahedral sp^3 . Oxidation totally destroys the electrical conductivity of graphene. However, the reduction of graphene oxide restored the sp^2 hybridized structure as well as the electrical conductivity [3]. Another way of GO preparation is the oxidation of graphite which made up of millions of layers of graphene. By oxidation of graphite using strong oxidizing agents, oxygenated functionalities are introduced makes the material hydrophilic and expand the layer separation. By using sonication, graphite oxide can be exfoliated in water producing single or few layers of GO. The main difference between graphite oxide and dispersed GO is the number of layers. A few layer

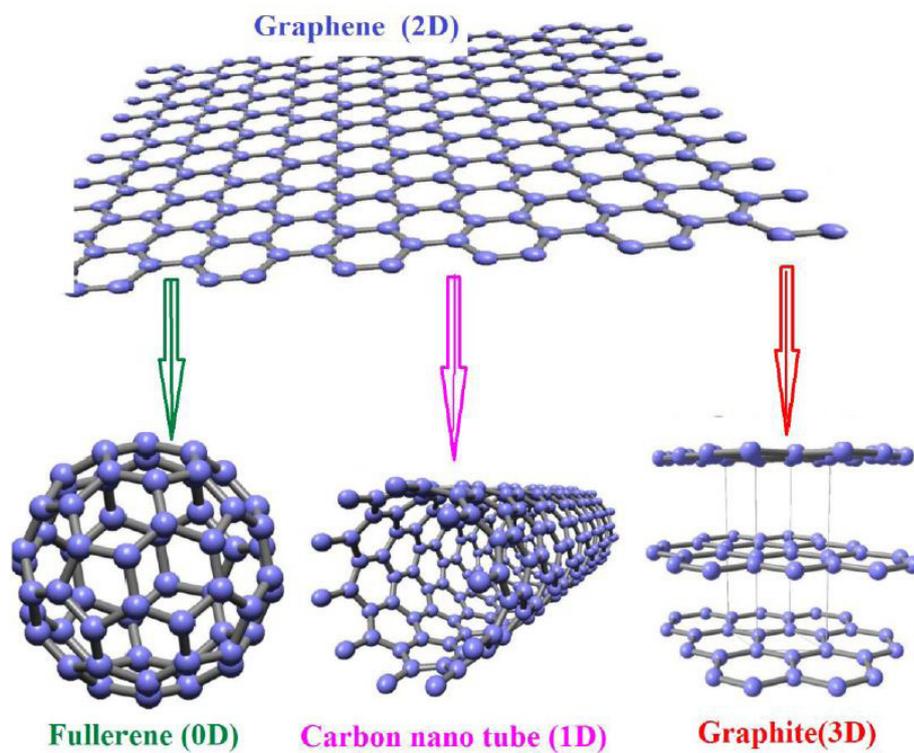


Fig. 1. Graphene and related structures [3].

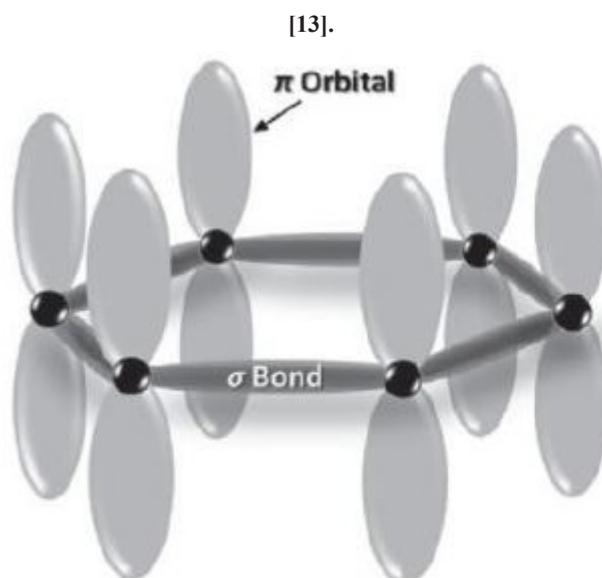


Fig. 2. The sp^2 hybridization between carbon atoms and formation of π bonds from the unoccupied p-orbital

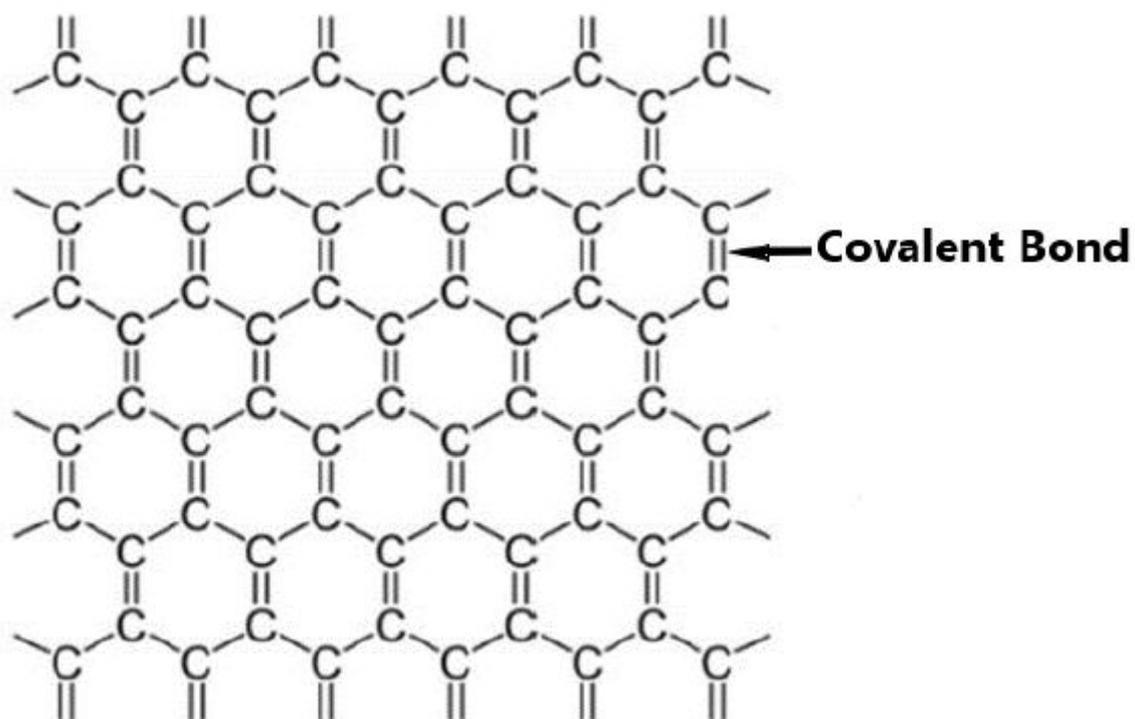


Fig. 3. Graphene structure.

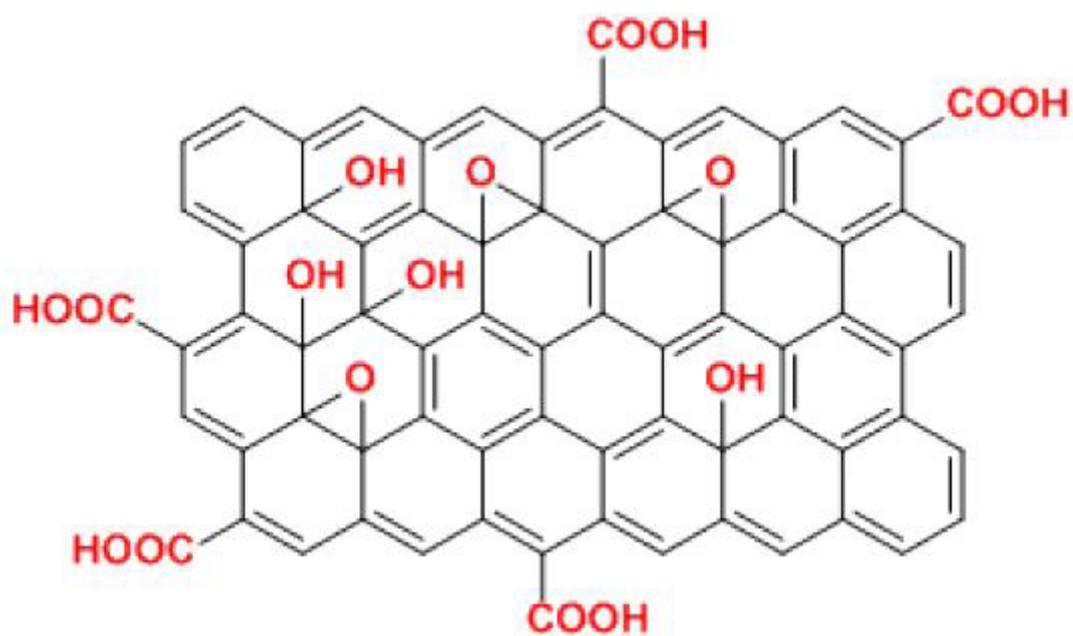


Fig. 4. Schematic structure of graphene oxide (GO) [15].

flakes and monolayer flakes can be found in a dispersed GO [3].

Synthesis

Graphene can be synthesized mechanically, chemically, or thermally. In general, two sources are used for the preparation of graphene: graphite and organic fragments. There are several approaches to prepare graphene. Recently, bottom-up methods of graphene preparation have been developed including chemical vapor deposition on metallic films. Other methods are top-down synthesis like micromechanical exfoliation method from graphite using the peel-off method by scotch tape. Every method has its own advantages and disadvantages. In chemical vapor deposition method, organic molecules as carbon source are used and needs high operating temperature and expensive substrate. In addition, the yield is low and the hydrogen released to atmosphere has the tendency to react with ozone. Micro cleavage method is a simple process and produces good quality of graphene but it is not a feasible method for mass production. Liquid exfoliation of graphite crystal and chemical reduction of graphene oxide methods are often liberating toxic gases and involve complex chemical process which leads to destruction of the basal plane structure. Consequently, the main challenge is the bulk production of graphene from inexpensive precursors by economic method with high yield. Biomass waste is a big challenge in smart cities. Lignin, cellulose, and hemicelluloses are the main components of plant fiber. Therefore, these materials are currently the hotspots due to their abundance, need for recycling and being ample source of carbon. The conversion of these materials into economically-worth products such as carbonaceous materials will help in the management of plant wastes. Lately, environmentally friendly methods using biomass precursors (*e.g.*, sugar, chitosan, plants, and other foodstuffs) have been suggested for charcoal preparation (carbonization) [17, 18].

Chemical exfoliation and Hummer's method

Low-cost natural and industrial carbonaceous wastes such as vegetation wastes (wood, leaf, bagasse, and fruit wastes), animal wastes (bone and cow dung), a semi-industrial waste (newspaper), and an industrial waste (soot powders produced in exhaust of diesel vehicles) were used for charcoal preparation (carbonization) to overcoming the use of expensive highly pure graphite (HPG).

Firstly, the agro waste materials were covered in an aluminum foil and carbonized at ~ 400–500 °C for 5 days. The obtained charcoal materials were grounded by a mortar into powders, which were then covered in an aluminum foil and heated at 450 °C for 24 hr. The obtained charcoal powders were used as raw materials to synthesize graphene oxide. Graphitization was achieved with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution and the pH of the solution was adjusted 2 by adding HCl. The mixture was stirred at 60 °C for 5 hr. In addition, water evaporation and drying takes place to obtain a graphitized material which grounded to obtain powder.

All the materials showed total residual impurities <5 %. The vegetation substances (such as the natural carbonaceous materials) yielded the lower residual impurities (<0.7 %), while the soot (as one of the industrial carbonaceous materials) resulted in a relatively high impurity level (5 %), substantially related to the residual S (sulphur) and N (nitrogen) impurities. The animal carbonaceous materials (*i.e.*, bone and cow dung) presented 2 % residual impurity level, substantially related to the residual Ca for the former and residual N and Na (sodium) for the latter. The newspaper (as a semi-industrial starting material) yielded a relatively high residual impurity level of 3 %, substantially due to application of Pb (lead) in printing the newspaper [17].

Also, biomass such as coconut shell, rice husk, and bagasse were used as raw materials to synthesize GO. These materials were placed and burnt in a furnace at 550 °C for 3 hr, under atmospheric pressure. GO was synthesized from the prepared graphitized powder by using a modified Hummers' method. For this purpose, graphitized powder was dissolved in H_2SO_4 at 80 °C for 24 hr. Then, NaNO_3 was added into the solution and stirred in an ice bath for 1 h followed by slowly addition of KMnO_4 into the solution and vigorously stirred for 4 hr. Then, it was warmed to room temperature while being stirred continuously in a water bath at 35 °C for 1 hr. The prepared solution was diluted by distilled water. In addition, H_2O_2 was added into the solution in order to reduce residual permanganate to soluble manganese ions and stop the gas evolution from the solution. Finally, a GO suspension was obtained by ultrasonication of the centrifuged graphite oxide suspension. For chemical reduction of the GO aqueous suspension by hydrazine (as a standard reductant), the pH of GO suspension was adjusted to 9.0 by adding a diluted ammonia solution. Then, hydrazine solution was added to the suspension while it was stirred at room

temperature. Finally, the suspension was refluxed at 90 °C for 3 hr in an oil bath [18].

Agro waste such as tea waste was used also for production of bio-char. Firstly, GO preparation started by pyrolysis process under N₂ atmosphere in a ceramic crucible. Tea waste was charred in N₂ atmosphere; the resultants graphite was cooled, crushed and sieved to obtain a homogenous powder of particle size less than 0.2 mm. The bio-char powder was acidified with concentrated H₂SO₄ then; NaNO₃ and KMnO₄ were added to the slurry with continuous stirring. The temperature was gradually increased from 50 to 100°C. Finally, 30% H₂O₂ was added to the heated mixture until the color was turned to bright yellow. The solution was sonicated, filtered and washed repeatedly with 5% aqueous HCl for metal ions removal and further washed with distilled water for removal of excess acid present and dried in oven. The GO prepared by this technique has porosity 0.62; yield 52.15%, bulk density 0.8 g cm³ and moisture content 5.6% [19]. For graphene production, hydrazine hydrate was added to a suspension of GO in distilled water with constant stirring. After 1 hour the slurry was filtered through a filter paper and dried in hot air oven at 60°C for 6 hr [20].

Muffled atmosphere for graphene (MA-G) and graphene oxide preparation (MA-GO)

After juice extraction of sugarcane bagasse (SCB), the remaining fiber was dried, grounded well in order to produce fine powder. Known amount of SCB powder mixed with ferrocene and placed in a porcelain crucible. The mixture put directly into a muffle furnace at 300 °C under atmospheric conditions. Next, the as-produced black solid was collected at room temperature. This method considered as simple and low-cost process for cost-effective production of graphene-based materials [12].

Rice husk ash (RHA), prepared by the combustion of dried rice husk in air, activated with KOH in a crucible and the mixture was covered with ceramic wool which in turn was set into a larger SiC crucible covered with carbon powder and ceramic wool. The fully covered carbon powder was used to protect oxidation against air at high temperature. The crucible was annealed at 750 °C for 2 hr in air. The resulting samples were washed with distilled water several times to remove impurities, filtered and dried at 100 °C for 24 hr. The yield of graphene by using RHA as

starting material was found to be ca. 10 wt% [18].

Thermal pyrolysis

Preparation of graphene by thermal pyrolysis of agro wastes, such as camphor leaves, is a simple technique to produce high-quality and large-scale graphene. Thermal method is always high yield and meets the requirements of various industries. Camphor leaves were washed with acetone and dried followed by pyrolysis under N₂ at 1200 °C for 4 min. At high temperatures, hemi-cellulose undergoes cleavage and arrangement under N₂, which leads to graphene formation. After that, the sample was cooled to room temperature then D-tyrosine and trichloro methane were added. Addition of D-tyrosine makes π - π interaction with graphene to ensure pure graphene synthesis with thickness of 2.37 nm. The slurry was sonicated in an ice bath and then centrifuged to precipitate amorphous carbons. Graphene was suspended in the solvent while other forms of carbon precipitated. Graphene could be extracted by filtration. D-tyrosine can be easily removed from the solution by washing with either a strong acid or base. The graphene yield from this procedure is 0.8%, which means we could get 0.8 mg of graphene from 0.1 g of dried camphor leaves [21]. Figure 5 shows the growing mechanism of graphene by thermal method. During thermal process, individual carbon atoms are released then they nucleate with others in the structure of benzene ring through sp² bonds instead of natural sp³ bonds linked carbon atoms. After that the nucleation grows into graphene, this means the thermal process is the split of molecules and recombination of atoms.

Chemical vapor deposition (CVD) or Copper foil method

The most popular technique for large-scale production of mono- or few-layer graphene films is CVD due to its scalability and potential to produce high-quality graphene film [22, 23]. However, it is an inefficient method because it requires high temperature [23]. Graphene could be prepared by CVD method from decomposition of methane/acetylene/ethylene on metal surface. Carbon is added in the form of a methane gas, epitaxial growth on electrically insulating surfaces, where the carbon source is added within the substrate surface, and carbonization of biomass/waste materials. These methods have better controllability of size, thickness and shape. However, the materials prepared by these methods

contain impurities and exhibit wide variability in surface and structural characteristics.

Foil is used to synthesize graphene where the sheet of graphene is synthesized based on the shape of one piece of foil. The first successful production of few layer graphene films using CVD was reported using the Cu as foils and camphor as carbon source. Metals with mediate-high carbon solubility (>0.1 atomic %) such as Co and Ni have been used to facilitate the diffusion of carbon into the metal thin film at high temperature and followed by precipitation of carbon out on the metal surface when cooling [22].

Production of high-quality monolayer graphene directly on the surface of Cu foils under a H_2/Ar flowing atmosphere was demonstrated. The pristine graphene was built on the bottom side of the Cu film. The front side of the Cu foil was etched away by floating the foil metal-down on an acidic $CuSO_4$ solution (made with $CuSO_4 \cdot 5H_2O$ (15.6 g), conc. HCl (50 mL), H_2O (50 mL), and H_2SO_4 (2 mL)) for 5s. The size of the Cu foil was 2 cm x 3.0 cm and the boat was 40 cm long and cut from a quartz tube with a 15 mm inside diameter [24]. Only high-quality pristine graphene with few defects and 97% transparency was grown on the bottom side of the Cu foil [25].

Plasma enhanced chemical vapor deposition (PECVD)

Use of plasma is considered as one of the most promising methods to produce graphene with desired properties. After completion of the pyrolysis process system was cooled down naturally in inert atmosphere and residual black powder was collected. Hydrogen plasma treatment on residual black powder was carried out at 350 °C for 3–4 min in a microwave plasma chemical vapor deposition apparatus operating at 2.45 GHz frequency. The effect of plasma on the structures of carbonaceous products was studied and it is revealed that the carbonaceous structures such as 3D nano GO, graphite nanodots, carbon nanotubes, and carbon onions were present in both pre-treated and plasma-treated residual black powder.

PECVD as compared to CVD for synthesis of graphene is preferred due to low reaction temperature which minimizes the cost production. First high amount of graphite was obtained after using a DC discharge PECVD in a fabrication of "nanostructured graphite". The first production of mono- and few layers of graphene on several

types of substrates by radio frequency PECVD was reported which used a gas mixture of CH_4 and H_2 at 900 W and in the reaction temperature of 680.

The primacy of PECVD over CVD is due to lower deposition time (≤ 5 min) and a lower growth temperature of 650 can be done. Also, PECVD have additional high-density reactive gas atoms and radicals which allows using low-temperature and rapid synthesis of graphene [22].

Mechanical exfoliation method

Graphene synthesis with abundance of micro as well as meso-pores was achieved via mechanical exfoliation method from an agricultural waste biomass such as peanut shell. Peanut shells wastes were collected, washed with distilled water to remove dust and dried in sunlight for a few days. Then it was dried in a vacuum oven at 80 °C for overnight to remove any moisture content. These dried shells were ground into a homogenous fine powder for the synthesis of carbon nano materials. The powder was pyrolyzed in a tubular furnace at 800 °C for 2hr under an argon atmosphere at a heating rate of 3 °C min^{-1} . The resulting product was washed with isopropanol to remove any unwanted organic deposition. Then it was activated with KOH (w/w 1:3) to get a homogeneous mixture which heated in a tubular furnace under an argon atmosphere at 800 °C for another 2hr to generate the required porosity and functionality to get peanut shell derived activated carbon materials. The activated sample was then washed with 1:1 HCl solution followed by distilled water until the pH reached neutrality and dried for overnight. The exfoliation of the product was performed in 10% H_2SO_4 aqueous solution through probe sonication for 1 hr with a power of 15 W and a pulse on-and-off time of 5 seconds. Then it washed until neutrality and the sonication step is repeated many times. The washed samples were centrifuged and dried at 80 °C for overnight. The yield was found to be 22.5 wt % with respect to peanut shell precursor. High specific surface area (2070 $m^2 g^{-1}$) with a sufficiently large pore volume of 1.33 $cm^3 g^{-1}$ was emerged by this method [26].

Improved graphene oxide method

The palm kernel shell (PKS), empty fruit bunch (EFB) and oil palm leaves (OPL) were collected, washed, dried in an oven at 70 and were grounded into a powder. Carbonization was carried out in an alumina boat under N_2

gas to achieve a carbon material that served as the precursor for rGO (reduced graphene oxide) synthesis. The precursors OPL, PKS and EFB were heated at a constant heating rate of 10 °C/min, to the temperatures of 400, 500, 600, 700, 800 and 900 °C and held for 3 hr for optimization.

After the synthesis, the as-produced materials were washed twice repeatedly in deionized water, 37% HCl and ethanol, each step followed by centrifugation. The materials were further coagulated with diethyl ether, and the resulting solutions were centrifuged and the supernatant (excess ether) decanted away. The residue was carefully removed from the centrifuging tubes and dried overnight at room temperature. The as-prepared GOs were subsequently reduced through thermal treatment using low-temperature annealing reduction of GO. The thermal annealing reduction was conducted at 300 °C in a furnace and operated in an inert atmosphere of nitrogen gas flow [27].

Carbon yield % prepared from precursors; OPL and PKS against carbonization temperatures showing that the yield tends to decrease as the carbonization temperature increased. In addition, GO could be reduced also by chemical reduction using hydrazine, NaBH₄ and hydroquinone on vigorous stirring at 80–100°C to produce graphene. In order to minimize the amount of defect produced from reduction of GO, solvothermal technique was developed by Dai and co-workers to reduce the GO in more effective manner. Solvothermal reduction was occurred in *N,N*-dimethylformamide (DMF) at 180 °C using hydrazine monohydrate and/or sodium borohydride (NaBH₄) as the reducing agent. The reduced GO film by hydrazine becomes rigid while NaBH₄ reduction caused the reduced GO film become fragile. To avoid this problem the reduction by hydrohalic acid was used for giving integrity and flexibility to the reduced GO film [28].

The chemical reduction techniques showed some drawbacks, such as toxic waste produced to the environment owing to the released poisonous hydrazine vapors, COOH (carboxyl group), OH (hydroxyl group), and >O (epoxy group) which highly affect environmental, and are not economically feasible, when scaling up for production. Thus, environment friendly reducing agents are needed such as vitamin C, aluminum powder, reducing sugar, amino acid and the aromatic rings of tea polyphenol that exists in green tea solution. Environmentally friendly

reduction process advantages such as low-cost procedure and no poisonous waste were released [22].

Liquid-phase exfoliation

The technique of this procedure is based on the use of natural and synthetic polymers as starting materials. The starting material gives rise to graphitic carbons and this technique mainly comprises the following stages:

a) pyrolysis of the starting polymer in a furnace in the absence of oxygen at temperatures between 400 and 1200°C; and

b) liquid-phase exfoliation of the pyrolyzed material which produced in the first stage. Several liquid-phase exfoliation cycles take place to promote exfoliation performance. Exfoliation performance is the percentage by weight of the pyrolyzed material which is suspended in the solvent. For solid graphene samples preparation, the solvent is removed and the resulting residue is dried.

Natural polymers used are biopolymers and their derivatives, for example polysaccharides (agricultural waste) which comprise chitosan, alginate. On the other hand, the synthetic polymers used are poly (furfuryl alcohol), poly (acrylate), polythiophene, poly (p-phenylene vinylene), polyaniline, polystyrene, polyacrylonitrile. The exfoliation stage carried out in solvents preferably, water, methanol, acetone, ethylene glycol, propylene glycol, dimethylformamide, methylpyrrolidone, ionic liquids or supercritical fluids. This procedure gives graphene sheets having dimensions between 1 and 100 microns from biopolymers. The graphene concentrations obtained in water suspensions may vary from 0.01 mg/ml to 0.2 mg/ml [29].

Graphene preparation with aid of ferric chloride solution

Glucose (C₆H₁₂O₆) is a renewable carbon source which used to prepare graphene with the aid of FeCl₃. Glucose and FeCl₃ were dissolved in water and then heated to 80 for carbonized glucose and FeCl₂ (H₂O₂) production. Then calcinations was achieved at 700 (argon atmosphere) for production of graphene and Fe₀, as shown in Fig. 6. Finally, the Fe₀ was removed with the aid of HCl [30].

Hydrothermal method

The fibrous hemp wastes can be converted

into a graphene-like nanomaterial. Hemp bast is a nanocomposite made up of layers of lignin, hemicellulose, and cellulose. It separates into nanosheets similar to graphene. Hemp is composed of three layers namely S1, S2 and S3 i.e. inner, middle and outer layers respectively. The S1 and S3 are composed of cellulose and lignin, the middle layer is primarily crystalline cellulose. The fibrous hemp wastes were heated for 24 h at 180 °C for ashing the cellulose and lignin components and then the resulting material was activated with KOH to give rise to porous graphene which are crumpled and contains holes that can be applied in super capacitors [30].

Characterization

XRD

The XRD analysis was performed to confirm the formation of various phases. In the XRD pattern, as shown in Fig. 7, pristine graphite shows a narrow peak with very high intensity at $2\theta \approx 26.05\text{-}26.6^\circ$ relevant to the (111) plane. With oxidation, to form GO, this peak shifts to a lower angle at $2\theta \approx 11.54\text{-}13.9^\circ$ relevant to the (002) plane due to the incorporation of oxygen functionalized group like epoxy, carboxyl, hydroxyl and carbonyl in graphene layers, which confirms the successful preparation of GO [31]. The interlayer distances, calculated using the Braggs equation, increase from 0.35 to 0.765 nm after graphene oxidation owing to interlayer spacing of oxygen containing functional groups [32].

TEM

The thickness of graphene can be determined accurately by TEM analysis as reported by Hernandez et al. by observing a large number of TEM images to generate a series of thickness statistics [33]. Single-layer graphene can be observed as transparent sheets by TEM analysis. When graphene sheets were fold back, cross-sectional can be viewed and the number of layers can be measured using TEM at several locations.

Figure 8 shows that monolayer and bilayer folded graphene can be observed as one and two dark lines, respectively when the folded graphene sheet are placed parallel to the electron beam. A more accurate identification way of number of graphene layer can be determined by nano area electron diffraction patterns by changing incidence angles between the electron beam and the graphene sheet [34, 35].

Fourier-transform infrared (FT-IR) and Raman spectroscopy

FT-IR is a rapid and easy way to identify functional groups, structure and quality of carbon

materials including graphenes. The graphene spectrum shows O-H broad peak at 3433 cm^{-1} resulting from -OH stretching vibrations of the hydroxylic group and chemisorbed water and C = C at 1630 cm^{-1} which can be assigned to the skeletal vibrations of graphene-like sheets. The peak at 3160 cm^{-1} stands for C=C-H stretching mode. Medium broad vibration observed at 2786 cm^{-1} is ascribed to the overtones of O-H bending. The peaks at 1397 and 1464 cm^{-1} appear due to the-CH₂ and -CH symmetric bending [12].

IR confirms the introduction of oxygen containing groups such as functional hydroxyl, epoxy and carboxylic groups after oxidation of graphene. The strong band at $1708\text{-}1728\text{ cm}^{-1}$ is attributed to stretching vibration modes of C = O in carboxylic acid and carbonyl groups. The peak at 1624.12 cm^{-1} is attributed to the skeletal vibrations of un-oxidized graphitic domains. The peak at 1594 cm^{-1} is assigned to the skeletal vibrations of un-oxidized graphitic domains. The band at 1059 cm^{-1} is assigned to C-O (epoxy) groups while the band at 1224 cm^{-1} is usually attributed to C-OH stretching vibrations. The strong peak around 3500 cm^{-1} can be attributed to the O-H stretching vibrations of the C-OH groups and water [36].

Raman spectroscopy is one of the most widely-used analytical techniques to characterize the bonding structure of carbon-based materials. Raman spectra confirm the lattice distortions; it illustrates D- and G-bands at 1365 and 1585 cm^{-1} , respectively as shown in Fig. 9. From the ratio between ID and IG bands, the number of layers of graphene can be accurately determined [37]. The G-band of the as-prepared GO shifted towards a higher wavenumber, indicating the oxidation of graphite-like material, which results in the formation of sp³ carbon atoms [38].

Conclusion

Industrialization production with low cost is one of the major challenges in graphene field. It is probably manifested in this review that the renewable and inexpensive agricultural wastes could be effectively converted into a wealth of products.

Graphene is a promising material for various applications in the fields of physics, chemistry, materials science and engineering, and biology. However, the graphene industry is still in its early stages, very significant progress in mass production and certain industrial applications has become obvious.

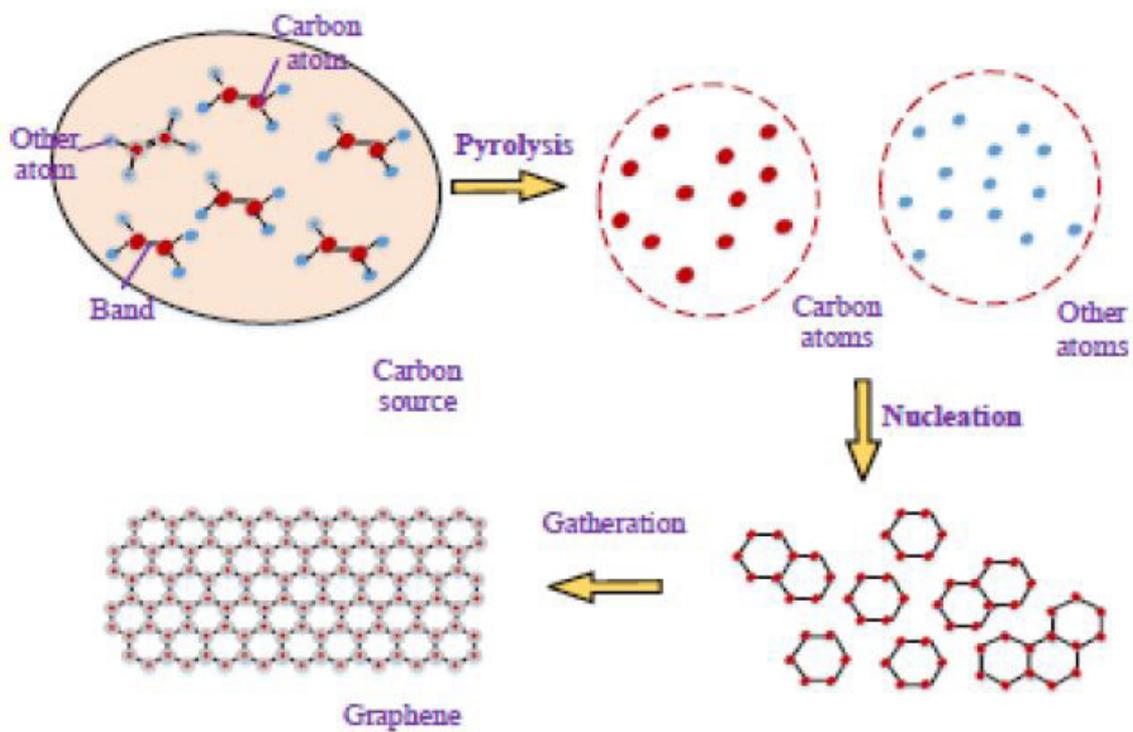


Fig. 5. Mechanism of thermal method for growing of graphene [21].

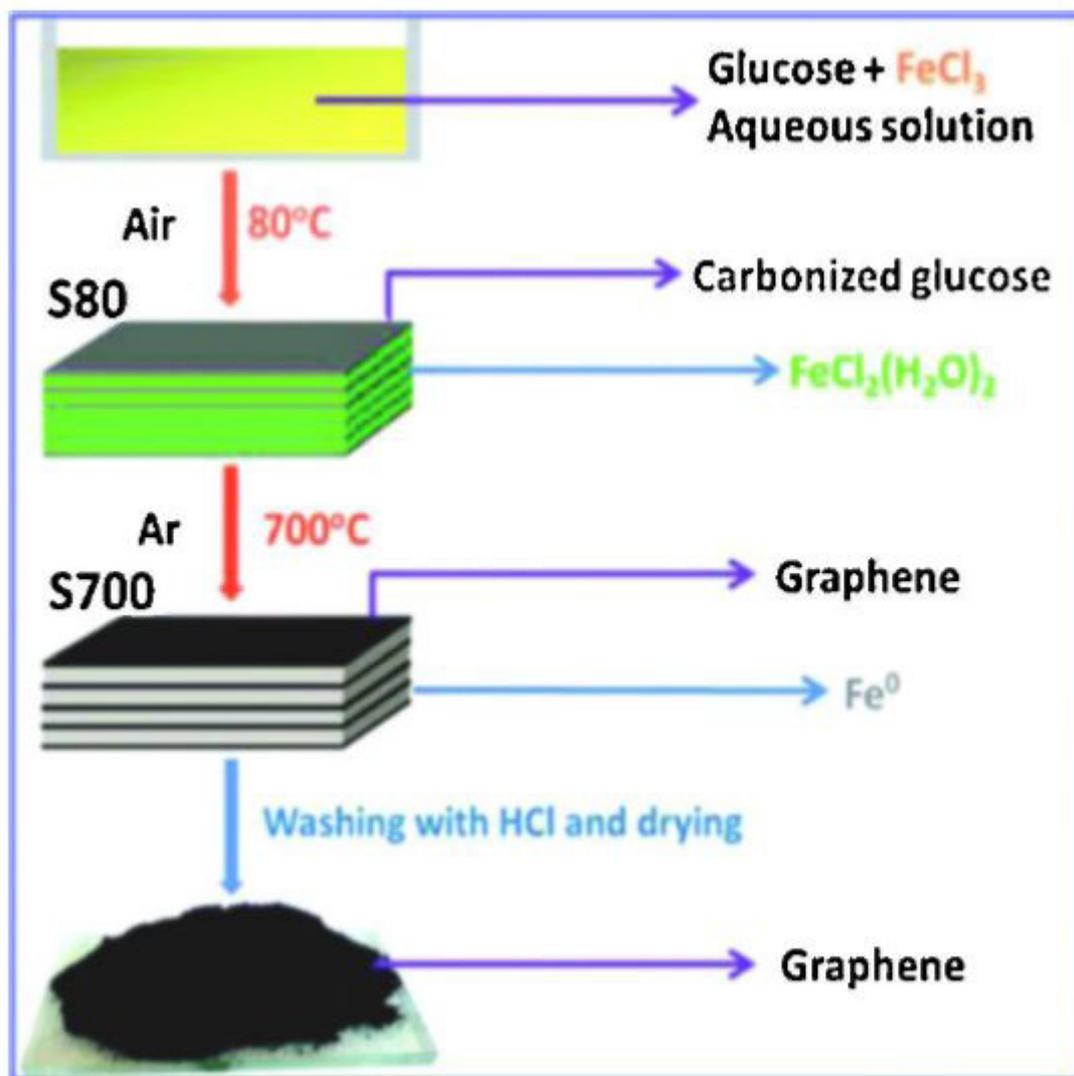


Fig. 6. Schematic representation of graphene preparation with aid of ferric chloride solution [30].

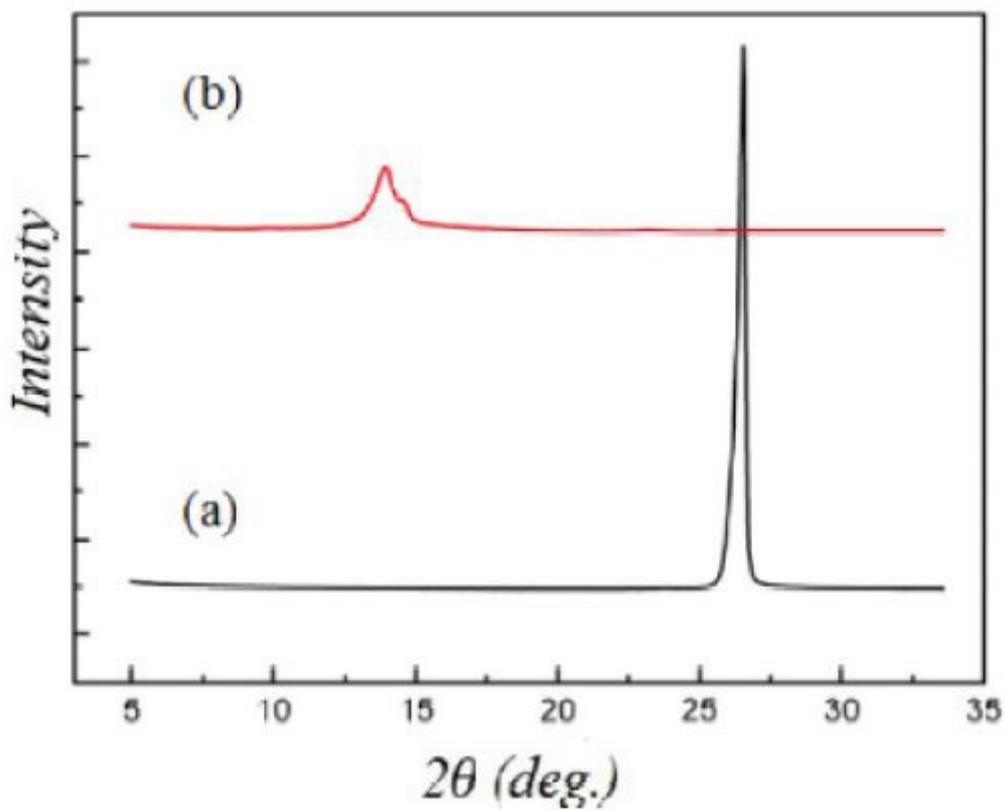


Fig. 7. XRD patterns of graphite (a), graphene oxide (b) [32].

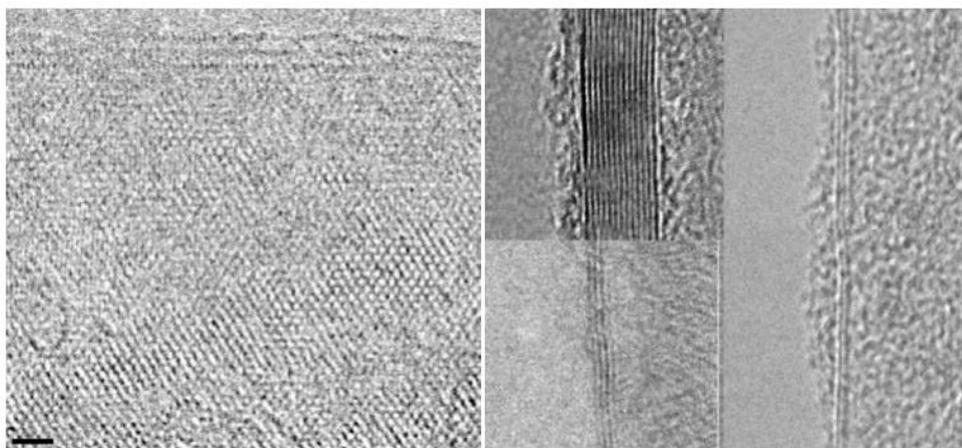


Fig. 8. TEM of graphene oxide [34, 35].

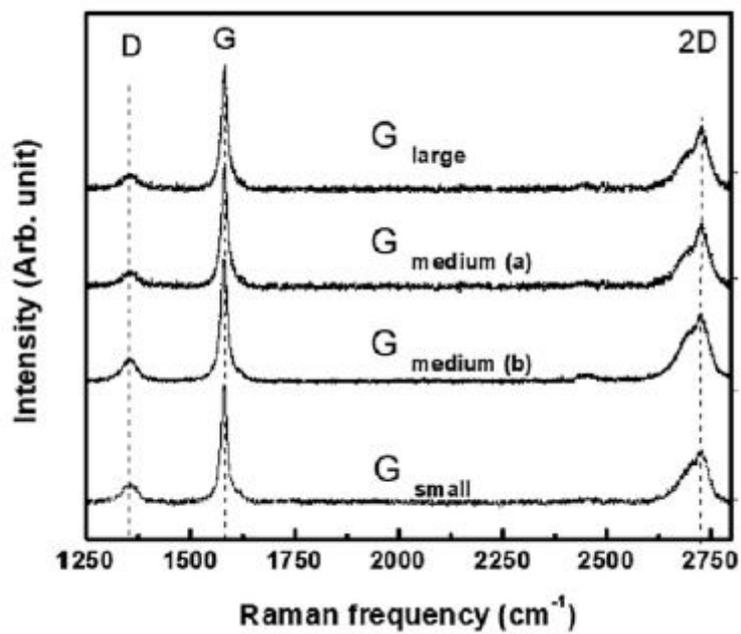


Fig. 9. Raman spectroscopy of graphene oxide [38].

Acknowledgement

The authors acknowledge the Academy of Scientific Research and Technology (ASRT), Egypt and Czech Academy of Sciences, for financial support of the bilateral research activities.

References

- Sadegh H., Development of graphene oxide from graphite: A review on synthesis, characterization and its application in wastewater treatment. *Reviews on Advanced Materials Science*, **49**, 38-43 (2017).
- Yahya M.A., Mansor M.H., Zolkarnaini W.A.A.W., Rusli N.S., Aminuddin A., Mohamad K., Sabhan F.A.M., Atik A.A.A. and Ozair L.N., A brief review on activated carbon derived from agriculture by-product. *AIP Conference Proceedings*. AIP Publishing, 1972 (1), 030023 (2018).
- Roy I., Sarkar G., Mondal S., Rana D., Bhattacharyya A., Saha N.R., Adhikari A., Khastgir D., Chattopadhyay S. and Chattopadhyay D., Synthesis and characterization of graphene from waste dry cell battery for electronic applications. *RSC Advances*, **6** (13), 10557-10564 (2016).
- Chalageri B.D., Archana and Kulkarni R.M., Denitrification of groundwater using graphene. *International Journal of Web Engineering and Technology*, **5** (15), 10-14 (2016).
- Darwish A., Ghoniem A., Hassaan M., El-Said Shehata O. and Turkey G., Synthesis and Characterization of Polyaniline/Mn₃O₄/Reduced Graphene Oxide Nanocomposite. *Egyptian Journal of Chemistry*, **62**, Special Issue (Part 1) December 2019, 251-265 (2019). doi: 10.21608/ejchem.2019.13194.1821
- Orlita M., Faugeras C., Plochocka P., Neugebauer P., Martinez G., Maude D.K., Barra A.-L., Sprinkle M., Berger C. and De Heer W.A., Approaching the dirac point in high-mobility multilayer epitaxial graphene. *Physical review letters*, 101(26), 267601 (2008).
- Stoller M.D., Park S., Zhu Y., An J. and Ruoff R.S., Graphene-based ultracapacitors. *Nano letters*, **8** (10), 3498-3502 (2008).
- Balandin A.A., Ghosh S. Bao W., Calizo I., Teweldebrhan D., Miao F. and Lau C.N., Superior thermal conductivity of single-layer graphene. *Nano letters*, **8** (3), 902-907 (2008).
- Lee C., Wei X., Kysar J.W. and Hone J., Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, **321** (5887), 385-388 (2008).
- Nair R.R., Blake P., Grigorenko A.N., Novoselov K.S., Booth T.J., Stauber T., Peres N.M. and Geim A.K., Fine structure constant defines visual transparency of graphene. *Science*, **320** (5881), 1308-1308 (2008).
- Randviir E.P., Brownson D.A. and Banks C.E., A decade of graphene research: Production, applications and outlook. *Materials Today*, 17(9), 426-432 (2014).
- Somanathan T., Prasad K., Ostrikov K., Saravanan A. and Krishna V., Graphene oxide synthesis from agro waste. *Nanomaterials*, **5** (2), 826-834 (2015).
- Riedl C., Epitaxial graphene on silicon carbide surfaces: Growth, characterization, doping and hydrogen intercalation. Dissertation, Faculty of Natural Sciences, Friedrich-Alexander-University Erlangen-Nürnberg, Germany (2010).
- Liu S., Graphene oxide & graphene based catalysts in photochemical reactions. *M Sc thesis*, Department of Chemical Engineering. Curtin University (2013).
- Alam S.N., Sharma N. and Kumar L., Synthesis of graphene oxide (go) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rgo). *Graphene*, **6** (01), 1-18 (2017).
- Eluyemi M., Eleruja M., Adedeji A., Olofinjana B., Fasakin O., Akinwunmi O, Ilori O., Famojuro A., Ayinde, S. and Ajayi E., Synthesis and characterization of graphene oxide and reduced graphene oxide thin films deposited by spray pyrolysis method. *Graphene*, **5** (3), 143-154 (2016).
- Akhavan O., Bijanzad K. and Mirsepah A., Synthesis of graphene from natural and industrial carbonaceous wastes. *RSC Advances*, **4** (39), 20441-20448 (2014).
- Muramatsu H., Kim Y.A., Yang K.S., Cruz Silva R., Toda I., Yamada T., Terrones M., Endo M., Hayashi T. and Saitoh H., Rice husk-derived graphene with nano-sized domains and clean edges. *Small*, **10** (14), 2766-2770 (2014).
- Roy S., Synthesis of graphene oxide using tea-

- waste biochar as green substitute of graphite and its application in de-fluoridation of contaminated water. *American Journal of Chemical Research*, **1** (1), 2-19 (2017).
20. Papita Das S.G. and Soumita M., Removal of naphthalene present in synthetic waste water using novel g/go nano sheet synthesized from rice straw: Comparative analysis, isotherm and kinetics. *Front Nanosci Nanotech*, **2** (1), 38-42 (2016).
21. Shams S.S., Zhang L.S., Hu R., Zhang R. and Zhu J., Synthesis of graphene from biomass: A green chemistry approach. *Materials Letters*, **161**, 476-479 (2015).
22. Liu W.-W., Chai S.-P., Mohamed A.R. and Hashim U., Synthesis and characterization of graphene and carbon nanotubes: A review on the past and recent developments. *Journal of Industrial and Engineering Chemistry*, **20** (4), 1171-1185 (2014).
23. Lee H.C., Liu W.-W., Chai S.-P., Mohamed A.R., Aziz A., Khe C.-S., Hidayah N.M. and Hashim U., Review of the synthesis, transfer, characterization and growth mechanisms of single and multilayer graphene. *RSC Advances*, **7** (26), 15644-15693 (2017).
24. Ruan G., Sun Z., Peng Z. and Tour J.M., Growth of graphene from food, insects, and waste. *ACS nano*, **5** (9), 7601-7607 (2011).
25. Titirici M.-M., White R.J., Brun N., Budarin V.L., Su D.S., Monte F., Clark J.H. and MacLachlan M.J., Sustainable carbon materials. *Chemical Society Reviews*, **44** (1), 250-290 (2015).
26. Purkait T., Singh G., Singh M., Kumar D. and Dey R.S., Large area few-layer graphene with scalable preparation from waste biomass for high-performance supercapacitor. *Scientific reports*, **7** (1), 15239 (2017).
27. Nasir S., Hussein M., Yusof N. and Zainal Z., Oil palm waste-based precursors as a renewable and economical carbon sources for the preparation of reduced graphene oxide from graphene oxide. *Nanomaterials*, **7** (7), 182 (2017).
28. Dai B., Fu L., Liao L., Liu N., Yan K. and Chen Y., High-quality single-layer graphene via reductive reduction of graphene oxide. *Nano Research*, **4** (5), 434-439 (2011).
29. Arnau A.M.P., Gómez H.G., Cortezón E.S. and Sánchez J.M.D., Method for obtaining solid graphene samples or suspensions. *European Patent Application*, EP 2 924 005 A1 (2015).
30. Raghavan N., Thangavel S. and Venugopal G., A short review on preparation of graphene from waste and bioprecursors. *Applied Materials Today*, **7**, 246-254 (2017).
31. Zhang H.-B., Zheng W.-G., Yan Q., Yang Y., Wang J.-W., Lu Z.-H., Ji G.-Y. and Yu Z.-Z., Electrically conductive polyethylene terephthalate/graphene nanocomposites prepared by melt compounding. *Polymer*, **51** (5), 1191-1196 (2010).
32. Yang H., Li H., Zhai J., Sun L. and Yu H., Simple synthesis of graphene oxide using ultrasonic cleaner from expanded graphite. *Industrial & Engineering Chemistry Research*, **53** (46), 17878-17883 (2014).
33. Hernandez Y., Nicolosi V., Lotya M., Blighe F.M., Sun Z., De S., McGovern I., Holland B., Byrne M. and Gun'Ko Y.K., High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, **3** (9), 563-568 (2008).
34. Meyer J.C., Geim A.K., Katsnelson M.I., Novoselov K.S., Booth T.J. and Roth S., The structure of suspended graphene sheets. *Nature*, **446** (7131), 60-63 (2007).
35. Kim K.S., Zhao Y., Jang H., Lee S.Y., Kim J.M., Kim K.S., Ahn J.-H., Kim P., Choi J.-Y. and Hong B.H., Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*, **457** (7230), 706-710 (2009).
36. Geim A.K. and Novoselov K.S., The rise of graphene. *Nature Materials*, **6**, 183-191 (2007).
37. Beams R., Cancado L.G. and Novotny L., Raman characterization of defects and dopants in graphene. *Journal of Physics: Condensed Matter*, **27**, 083002 (2015).
38. Silva L.I., Mirabella D.A., Tomba J.P. and Riccardi C.C., Optimizing graphene production in ultrasonic devices. *Ultrasonics*, **100**, 105989 (2020).

الجرافين: التركيب والتحضير والتوصيف، استعراض موجز**سمير كامل^١ ، محمد السخاوي*^١ ، بدوي أنيس^٢ ، وهبة الله سرحان تهامي^١**

قسم السليلوز والورق ، المركز القومي للبحوث ، ٣٣ ، شارع البحوث ، ص.ب. ١٢٦٢٢ ، الدقي ، الجيزة ، مصر
قسم الطيف ، شعبة الفيزياء ، المركز القومي للبحوث ، ٣٣ شارع البحوث ، ص.ب. ١٢٦٢٢ ، الدقي الجيزة ، مصر

في عام ٢٠٠٤ . استخدم العالمان أندريه جيم وكوستيا نوفوسيلوف تقنية بسيطة لفصل طبقة الجرافين من الجرافيت. وقد حصلوا على جائزة نوبل في الفيزياء في عام ٢٠١٠. وبعد ذلك ، تزايد النشر عن الجرافين عاما بعد عام . وأصبح من الموضوعات الأكثر ظهورا في مجال البحث مما يشير إلى أهمية أبحاث الجرافين. نظراً للخصائص الفريدة للجرافين . يمكن اعتباره مادة واعدة للتطبيقات المختلفة في مجالات الفيزياء والكيمياء وعلوم المواد والهندسة والبيولوجيا. وبالتالي . سيركز هذا البحث المرجعي على استخدام الكتلة الحيوية والنفايات الأخرى كمواد أولية لتحضير الجرافين. نأمل أن تكون هذه الدراسة مفيدة للأشخاص المهتمين بهذا المجال. كما اخذ في الاعتبار أيضا آفاق الجرافين المستقبلية.