REVIEWS

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Graphene synthesis, fabrication, characterization based on bottom-up and top-down approaches: An overview

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Abstract: This study presents an overview on graphene synthesis, fabrication and different characterization techniques utilized in the production. Since its discovery in 2004 by Andre Geim and Kostya Novoselov several research articles have been published globally to this effect, owing to graphene's extraordinary, and exclusive characteristics which include optical transparency, excellent thermal, and mechanical properties. The properties and applications of this two-dimensional carbon crystal composed of single-layered material have created new avenues for the development of high-performance future electronics and technologies in energy storage and conversion for the sustainable energy. However, despite its potential and current status globally the difficulty in the production of monolayer graphene sheet still persists. Therefore, this review highlighted two approaches in the synthesis of graphene, which are the top-down and bottom-up approaches and examined the advantages and failings of the methods involved. In addition, the prospects and failings of these methods are investigated, as they are essential in optimizing the production method of graphene vital for expanding the yield, and producing high-quality graphene.

Key words: two-dimensional material; nanomaterial; carbon material; nanostructure

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1. Introduction

Graphene is an exceptional carbon crystal composed of single-layered materials made up of six bonded sp^2 carbon atoms, configured in a honeycomb lattice nanostructure with an atomic spacing of 1.42°. It is the underlying element present in graphitic materials: fullerene (0D), nanotubes (1D), graphite (3D). Andre Geim, and Kostya Novoselov discovered this material in 2004 at Manchester through a method called "Scotch tape peeling" by using adhesive tape to separate an isolated monolayer graphene from graphite. Hence, the graphene layers produced are greatly ordered; possess unique and excellent electrical, mechanical, optical and thermal properties and this has meant that it has drawn lots of attention to itself[1–3]. Furthermore, it has a high specific surface area of 2630 m^2/g, a high intrinsic electron mobility of 2.5×10^5 $cm^2/(V{\cdot}s)$, a superior thermal conductivity with a value ranging from 3000 to 5000 W/(m·K). In addition, it has an extremely good Young's Modulus with a value of 1 TPa, a high current density, 10^8 A/cm^2 and a good optical transmittance of 97.7%[4, 5].

Since its discovery, the major challenge to the productive future application of graphene as an alternative to silicon in new generation electronics commercially is the absence of an energy band gap due to its symmetry, which unites two types of distinct carbon atoms. Therefore, there is a need to open a finite gap of graphene in the energy dispersions at K-point through several techniques. These techniques should be cost effective in manufacturing or fabricating high quality and large area graphene sheets[6, 7]. However, the most commonly used techniques nowadays include chemical vapor deposition (CVD)[8], chemical via reduction of graphene oxide (GO)[9], epitaxial growth[10], and mechanical exfoliation[11].

Furthermore, in recent reports (CVD) and epitaxial methods are adopted in the synthesis of graphene to open the band gap and are promising in the generation of monolayer area quality graphene on a large scale. These methods are not without its challenges, because the reduction of graphene oxide chemically includes the use of hydrazine, dimethyl hydrazine and its derivatives that are highly poisonous and harmful to humans and the environment. In addition, other negatives of CVD are that these chemicals have adverse effect on biomaterials, electrochemical storage device and polymers and these contributes to increase in the cost of production of graphene on an industrial scale[12, 13].

Hence, most recently the biological reduction of graphene through plants extracts and microorganisms are developed as alternative to the use of hydrazine as a natural re-

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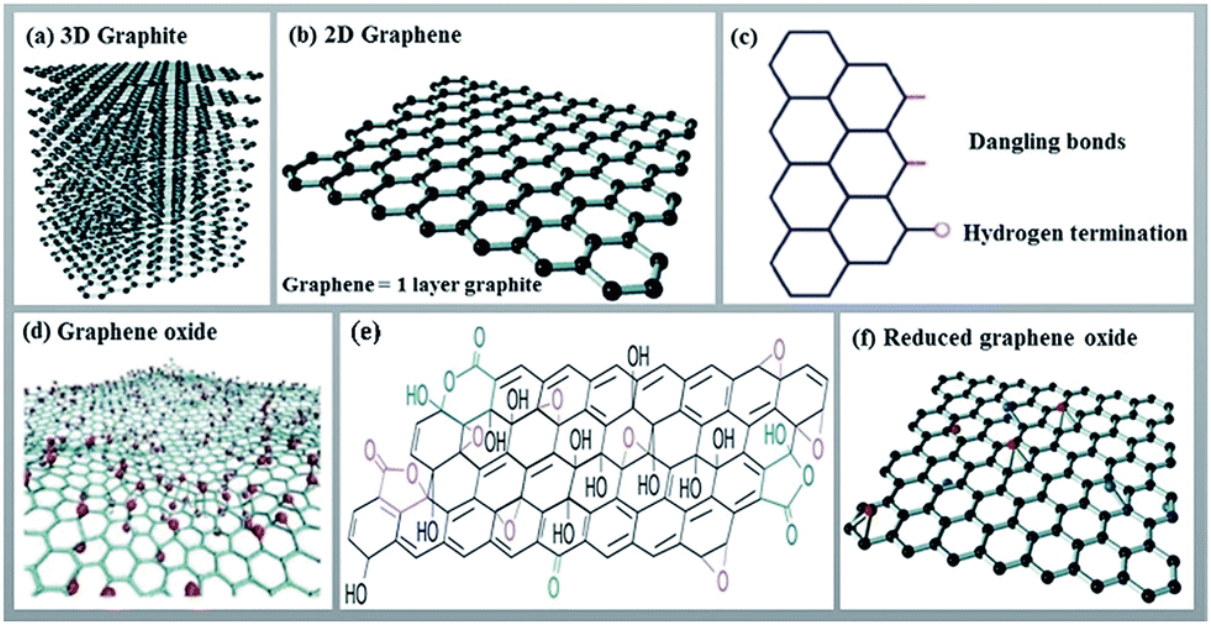

Fig. 1. (Color online) Structures of (a) 3D graphite, (b, c) 2D graphene and its edge, (d, e) graphene oxide, (f) reduced graphene oxide[22].

ducing agent in the reduction of graphene oxide to manufacture graphene on a large scale[14]. Therefore, the report shows that cocos nucifera L. can serve as reducing agent in the green synthesis of graphene (Kartick *et al*., 2013). The thermogravimetric analysis showed that the graphene produced was thermally stable with lower charge density on the graphene surface. It was also determined that phytoextracts have the potential to reduce graphene oxide in an environmentally friendly process with potentials in diverse areas like biomedical applications (Lee & Kim, 2013).

Besides, the preparation of graphene at the macroscale by liquid phase exfoliation to form a graphene oxide (GO) halfway, which is followed by reduction to maintain the graphene structure (RGO). Nevertheless, it was determined that the composition of poor dispersion, sheet defects restacking and multilayer thickness could limit the complete realization of the high surface area and electronic properties of graphene[9]. Therefore, this overview discussed chemical and green methods with their applications on nanomaterials, biomaterials, and polymers. The advantages and limitations of these techniques in producing safe, high quality and cost-effective monolayer graphene in large scale with these techniques are discussed.

2. Production of graphene

Synthesis of graphene is the process of contingent on the preferred purity, size and crystallinity of the individual by-product. Interestingly, the synthesis of graphite was reported in 1975 when Lang showed the formation of single- and multi-layered graphite by thermal decomposition of carbon crystal on platinum substrates but was not classified as graphene owing to lack of techniques on characterization[15, 16].

The challenge was the inability to identify the applications of the by-product and the properties of the layers produced on the crystal planes of platinum were not uniform, this prevented a thorough study on the material in the early days. However, after a long while, in 1997 respectively, it was reported that graphene was grown on a crystal substrates of a transition metals and metal carbides by decomposing hydrocarbon gases at elevated temperature. In addition, in 1999 the physical properties of the edges of graphene were studied by growing epitaxial nano-sized films with a ribbon structure on a Ni substrate by Oshima *et al*.[17]. The success was few and far between during this period not until 2004 when Novoselov *et al*. was credited to have discovered graphene through Mechanical Exfoliation of graphite[18, 19].

Furthermore, the study on graphene synthesis has grown since the early studies of graphene on Pt substrates; this is because it is believed that it can herald the development of next generation electronics and technologies owing to its extraordinary properties[20]. Therefore, its application in novel electronic devices demands high quality large-area single graphene, which can be maneuvered to create complex appliances homogenized into silicon device flows[21]. Moreover, the graphene synthesized by mechanical exfoliation from highly ordered pyrolytic graphite, is recognized as the graphene with the finest electronic properties and highest quality but for large-production, the fabrication method is required and optimized to synthesize size wafer scale graphene (Novoselov *et al*., 2004). The structures of the different forms of graphene are illustrated in Fig. 1[22]. However, herein, the recent progress in the large-scale production of graphene via the top-down approaches, which include reduction and exfoliation methods and bottom-up approach, which include CVD and epitaxial growth etc., are discussed and both compared with green approach in the synthesis of graphene.

However, to circumvent the production of undesirable and toxic by-product with the adoption of sustainable, dependable and environmental approach. The green synthesis of graphene is backed to aid several biological materials like phytoextracts, algae, fungi and bacteria[23]. The plants extracts is an easy and facile process for mass-production of graphene and can also prevent the sizeable aggregation. Therefore, the green synthesized RGO is highly soluble in water and suitable for practical application[9].

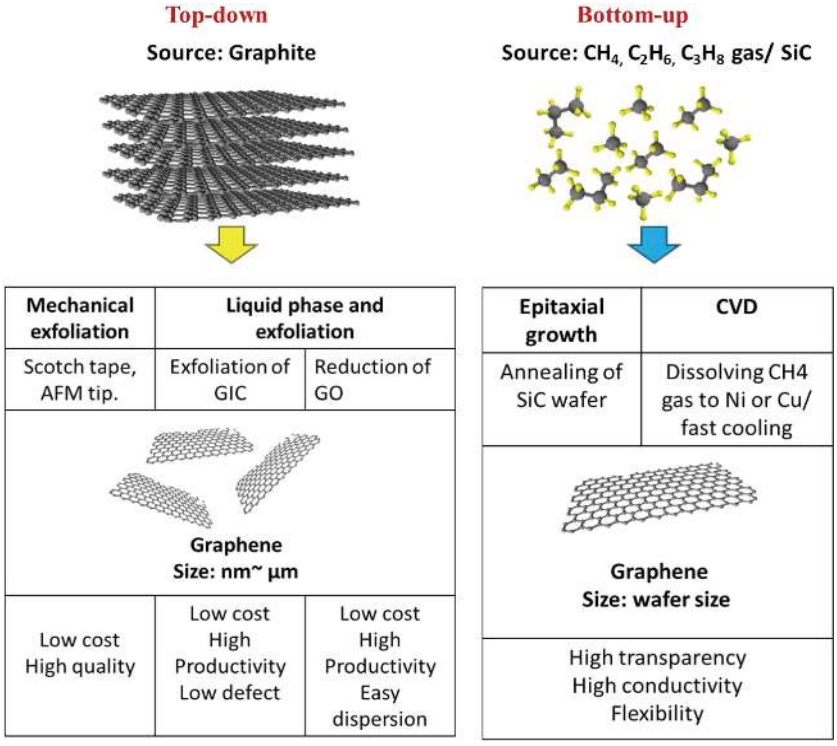

Fig. 2. (Color online) Top-down and bottom-up approaches for synthesis of graphene[23].

2.1. Top-down approach

This is the process of breaking down or reducing graphite into nano sized graphene sheets, which are easily complexed with separate functional materials to produce novel materials[24]. The benefits of top-down methods embody substrate transfer, price effectiveness and high dependability compare to bottom-up approach. Moreover, it has become very important to reduce the gap between research findings and commercialization of products of top-down approach[25]. As illustrated in (Fig. 2), the graphene synthesis is based on two main approaches: bottom-up and top-down techniques[26].

2.2. Mechanical exfoliation

This is the first and one of the most widely utilized method employed to synthesize graphene from graphite, which uses mechanical forces to separate the layers from each other to obtain graphene. However, within the graphite sheets are Van der Waals bonds, which can be broken down when exfoliating graphene using normal or lateral forces[27, 28]. The gap between successive planes was said to 3.35 Å by Coulson in 1961 in his book titled Valence, a value so huge that it can only stem out of Van der Waals forces. In addition, the force required to break Van der Waals bonds is 25% less than the force required to restack graphite layers, and twice less than the force for splitting graphite layers by breaking covalent bonds. However, the exfoliation technique can lead to adhesion in the sheets of the graphite which results in the restacking of the layers rather than separating the graphene layers as exfoliation progresses[29, 30]. In summary, mechanical exfoliation can produce single layer graphene of high quality from highly ordered pyrolytic graphite but this has only been proved in the laboratory and not in production on a large scale. The different mechanical techniques include ball milling, sonication while the adoption sonication as a mechanical wave is the most widely used technique to separate graphite[31, 32].

2.3. Ball milling

Ball milling is an emerging method to fabricate high-quality graphene by breaking down stacked graphite into graphene. Interestingly the ball-milling process was reported to have started about 150 years ago where it was employed in the talc powders, size communications of ore and several other applications. However, in the last two decades, the technique is proposed for the creation of nano-sized particles at room temperature[33, 34]. Hence, it is facile and very effective solid-state method of grinding several materials into fine powders, nanocomposites synthesis and for oxides making it a promising method for mass generation of graphene at low-cost[35]. During milling, the large graphite sheets are subject to shear forces, while normal force is exerted to reduce the graphite flakes into nano-sized materials and present a fault in the basal plane. The milling technique can be done using wet and dry conditions. As shown in Fig. 3 below, Lv *et al.* used Na_2SO_4 salt to create graphene nanosheets with ripple-like corrugations in the hundreds of square nanometers range[36, 37]. In contrast, in the presence of graphite, dry ice, and stainless-steel balls, ball milling was conducted in a planetary ball-mill machine as illustrated in Fig. 4[38]. Hence, the size and quality of the materials produced depend on the media used[36]. However, Zhao *et al.* gave a new outlook to ball milling process by exfoliating graphite into graphene flakes in a liquid medium using wet ball milling. The result obtained revealed a thickness of about 0.8–1.8 nm, which corresponds to discrete monolayer and few-layer graphene (⩽ 3 layers). Hence, this result has encouraged a lot of research activity in ball milling recently[39]. Subsequently, Dash *et al.* also presented a facile, cost effective and environmentally friendly approach for synthesizing graphene oxide from high pure natural graphite flake powder using the new horizontal high-en-

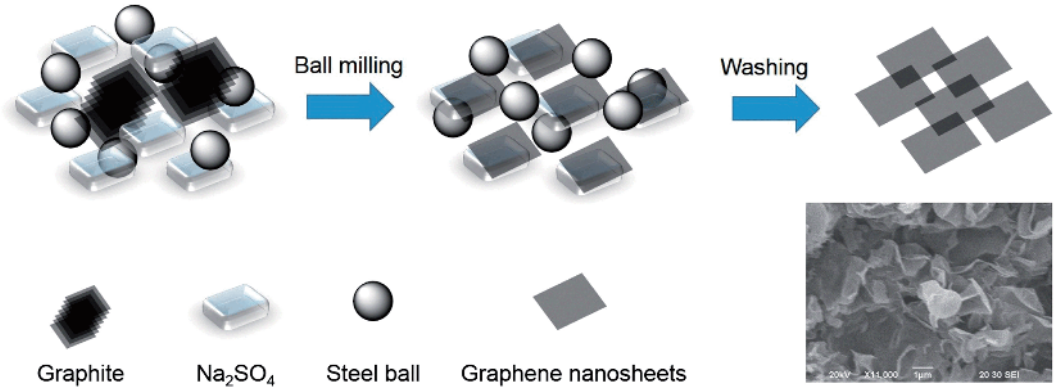

Fig. 3. Schematic diagram of the soluble salt assisted (Na_2SO_4) wet ball milling approach for synthesis of graphene nanosheet powder[36].

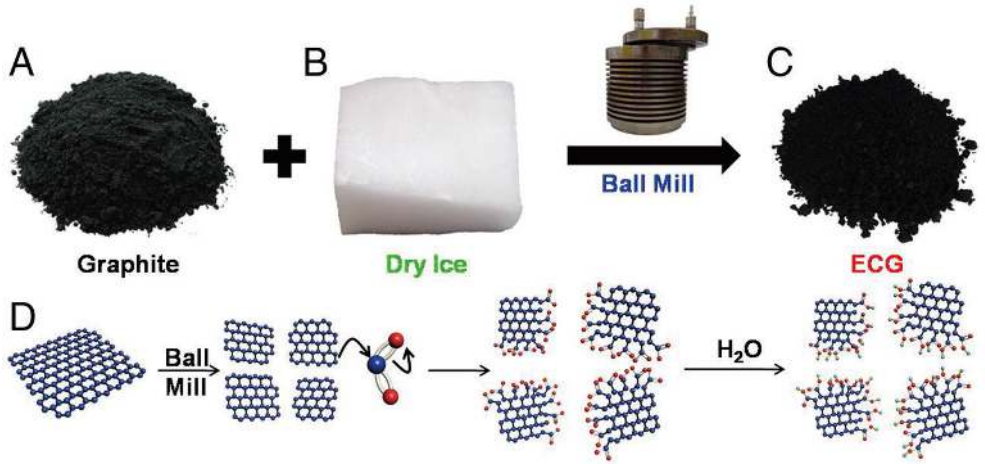

Fig. 4. (Color online) (a) Pure graphene. (b) Dry ice. (c) Edge-carboxylated graphite prepared by ball milling for 48 h. (d) Schematic view of physical cracking and edge-carboxylation of graphite by ball milling in the presence of dry ice, and protonation[38].

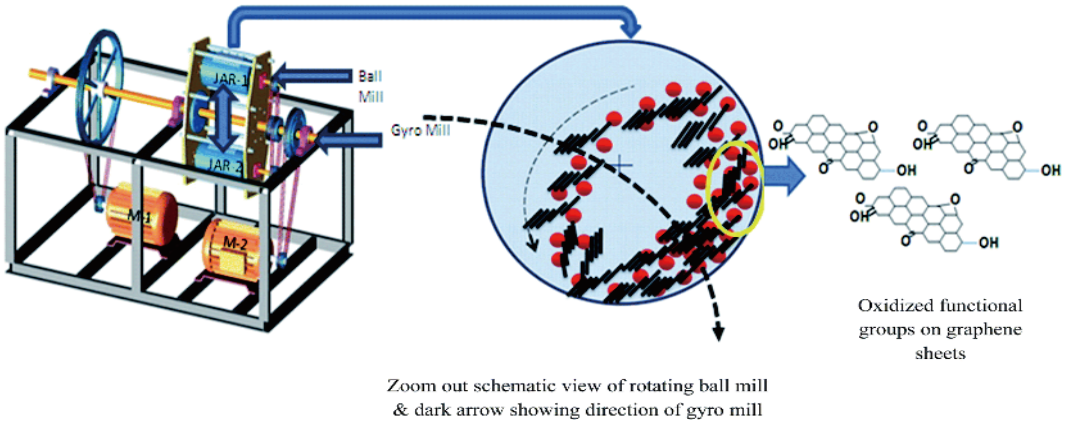

Fig. 5. (Color online) Schematic view: preparation of graphene oxide in laboratory designed ball mill[40].

ergy dry planetary ball milling approach without the use of catalyst or toxic chemicals as schematized in Fig. 5. Here, the specific surface area of the resulting GO samples increased (188.25 m^2/g) as the milling time of the FEED enhances[40]. The sample obtained after 16 h of milling showed better level of oxidation, time and energy usage factors. Hence, as the milling time increases the amount of oxygen increased without changing the structure of the lattice.

In addition, Casallas Caicedo *et al.* reported the oxidation of graphite by the ball-milling method with the aid of potassium perchlorate and purified water to exfoliate graphene from graphite (Figs. 3–5). It was discovered that the degree of oxidation increased as the milling time increases. In addition, the effects of the oxidation were examined based on the grinding time intervals (6, 12, 18, 24, 30 h) in this approach and the obtained samples in the ball milling are compared with the outcome of the Hummers methods. Hence, the sample showed better dispersion and a darker color after 18 h of milling which is due to removal of functional groups like carboxyl, hydroxyl and epoxy[41]. Here, the sample obtained after 16 h of milling is considered the best sample in terms of the level of oxidation, duration and energy usage factors are

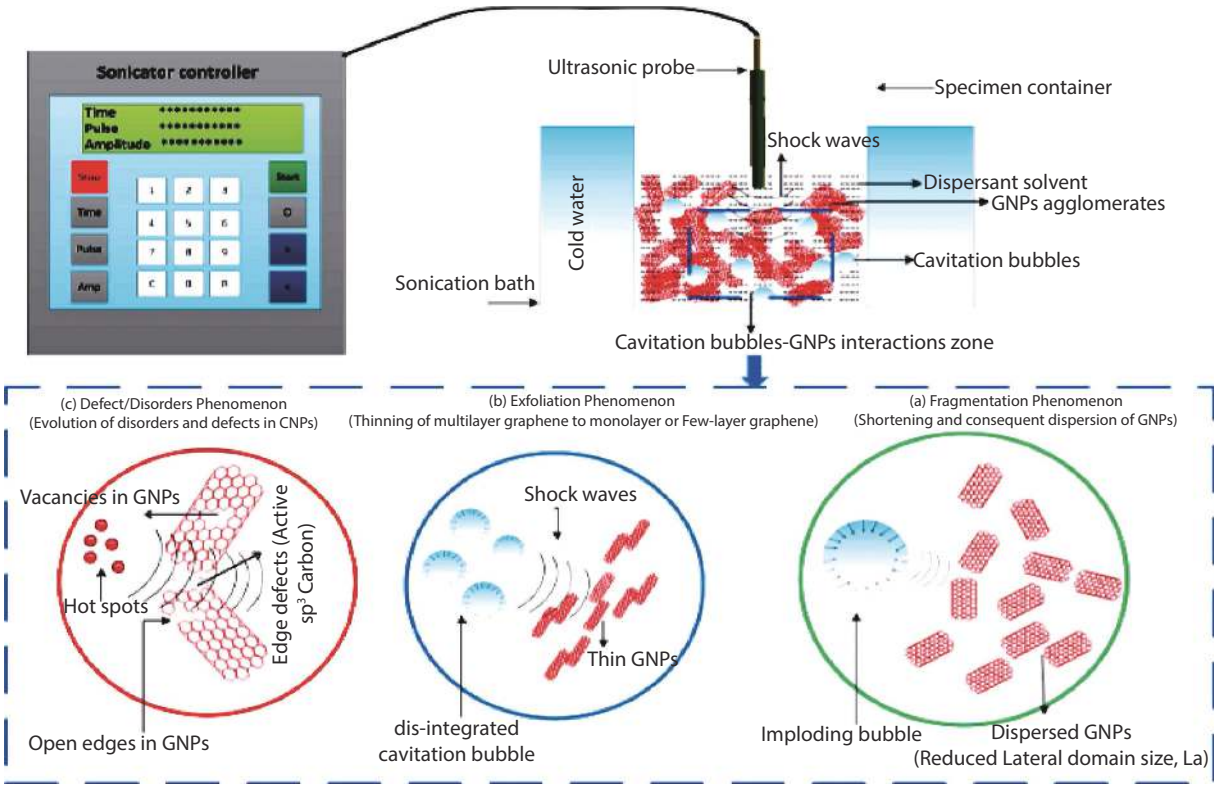

Fig. 6. (Color online) Schematic view of tip sonication processing with parameters that influence graphene nanoplatelets dispersion in a liquid medium with obtained phenomena. (a) Fragmentation. (b) Exfoliation. (c) Defect[46].

examined. Finally, the attractions of the ball milling technique are its ability to produce low-cost and high-quality graphene. It is an effective tool in functionalizing graphene and indulge effective exfoliation. However, the long processing time has greatly contributed to the reduction in the yield of graphene synthesis.

2.4. Sonication

Sonication-assisted liquid-phase exfoliation is an efficient method, which can synthesize mass production of high-quality single- or few-layer graphene[42]. However, sonication is of two types bath sonication and tip sonication. Hence, they are used singly or concurrently to synthesize single- or few-layer graphene. However, the low efficiency and low energy input associated with bath sonication has made it not suitable for large-scale production of graphene. In contrast, research shows that high-power tip sonication method is an efficient or rather by combining shear mixing can scale-up graphene production in a short time though may cause breakdown in the structure of the graphene. There are three phases associated with liquid-phase exfoliation which include dispersion of graphite in a solvent, exfoliating graphite and purification[43]. Coleman *et al.* first investigated this method (liquid phase exfoliation) using a bath sonicator to sonicate graphite in an organic solvent. Sonication occurs because of gap (small sized bubbles) in pressure fluctuations, which acts on the bulk material to create exfoliation[44, 45]. Baig *et al.* investigated tip sonication effects on the characteristics of structural qualities of graphene nanoplatelets by modifying the sonication time and individual energy time at three distinct amplitudes (60%, 80%, and 100%). In their work, graphene nanoparticles were characterized with the aid of Raman spectroscopy (highly sensitive in detecting defects in graphite) to determine the disorders in graphene structures. However, during the dispersion or exfoliation stages, stacked 2D graphene is prone to significant damage, which results in amorphous carbon production and a low aspect ratio of graphene particles, making it unsuitable for reinforcing. Fig. 6 shows a schematic diagram of GNP tip sonication in a dispersing solvent (ethanol) utilizing a high-performance horn sonicator[46, 47]. In addition, as the sonication time and amplitude increase the more graphene nanoplatelets were produced due to increasing effect of the shearing force.

Krishnamoorthy and his group also reported a simple sonochemical method of the reduction of graphene oxide into graphene nanosheets in a small reaction time. However, graphene oxide was reduced to graphene nanosheets, which resulted in the agglomeration of graphene oxide, which inhibits the efficiency of reduction; thereby the removal of oxygenated functional group was not entirely realized. Hence, ultrasonication is used to exfoliate graphitic oxide into graphene oxide, as indicated in Figs. 7 and 8[48]. In summary, the efficiency of the exfoliated graphene nanosheets relies on the sonication time, temperature, liquid medium and the power of the sonication. Scientists to ensure the graphene solution is stable by improving on the dispersion in the graphene sheets have used surfactants. Hence, so far, the downside of this technique is low yield, poor dispersion, high-energy consumption and the use costly layer[49].

2.5. Electrochemical exfoliation

Electrochemical method is increasingly gaining attention in the production of graphene. It is different from wet chemical exfoliation method, as it does not require the use of harmful oxidants[50]. However, a fixed potential applied on a stacked graphitic material force the ions to intercalate into

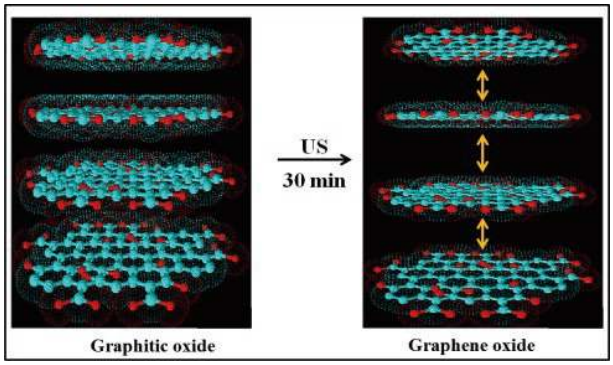

Fig. 7. (Color online) Separation of graphitic oxide by sonication for 0.5 h.

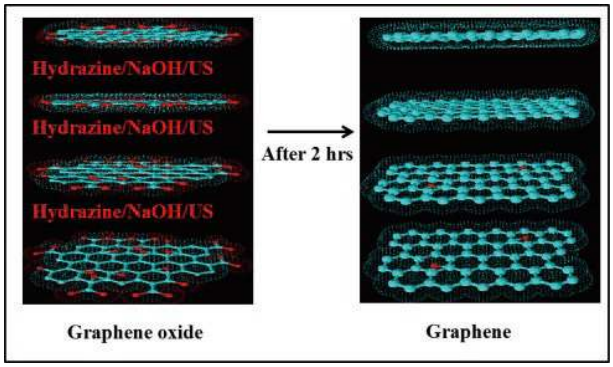

Fig. 8. (Color online) Sonochemical synthesis of graphene oxide into graphene nanosheets in the presence NaOH[48].

graphene layer reducing the Van der Waals forces between the surfaces, which separates, and exfoliate discrete graphene layers. This operation holds in a liquid medium or organic solvents, and it can be pegged in to anodic, cathodic and double-electrode exfoliation that is contingent on exfoliation plate[51, 52]. Pervez *et al.* studied a highly efficient electrochemical anodic exfoliation of graphite in different aqueous inorganic salts which include the following ($(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4). Hence, the oxidation level was reduced which enhanced the chemical and electronic properties of graphene. In addition, this approach is scalable and suggests it can be utilized for large-scale production of graphene because high yield graphene nanoplatelets with large graphene flake size was obtained as shown in Fig. 8[53]. Munuera *et al.* investigated how NaCl (table salt) can be an effective additive (co-electrolyte) based on ordinary sulfate-based electrolytes producing anodically exfoliated graphene with a negligible oxidation (O/C ratio ~ 0.02–0.03) the synthesis of high quality and low-oxidized graphene nanoplatelets with a high structural grade. The resulting low-oxidized graphene showed a remarkable ability to absorb towards organic dyes in a solvent (e.g., ~0.450 g/g for methyl orange), a considerable potential to absorb non-polar substances and non-polar solvents (15–30 g/g) and showed a reliable capacitive energy storage response. In contrast with previous study, this work presents a facile, a relatively cheap with easily accessible materials as a substitute oxidation-inhibiting co-electrolyte[54, 55]. Yang *et al.* presented a cathodic electrochemical technique employing ionic liquid, N-butyl, methylpyrrolidinium, bis(trifluoromethylsulfonyl)imide at room temperature ($BMPTF_2N$) was produced for few-layer graphene layers. The as-produced graphene sheets are majorly two to five layers thick, nonoxidative and are free of defect. Permeable graphene layers obtained by activating few layers graphene layers in potassium hydroxide revealed improved electrochemical process. Hence, it can be utilized in fields like energy conversion and storage[56]. Dalal and his group also presented a new approach on cathodic exfoliation for mass production of graphene nanoplatelets. However, this work still requires further study to improve the properties of aqueous cathodic exfoliated graphene. In addition, a relatively high yield and low defect graphene of ~10–13 layers of high quality ACEGNPs in aqueous solution of alkali metal salt electrolytes with suitable cation size[53]. Li *et al.* presented a new electrolysis to produce high-quality graphene applying a dual foil as an electrode and alternating currents to power the system Fig. 9. This report supported that a decrease in temperature would potentially control free radicals[57]. This approach is really gaining attention in the synthesis of graphene owing to its potential in mass production of environmentally friendly, cost effective and high-quality graphene.

2.6. Bottom-up approach

This approach is a layer-by-layer method that begins with the formation of small molecular carbon atoms to derive graphene. However, epitaxial growth of graphite on SiC, chemical vapor deposition, chemical reduction are the prominent method used[58, 59]. However, these methods use harmful oxidizers or carboxylic acid and organic solvents, which are not ecofriendly. Hence, the use of phytoextracts and microorganisms are viable alternatives employed in this approach due to its green nature and eco-friendly in production[60]. The advantage of bottom-up approach is the controlled thickness of the graphene layer achieved with the aid of separate surface catalysts and growth criteria[61, 62].

2.7. Epitaxial growth on SiC

In this approach monolayer and few layers graphene sheet can be grown by the depletion of the surface of Si on SiC substrates at a high temperature in a vacuum[63]. Howbeit, the nature of the obtained graphene in ultrahigh vacuum is poor due to high sublimation rates at low temperature. Therefore, multiple layer graphene epitaxial layers formed on SiC(0001) face can orient in the 30 phase or the 2 phase with respect to the substrate, as shown in Fig. 9[64]. Badami investigated the graphitization of α-Silicon Carbide that can be trace the method back to as early as 1962. Consequently, Van Bommel and his group presented that low-energy diffraction (LEED) experiments reveal the structure of graphite was crystallized on a hexagonal SiC(0001) surface by $(6\sqrt{3} \times 6\sqrt{3})$ R 30° structure. It was discovered that separate graphitization of the two discrete polar force. The initial state of Si-face produces monocrystalline sheets while C-face produce. Hence, the study could not reveal the presence of 2D crystals[65, 66]. In 2011, De-Heer and his group presented confinement-controlled sublimation method to produce high quality epitaxial single or multi-layer graphene on either the polar faces of the SiC crystal with applications in electronics. The Georgia Institute of Technology initiated this study of graphene electronics: they started and presented a serious pursuit on epitaxial graphene for graphene-based electronics. The method allows that the graphitization temperature to be regulated

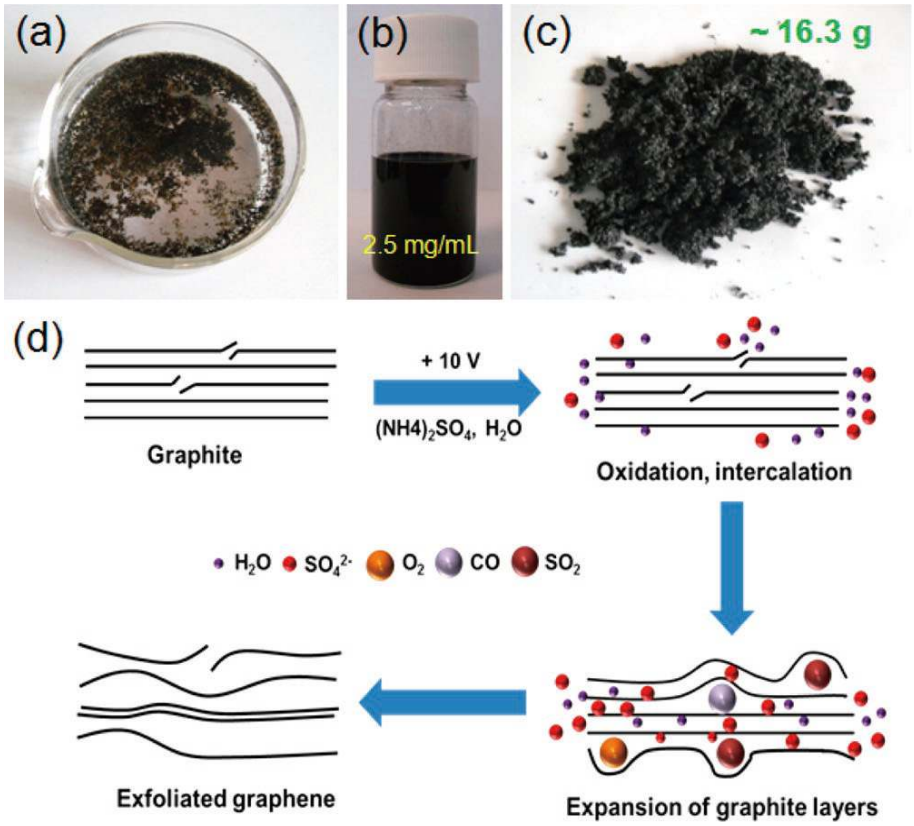

Fig. 9. (Color online) Image of graphite flakes after electrochemical exfoliation. (b) Dispersed EG in DMF solution (concentration 2.5 mg/mL). (c) EG size on a bulk scale (163 g). (d) Diagrammatic representation of the principle of electrochemical exfoliation[53].

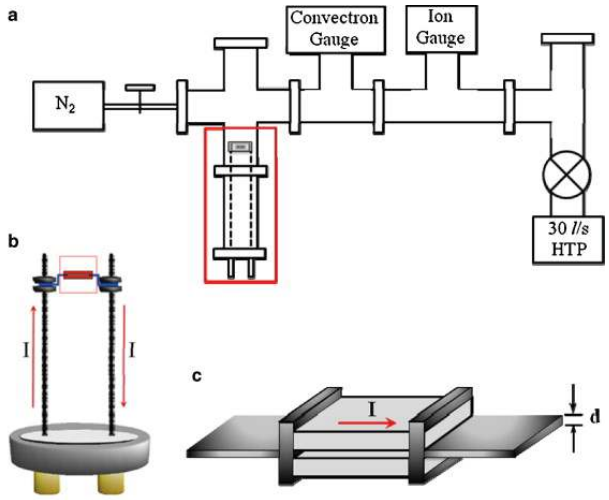

Fig. 10. (Color online) (a) Schematic view of the configuration used for face-to-face growth technique setup; (b) magnified view of the sample set up highlighted in panel (c) enlarged view of mounted SiC substrates highlighted by red lines in panel[64].

which is an improvement to growth at low temperatures plagued with production of defects in the graphene layers. Despite the success recorded in this research, production of graphene-based is yet to be realized[67, 68]. In 2011, Srivastava and Feenstra examined the effect of the annealing environment on the structure, shape and thickness of graphene produced on SiC(0001) surface. The graphene produced via this process can be applied in future electronic devices[69]. Real *et al.* also reported the use of Face-face and face-graphene process, the rate of diffusion is reduced by trapping the vapor between SiC(0001) surface and the corresponding surface in contact. It was discovered that it restricts the sublimation of Si by ensuring the formation of the graphene is regulated and uniform Fig. 10. The results obtained revealed that FTF/FTG approach is essential for producing single-layer EG growth at very high temperature and 101-kPa Ar pressure[70]. Zimbone *et al.* investigated the properties of cubic silicon carbide (3C-SiC) epitaxially produced on a patterned silicon substrate compressed of squared inverted silicon pyramids (ISP). This compliant substrate inhibits stacking faults associated with SiC/Si bond from contacting the surface. Be that as it may, a hole which appear on the epitaxial layer is caused by anti-phase boundaries created at the highest point of the pyramid. Along these lines, it was shown that by controlling the growth parameters permit the reduction of the height of the vacancy and the thickness of APBs, which enhances the SiC epitaxy quality. Howbeit, the thermal decomposition of 3C-SiC should beat the constraints of cost, wafer sizes, and micromachining operations[71, 72].

2.8. Chemical vapor deposition (CVD)

The CVD method is a bottom-up approach and is one of the main techniques utilized for preparing large-area high quality graphene. Graphene is created on surfaces of various transitions metals surfaces for example, Ni and Cu foils used as substrates from different vapor classes as a carbon source through chemical reactions. Optimizing the parametric growth process like energy, pressure, flow of carrier gas has been utilized to regulate the growth process[73–75]. Juang *et al.* are among the earliest, which synthesized single layer graphene (SLG) to few layer graphene (FLG) films by the CVD

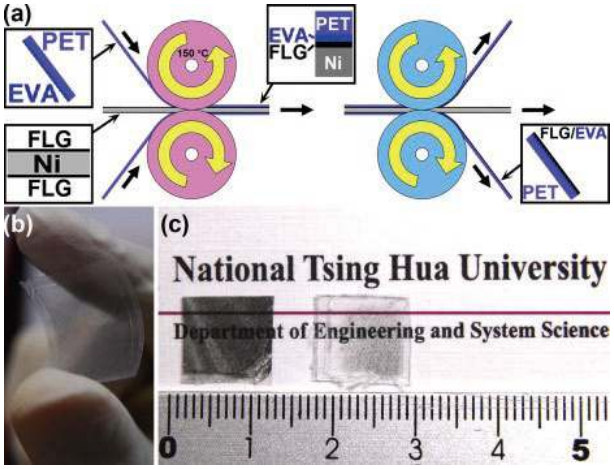

Fig. 11. (Color online) (a) Roll-to-roll process for the transfer of FLG from Ni foil to EVA/PET metal surface[76].

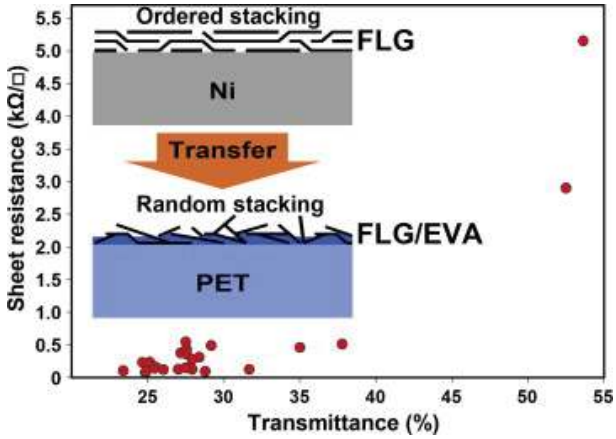

Fig. 12. (Color online) The graph of the sheet resistance versus the transmittance of the FLG/EVA/PET samples[76].

method on Ni foils. The transfer of centimeter scale FLG by means of Ni foil to transparent flexible polyethylene terephthalate substrates using an efficient roll-roll-process[76, 77]. Moreover, the result obtained indicate that regulating the cooling rate of the CVD technique will not be a suitable parameter for controlling the size of the graphene films, because of deposition and precipitation procedure will take place simultaneously in the graphene growth. The roll-to-roll technique for transferring FLG from Ni foil to EVA/PET substrates is depicted in Fig. 10 and a translucent flexible FLG/EVA/PET sample measuring 2 × 3 cm^2 and transferred samples of 1 cm^2 with varied transmittances. In addition, the sheet resistance versus transmittance plot of the FLG/EVA/PET samples is shown in Fig. 11.

In 2011, Hesjedal investigated the continuous growth of few-layer, and potentially single-layer, graphene on Cu foils, which run through an atmospheric CVD system in a roll-to-roll process[78]. Here, Cu was chosen as the substrate material because the low solubility of carbon in copper led to self-limited few-layer graphene growth. Hence, it was determined that the few-layer graphene films on Cu reveal a sizeable scale of few-layer graphene and the process can enable the fabrication of graphene for the diversity of electronics applications.

Zhao *et al.*[79] demonstrated in 2013 that low-pressure CVD on Cu surface from a carbon precursor aside methane and examined the growth of graphene through ethanol and self-limiting behavior over the copper surfaces compared in less than 30 s growth time. The timing used was to keep the framework from yielding multilayer graphene. More so, the choice of Cu here as the catalytic substrate is premise on the low solubility of carbon in copper, which limits the growth of graphene to the outer layer of the material to facilitate yielding of high-quality graphene. The graphene grown on the Cu foil exhibits properties related to that grown on methane under low-pressure conditions. Hence, arrangement of the graphene domains isn't reliant on the structures of the precursor (ethanol and methane) when the carbon flux is moderately low.

In the same vein, Dong *et al.*[80] investigated the growth of Graphene by plasma improved CVD at a low temperature (600 °C). The Ni–Cu alloy was chosen to work on the homogeneity and nature of graphene. The carbon diffusion rate was enhanced with Cu while Ni presented a good catalytic activity. Hence, a uniform and great quality wafer-scale graphene film was obtained from the SiO_2/Si substrate at low temperature (600 °C) due to the enhanced growth parameters and joining them with in-situ growth process. It was likewise found that plasma had a tremendous impact on the nature of

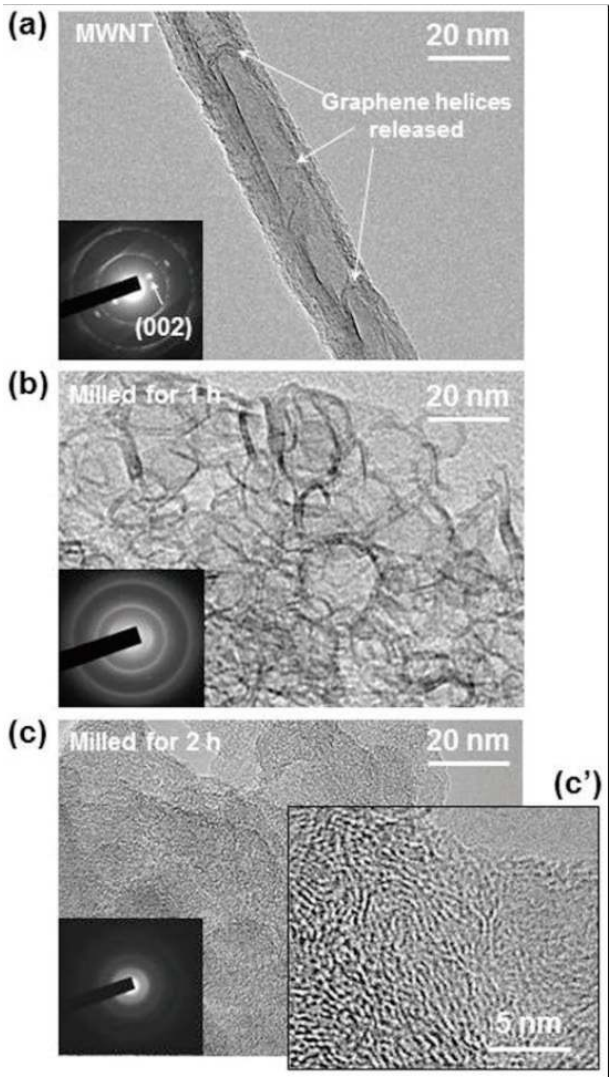

Fig. 13. (a) Pure VCCD-MWNT revealed the graphene helices released from the walls. (b) Milled for 1 h. (c, c') Milled for 120 min[83].

Table 1. Indicating the different graphene produced using CVD method.

Metal surface	Pressure	Temp. (K)	Size & shape	H_2/CH_4(/Ar)	Methods or annealing pretreatment	Mobility ($cm^2/(V·s)$)	Growth time	Reference
Cu foil	LPCVD	1308.15	0.5×10^{-3} m, dendrites	2/1.3	Inside surface of copper-foil enclosures	4000 (e)		[87] (2011)
Cu foil	APCVD	1323.15	~15 μm hexagonal	H_2/Ar, 10/300 CH_4 in Ar 8 ppm	H_2/Ar, 10/ 300 sccm, 1323.15 K, 30 min annealing	$<10^3$–10^4	~0.167 h	[88] (2011)
Cu foil	LPCVD	1350.15	$\sim 2.3 \times 10^{-3}$ m, $\sim 4.5 \times 10^{-6}$ m	70/0.15	High pressure annealing (1500 torr, 500 sccm H_2, 1350.15 K, electrochemical polishing	~11000	2.083 h	[89] (2012)
Ni (111)	UHV	873.15–1073.15	Millimeter size	Propylene ga(C_3H_6)	Ni(111) hetero-epitaxially grown on MgO(111)	–	0.0833 h	[90] (2011)
Cu foil	LPCVD	1273.15	100 μm, six-lobed flower	12.5/1	0.667 h; vapor trapping	4200; 20000 (hbn)	0.5 h	[91] (2012)
Liquid foil	APCVD	1433.15	>100 μm, hexagonal	300/6	200 sccm H_2, 1373.15 K, 0.5 h	1000–2500	0.5 h, 10–50 μm/min	[92] (2012)
Liquid foil	APCVD	1363.15	>200 μm, hexagonal	80/10, CH_4:Ar, 1.99	100 sccm (1.3 H_2/Ar mix) 1090 °C, 0.5 h	–	–	[93] (2012)
Cu foil	LPCVD	1308.15	Centimeter size	10/0.1	0.1 torr H_2, 1308.15, 0.5 h; 1×10^{-3}	40000-65000 (1.7 K); 15000–30000 (r.t)	12 h	[94] (2013)
Cu foil	APCVD	1273.15	25×10^{-3} m diameter quartz		10–15 sccm Ar, 600 sccm for H_2, and 10–50 sccm for CH_4	10–3700 (1273.15)	0.333–0.16 h	[95] (2011)
Cu foil	LPCVD	1308.15	$\sim 2 \times 10^{-3}$ m	10/0.1	Inside surface of Cu tube electroplating	5200	6 h	[96] (2013)
Cu foil	LPCVD	1273.15–1318.15	0.25-inch-wide, 0.002 inch thick	10/315	1010 °C and a pressure of 533.289 pascals with flows of 100 sccm H_2 in both the inner tube were changed to 300 sccm H_2 for the tube gap	25 mm/min (1273.15–1318.15)	24 h	[97] (2015)

graphene created.

Al-Hilfi *et al.*[81] hypothetically examined, from both a thermodynamic and a Kinetic viewpoint, the process of CVD growth on Cu–Ni surfaces. In their work, two temperature was considered in the gas phase, below 800 °C and beyond 800 °C. Earlier in 2006, Somani likewise researched the synthesis of planar few layer graphene (PFLG) films where a camphor pyrolysis on Ni foil[82]. Despite the success recorded in reducing the layers of the graphene the drawbacks are the inability to achieve a monolayer graphene. Furthermore, the method of deposition of PFLG on Ni foils utilized in this work is not appropriate for the fabrication of electronic devices like FET.

Lee and his group[83] successfully synthesized graphene sheets larger than 100 nm^2 in an area realized at a plasma-enhanced (PE)-CVD condition. Multi-wall carbon nanotubes (MWCNTs) were taken for a ball milling process to produce graphene nanopowders. Consequently, the graphene nanopowders are used as the precursor of the PE-CVD process. HRTEM pictures of MWNTs before and after mechanical milling for varied periods of time are shown in Fig. 12. The characterization by electron and diffraction, high-resolution microscopy indicates the presence of high-quality pure monolayer graphene sheets.

Vlassiouk *et al.* examined that large-scale high-quality synthesis can be executed utilizing atmospheric pressure chemical vapor deposition on Cu foil Fig.13. The results show that an atmospheric approach can annihilate the difficulties related with low-pressure CVD process while enabling the development of this innovation to the roll-roll industrial scale graphene generation[84]. Thus, the incombustible nature of the low concentrations of the mixed flow of stock gases (H_2 and CH_4) as the methane source of the atmospheric CVD is an advantage over the low-pressure CVD method. In this work, a 40" monolayer graphene with graphene areas mostly larger than 100 μm was effectively accomplished.

Despite the significant progress with the CVD method to grow graphene on the transition metal surface to produce graphene with high quality, fine grained and better hardness over other coating methods, a portion of the under recorded difficulties endures. The gaseous by-product of the process is for the most part destructive. This is on the grounds that the precursor gases used are highly volatile for it to react with the metal surface, yet it should not be too volatile to transport them to the reaction chamber[85]. It additionally requires high temperature in this manner making it an ineffective method. Thus, the inclusion of plasma in the CVD operation in the production of wafer-sized monolayer graphene films can be accomplished at lower temperature[86]. In this way, the creation of graphene with large and uniform grain size with controlled thickness is fundamental in diverse applications in electronics Table 1.

Fig. 14. (Color online) Image of powder and the aqueous dispersion of graphene oxide (0.5 mg/mL) before (left) and after reduction (right)[104].

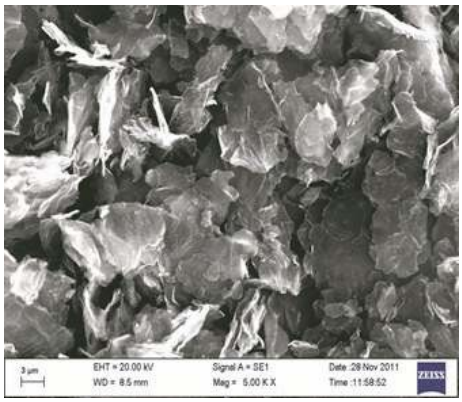

Fig. 15. SEM image of graphite-oxide[97].

2.9. Non-toxic reducing agents

The chemical method in the reduction of graphite oxide (GO) is one of the most important, and generally accepted process to obtain quality and uniform graphene film. Despite this success, the evidence of trace amount of toxic reducing agents in the produced graphene film are harmful to humans and are not environmentally friendly[98]. Therefore, the use of natural reducing agent in the reduction of graphene oxide will serve as a viable alternative, reduce cost and offer a green approach in the synthesis of graphene. As of late studies shows that caffeine[99], melatonin[100], ascorbic acids[101], wild carrot root[102] and amino acid[103] can supplant hydrazine. In lieu of this, the biological reduction of graphene oxide from plants extracts and microorganisms is proposed as substitutes to the chemical methods.

However, the significant qualities of these plant extracts are their superabundance in nature, cost effectiveness with their distinct physicochemical attributes. More so, the plant extracts contain a few carbolic compounds like chlorogenic acids, gallic acids, salicylic acids and vanillic acids etc. The phytoextracts will assist with turning away the accumulation

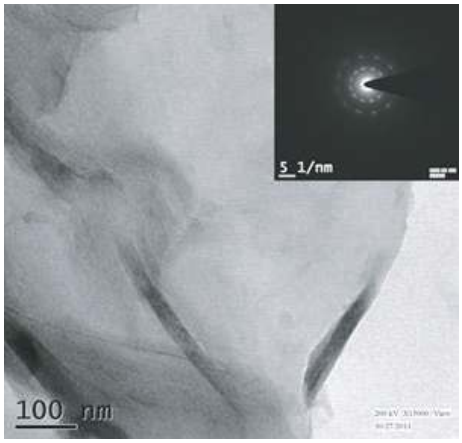

Fig. 16. TEM images of graphite oxide[97].

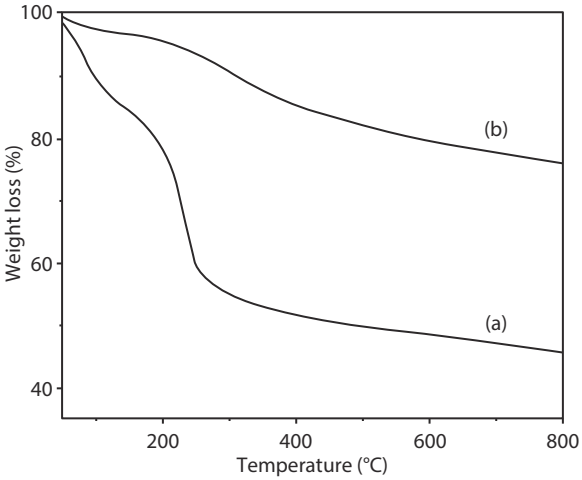

Fig. 17. Plot of thermogravimetric analysis of (a) graphite oxide and (b) graphene[97]

in an aqueous dispersion of the arising RGO through electrostatic repulsion exchange of the negative charge densities of the diverse carboxylic group[9]. The plants-based method is preferred to the microorganisms method because it obliterates the need to have high maintenance cell cultures and can be easily utilized for mass production of graphene[104]. Though the plant-based method is very encouraging, there is no record of optimization of reaction conditions and screening of plants to reduce graphene oxide.

Lee & Kim studied seven plant extracts, which include cherry, platanus, persimmon, magnolia, maple, pine, and ginkgo and compared their potentials to reduce graphene oxide[105]. There was an obvious change in the color of the mixture on reduction of the graphene oxide as schematized in Fig. 13 below. Furthermore, several characterization techniques such as UV–Vis spectroscopy, Raman spectroscopy, FT-IR, XPS, XRD, TEM and TGA established that cherry leaf extract reduced graphene oxide.

In 2011, Kartick *et al.*[14] demonstrated that C. nucifera (cocos nucifera) a natural reducing agent via a green method to produce graphene by reduction of graphite oxide. X-ray diffraction, UV–Vis and Raman spectroscopy was utilized to uncover the formation of graphene. Furthermore, SEM and TEM analyses were used to evaluate the morphology of the sheet, transparent character of graphene as illustrated in Fig. 14 respectively. Furthermore, the thermogravimetric analysis confirmed

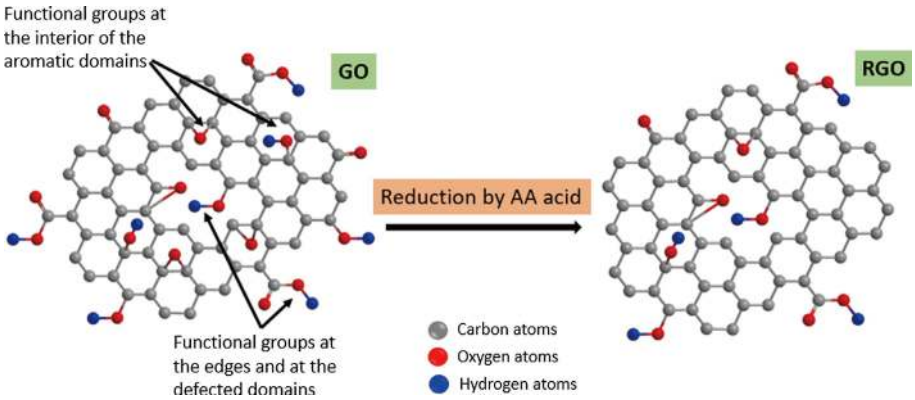

Fig. 18. (Color online) Schematic view of the oxygen functionalities in GO and RGO [108].

Table 2. Different strategies on green synthesis of graphene.

Source	Preparation	Morphology	Advantage	Properties	Application	Ref.
citrullus colocynthis (leaf extract)	RGO was prepared from graphite powder using the modified hummers method	Stabilized reduced graphene sheets	Low cost, facile, green method for deoxygenation of GO.	Sharp diffraction peak increase in interlayer spacing of GO	Anticancer drugs	[110] (2017)
c. nucifera (*cocos nucifera* l.)	Graphite oxide was prepared by oxidation of graphite with a mixture of sodium nitrate, concentrated ssulfuric acid and potassium chlorate	SEM and TEM images showed transparent and stable layers towards electron beam. AFM showed the bi-layer graphene.	Environmentally friendly non-toxic reducing agent	Low surface charge density	Biological materials	[111] (2013)
Plants extracts (cherry, platanus, magnolia, persimmon, maple, pine and ginkgo).	Graphene oxide was prepared using the modified hummers method, which was followed by ultrasonication.	Reduced graphene oxide	Environmentally friendly	Increase in hydrophilicity which was caused by the reduction in polar functionality on the surface of the layers	Biomedical applications	[110] (2013)
Pomegranate juice	Improved hummers method was used to oxidize graphite for the synthesis of graphite oxide and followed by reduction of as-produced graphene oxide by pomegranate juice to form graphene nanosheets	Single or few layer graphene sheets	Facile and green method	Presence of several oxygen containing group in the presence of graphene oxide	Biological and optoelectronics.	[109] (2014)
Ascorbic acid	Modified hummers method	Single layered graphene is 1 nm thick.	Low cost, green and efficient method, naturally available	Removal of oxygen functional group	Water purification	[111] (2017)
Wild carrot root	Modified hummers method	Few layers graphene	Environmentally friendly reduction method, cost effectiveness, simple approach	Partial removal of oxygen functionality	Electronic devices	[112] (2012)
Lime juice (*citrus aurantifolia*)	The oxidization of graphite using hummers method to form GO and then the graphene oxide was reduced where lime was used as the natural reducing agents	Reduced graphene oxide	Low cost, environmentally benign method	The high intensity of the main peak in GO shows a sizeable number of oxygen containing groups, which occur after the deposition.	Biological materials	[113] (2019)
magnifera indica	Mango leaves was cut down into tiny pieces (1–2 cm) and dipped in ethanol	Few layers graphene	Environmentally friendly, scalable, far and green method.	Biocompatible, photostable, excellent cellular uptake, good resolution	Biomedical nanotechnology applications	[114] (2016)

Table 3. Different ways of synthesis for graphene.

Method	Size	Advantage	Disadvantage	Application	Ref.
Epitaxial growth	50 μm	High quality, suitable for electronics	Highly expensive, low yield, wafer size, introduces voids in the transfer process	Field effect transistors, photodetectors	[115,116]
Chemical vapor deposition	0.2–10 μm	High quality and mass production, easy to transfer to other materials.	The use of harmful oxidizer or carboxylic acids, cost of the substrates may be high. The formation of graphene via high temperature on metal surface.	Electronics: light emitting diode, biosensors	[117,118]
Green synthesis	200–800 nm	Low cost, facile (simple), Green method for deoxygenation of GO, reduces waste, the use of harmless solvent, suitable for large scale production of graphene nanoparticles, high temperature and pressure are not required, environmentally friendly		Dye removal, electrochemical storage, Photocatalysis	[119,120]
Mechanical exfoliation	5–10 nm	Cost effective, high quality graphene layers and laborsaving	Low yield, defects and in the flakes produce are inconsistent.	Space protection, energy	[121,122]
Electrochemical exfoliation	2–3 nm	High quality single layer	Difficulty in removing the surfactants molecules, inconsistency in the produced graphene layer	Supercapacitors, batteries	[118,119]

that graphene was all the more thermally stable when compared with graphite oxide. The schematic diagram of the thermogravimetric study of graphite oxide and graphene in a nitrogen atmosphere is shown in Fig. 15. Thus, the graphene produced through this method gives incredible significance to different applications mostly in bioelectrical materials.

The deoxygenation of GO by means of C. Colocynthis leaf extract polyphenols as a reducing agent was presented by Zhu *et al.*[106, 107]. The change in the color of the suspension from brown to black in their study indicates successful removal of oxygen from GO. The different imaging techniques employed (Raman spectra, XRD and XPS data) affirmed the effective deoxygenation of GO. The plant extracts played an important role to stabilize and prevent the aggregation of reduced graphene oxide nanosheets. In addition, the cytotoxicity tests confirmed that synthesized RGO can be used as anticancer agent and cytotoxicity does not rely on the dose. Henceforth, the method revealed the commercial production of RGO in an environmentally friendly approach using plant extracts Fig. 16.

Besides, De Silva *et al.*[108] studied the production of graphene oxide by oxidizing natural graphite and ascorbic acid. The outcome demonstrates the graphite was successfully oxidized to vastly oxygenated and exfoliated layers. The different characterization techniques (AFM, XPS) employed in this study shows the presence of residual oxygen functionalities. Nonetheless, XRD results show an absolute removal of the GO peak after 50 min[123]. The types of oxygen functionalities existing in the GO and RGO is schematized in Fig. 17 below. In synopsis, this study provides a green, savvy and scalable way in the synthesis of quality graphene from natural graphite with ascorbic acid Tables 2 and 3. Furthermore, Tavakoli *et al.*[109] effectively synthesized graphene nanosheets with pomegranate juice where the pomegranate juice acted as both a reducing agent and a capping agent to form graphene nanosheets Fig. 18.

3. Conclusions and perspective

The carbon material 'graphene' has gained significance in the field of micromanufacturing, nanomaterials, biomedical, and composite materials owing to its high surface area thermal, electronic and physical properties. Be that as it may, the mass production of graphene for its wide range of applications rely on the production techniques and attracted with significant attention recently. Therefore, optimizing the production method is vital for expanding the yield, producing high quality graphene and most importantly adopting facile, cost-effective and environmentally benign method is the way forward. Hence, future study should be fixed on working with the measure of yield, biocompatibility as the use of poisonous chemicals, high energy, pressure and poor transfer process in chemical approaches that have contributed significantly to high-cost of production, poor yield and imperfections in the obtained graphene. All things being equal, the headway of novel methods and green sources is essential for synthesis of graphene materials in electronics, nanomaterials and biomaterials. The production creation methods and carbon sources are important in determining the size, morphology and optical characteristics of the obtained material. In a nutshell, despite myriads of research on the production of graphene since its discovery, none of the approaches fully satisfy its production on an industrial scale. This overview provided a comparative study as well as possible applications of graphene and discussed the potential methods.

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