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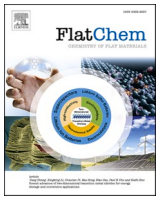

A critical review on vacuum and atmospheric microwave plasma-based graphene synthesis

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ABSTRACT

Nanotechnology has brought about a paradigm shift in material science, opening a wide range of potential applications in daily uses. Graphene is one of the most important nanomaterials that have applications in electronics, optoelectronics, energy storage, health care and aerospace industries due to its unique and remarkable properties. However, the synthesis of graphene since its discovery has encountered numerous struggles and each method has its advantages and shortcomings. Plasma-based synthesis of graphene, utilising various sources such as radiofrequency (RF) plasma, direct current (DC) plasma, and microwave (MW) plasma, stands out as a promising method due to its controllability, flexibility, and scalability. Among these, microwave plasma-based synthesis is gaining rapid popularity. This method, applicable under both vacuum and atmospheric pressure conditions, offers numerous advantages over other techniques, further enhancing its appeal in the field of graphene production. However, a comprehensive assessment of these methods in terms of equipment, process parameters and their effects on graphene production and quality has not been reported. Therefore, this literature presents a clear comparison of these methods along with the future outlook.

1. Introduction

Carbon is an abundant element on earth and exists in various types of allotropes. Carbon allotropes exist in different dimensions, sizes and shapes. Carbon dots, single-walled carbon nanotubes, graphene and diamond are a few to describe and they belong to zero, one, two and three-dimensional carbon nanostructures respectively [1]. Among carbon nanostructures, the graphene family constitutes an important class of compounds widely utilized in both research and industrial sectors. The graphene family of materials comprises not only pristine graphene but also graphite oxide, graphite, reduced graphene oxide and graphene oxide. Each member of the graphene family of materials comprises a variety of properties and structures. These differences in their structure and properties make them prospectively valuable materials [2]. Pristine graphene among the family of graphene materials is an emerging research topic.

Graphene is regarded as a 'wonder' material because of its myriad properties. This nanomaterial has outstanding electrical conductivity, extraordinary thermal conductivity, exceptional mechanical strength, biocompatibility, quantum hall effect, variable optical properties, and a high surface-to-volume ratio. Graphene exhibits distinctive electronic characteristics and is acknowledged as the best thermally conductive material currently identified [3,4]. This material has flexible surface properties, resistance to harsh chemicals and high temperatures [5]. Moreover, graphene is the strongest and thinnest material known so far [1]. Graphene is a single layer of graphite with a two-dimensional array of sp^2 hybridized carbon atoms. They also have a honeycomb-like structure and are hexagonally arranged [2,6]. The bond angle between them is 120° and the carbon–carbon bond length is 0.142 nm [7]. Owing to these exceptional properties and structure of graphene, it is widely used in a broad application spectrum such as in electronics, optoelectronics, photonics [8], energy storage [9], health care [10] and aerospace [11].

The journey to the fabrication of graphene commenced in the 1840 s with the synthesis of graphite oxide using various methods such as Hummer's, Brodie's, and Staudenmaier's methods [12]. A pivotal moment unfolded in 1970 when a single layer of graphite was created by segregating carbon on a nickel substrate [13]. The term 'graphene' was

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proposed by Boehm and co-workers [14] in 1986 to describe a carbon monolayer, resembling graphite. The International Union of Pure and Applied Chemistry (IUPAC) officially adopted the term 'graphene' in 1997, declaring its usage exclusively when discussing the reactions, structural relations or other properties of a single layer [15]. An impactful breakthrough in this field occurred in 2004 when Geim and Novoselov significantly advanced material science by isolating graphene through the micromechanical cleavage of graphite. For this incredible discovery, they were awarded the Nobel Prize in Physics in 2010 [16].

Since the breakthrough in graphene, several methods have been adopted for graphene synthesis, broadly classified into top-down and bottom-up approaches. As the name suggests, a top-down approach is a destructive synthesis in which the bulk material is brought to its simpler units by different means. It involves graphite as the starting material, which is then exfoliated or reduced. In comparison, the bottom-up approach is a constructive process that mainly depends on the - assembly of atoms and molecules together to form the bulk material. The bottom-up involves using precursors such as hydrocarbons or natural resources for graphene preparation [17,18]. The top-down method has limitations such as poor-quality graphene, use of toxic chemicals, long processing time and low production rate. However, the bottom-up method is the most widely used due to its advantages such as scalability, efficiency and the production of large-area, high-quality graphene.

This review compares two different bottom-up methods such as microwave plasma-based synthesis of graphene in vacuum and atmospheric conditions. The instruments used, the process parameters, and the quality of the synthesised graphene all differ among these techniques. This review can be classified into different sections. Section 1 introduces graphene with its properties and structure. Section 2 gives an overview of the several methods used in graphene synthesis since its discovery. Section 3 explains the microwave plasma-based synthesis of graphene in vacuum conditions and the factors influencing the synthesis. Section 4 describes the atmospheric pressure microwave plasma method of synthesising graphene and its influencing factors. Section 5 explains the structural differences of graphene synthesised in both techniques. Section 6 is a brief section that details on the carbon footprints in graphene synthesis. Section 7 concludes by comparing both techniques. Lastly, section 8 ends with the future perspectives.

2. An overview of graphene synthesis techniques

The important graphene synthesis techniques used in the literature are shown in Fig. 1 and following this, a brief introduction to these different techniques is given.

Micromechanical or mechanical cleavage is one of the key methods for the synthesis of graphene using scotch tape from highly ordered pyrolytic graphite (HOPG). Mechanical exfoliation has a simple mechanism. Breaking the van der Waals forces with a shear force or nominal force between the graphene layers of a bulk precursor [16,19]. The produced graphene maintained not only high quality but also a large surface area [20,21]. This method is labor-centered, time-consuming, and unsuitable for commercial production [21,22].

Another method that scientists employ to create graphene from graphite is chemical exfoliation via intercalated compounds. This is mainly a two-step process, which includes increasing the interlayer distance and forming intercalated compounds followed by strong heating or sonication. The introduction of alkali metals can decrease the van der Waals forces of attraction in graphitic solution and hence increase the interlayer separation because of the difference in ionization potential between the graphite and alkali metal [23–25]. Alkali metals such as potassium (k) [23], sodium–potassium alloy (NaK_2) and cesium (Cs) [26] were used for intercalation.

Chemical exfoliation progresses in two ways, supercritical fluid exfoliation and liquid phase exfoliation. The major difference between the two methods is that in the former the forces of attraction are overcome by sonication whereas, in the latter, there is penetration of fluid to graphitic layers [24]. This method has one major limitation of reassembling back to graphite. This has led researchers to the incorporation of immiscible liquids like heptane and water and the use of surfactants [27,28].

Two-dimensional nanosheets like graphene can be successfully prepared by using electrochemical exfoliation. This technique creates monolayer or few-layer thin nanosheets by broadening the structure and disrupting weak interlayer connections using a liquid electrolyte and by a redox potential [29]. This method consists of five types of electrochemical exfoliations namely anodic exfoliation [30], cathodic exfoliation [31], simultaneous dual electrode exfoliation [32], alternative intercalation [33] and multistep intercalation [34]. The thickness and lateral dimensions of the graphene film, as well as its physical and chemical characteristics, can be controlled by adjusting the electrolyte, bias, and exfoliation time. This is a simple, effective, and inexpensive way to prepare graphene [35].

One of the traditional approaches for synthesizing graphene is the chemical reduction of graphite oxide. For instance, Brodie's method [36], Staudenmaier's method [37], and Hummer's method [38] are used to produce graphitic oxide. These methods utilized oxidants and strong acids such as potassium permanganate, nitric acid, and concentrated sulphuric acid in their synthesis technique. After oxidation, graphitic oxide is reduced to graphene or graphene oxide depending on the reaction conditions. The reduction of graphitic oxide to graphene is obtained by using hydrazine or dimethyl hydrazine in the presence of a surfactant or a polymer [39]. The other reducing agents used in this process are ascorbic acid [40], hydroxyl amine [41], sodium borohydride [42] and hydroquinone [43]. When compared to Brodie method and Staudenmaier method, Hummer's method is more efficient, quicker, and safer. The production of hydrophilic and highly oxidation-efficient graphene-based products is a significant benefit of the modified Hummer's process. This method has been modified by Marcano et al. [43] and is widely used in synthesizing graphene oxide. The production of hydrophilic and highly oxidation-efficient graphene-based products is a

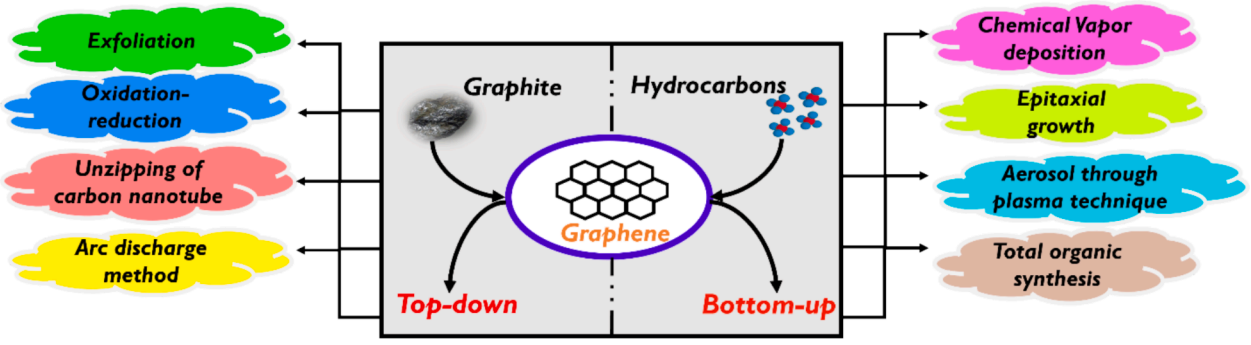

Fig. 1. Various top-down and bottom-up techniques for graphene synthesis.

significant benefit of the modified Hummer's process.

Thermal reduction, hydrothermal reduction, photochemical reduction, microwave-assisted reduction, chemical reduction, and electrochemical reduction are some synthesis techniques used in the production of graphene. Chemical reduction is the best method to remove most of the functional groups that are present in the graphene oxide and thus create the desired product, graphene. Yet, there might be a defect in the electronic structure of graphene due to the functional groups like carboxylic and hydroxyl groups. This affects the electrical conductivity of the produced graphene [44].

Single or few-layer graphene can be obtained by the axial or longitudinal incision of cylindrical carbon nanotubes (CNT). Either multi-walled (MWCNT) or single-walled carbon nanotubes (SWCNT) can be used in this process. Chemical unzipping, intercalation and exfoliation, metal-catalyzed cutting, and plasma etching are some of the methods used to unzip CNT [45]. By adopting the appropriate type of nanotube, the size of the graphene nanoribbon can be modulated. It is a flexible approach to graphene synthesis, but it has certain drawbacks that prevent it from being used. Significant drawbacks of this process include the high cost of precursor and chemicals, oxidation and defects along the splitting edges [46].

Chemical vapor deposition (CVD) is a bottom-up process and is the most adapted method for the synthesis of graphene with better quality. The synthesis of graphene occurs in a substrate via solid, liquid and gas precursors. Different kinds of CVD promise large-scale production and high-quality graphene such as atmospheric pressure CVD (AP-CVD), low-pressure CVD (LP-CVD), plasma enhanced CVD (PECVD), and thermal CVD (T-CVD). Bio-based precursors are also utilized in the production of graphene in addition to chemical precursors. The precursor must be in its gaseous state before contacting the metal substrate. The control over thickness is a challenging task when synthesized using transition metals with strong carbon solubility because of carbon diffusion and multilayer product development; in contrast, homogenous graphene films are produced by employing transition metals with low solubility, such as copper [47,48]. Apart from the transition metals, metal alloys like Cu-Ni, Ni-Au and dielectric substrates are also used in various processes [49].

Graphene of high quality with consistent thickness and greater area can be produced by the epitaxial growth technique. Surface depletion of silicon carbide (SiC) is the primary process involved. A carbon-rich surface is left behind during SiC annealing. Due to the high vapour pressure of Si, it first desorbs from the substrate [50]. This is followed by the graphene growth called epitaxial layers. The produced graphene can be applied to a wide range of devices, including integrated circuits, radio-frequency transistors, field effect transistors, and sensors. The challenge faced in this technique is to control the layer thickness as it requires an ultra-high vacuum. Another limitation of this method is that it must have a very high annealing temperature and high Ar pressure which will also be a threat to safety concerns [51].

The total organic synthesis capitalizes on the structural resemblance of polycyclic aromatic hydrocarbons (PAHs) employed in the synthesis of graphene. PAHs, with their dimensions falling between the molecular and macromolecular phases, also exhibit 2D graphene segments comprised of carbon atoms with sp^2 hybridization [52]. By employing H_2 gas-free self-assembly of PAHs with different motifs, such as coronene, pentacene, and rubrene, Wan et al. [53] were able to construct large-area and low-defect graphene sheets. On Cu foil, the graphene was synthesised under extreme vacuum. The graphene derived from coronene has the best results when compared in terms of quality, with a carrier mobility of $\sim$ 5300 $cm^2V^{-1}S^{-1}$. Different reactions that occur at the Cu surface are precursor decomposition, diffusion of gas into the surface, nucleation, growth of island and island coalescence [54]. This method of graphene synthesis demonstrates good advancement yet the side reactions that occur simultaneously retard its use in commercial applications [52].

2.1. Plasma-based graphene synthesis

Plasma-based synthesis of graphene offers several advantages when compared to the other techniques. Plasma can be formed from any material. This free-choice of selection of the carrier medium makes this method novel when compared to other conventional synthesis techniques. Plasma-based synthesis of graphene is a rapid and facile process which can use renewable feedstock that makes this method cost-effective and eco-friendly [55]. In the plasma-based CVD technique, graphene is mostly synthesized under low-pressure circumstances. This technique uses a variety of plasma sources, including direct current (DC), microwave (MW, 2.45 GHz), and radio frequency (RF, 13.56 MHz) plasma. The plasma-based approach for graphene production has been widely used. The other derivatives including diamond films, carbon nano-tubes and nano-walls can also be synthesized by this method [56].

Controllability is one of the notable advantages of using DC plasma. The geometry including the shape, size and thickness of the graphene synthesized can be varied [57]. The temperature of the system must be sufficient to transform the solid material into gaseous form. In the next step, the precursor in the gaseous form interacts with highly excited particles such as radicals, ions and electrons. This interaction leads to the formation of gaseous products. In the final step, these gaseous intermediate products condense to form the desired product. The size, shape and composition of the synthesized graphene depends on the rate of cooling [58].

The atmospheric pressure microwave plasma (APMP) method is an emerging bottom-up method that is used in the synthesis of graphene. The highlight of this technique over other methods is the capability of synthesising self-standing graphene. The temperature and atmospheric pressure conditions inside the plasma facilitate the growth and nucleation of graphene without the need for external heating of the system [59]. Edward et al [46] reported that the plasma temperature in an APMP method will reach around 3000 K. At that temperature, they decompose and nucleate to form graphene. This method allows the synthesis of graphene sustainably within a short time without any post-treatment to the synthesised material. The graphene-metal nanocomposites and heteroatom-doped graphene can also be prepared effortlessly using this method. Owing to these reasons it can be used as the best method for graphene synthesis [60]. This method is mainly dependent on certain factors such as microwave power, precursor and plasma gas flow rate and the reactor type which will be explained later in this review.

RF-PECVD method of graphene synthesis was first developed in 2004 by Hiramatsu et al [61]. This method provides mainly two ways for energy generation such as capacitive coupling and inductive coupling. RF-PECVD helps in the production of vertical graphene [62]. RF plasma reactors mainly composed of four major parts which includes a generator, vacuum system, gas passage system and a heating chamber. One of the major advantages of RF plasma is the large volume of plasma and high energy density [63]. Owing to the high density of RF plasma the deposition and the etching of the materials takes please simultaneously. The high quality graphene can be synthesised if there exist an equilibrium between the etching and the deposition of the materials [64].

The arc discharge method is also a typical plasma-based method used for producing defect-free graphene. The system consists of a reaction chamber where an anode and a cathode are immersed in a liquid or a gas medium. A high-temperature plasma is created when an electrical current is applied which dissociates the medium [65]. The factors that determine the quality of graphene are precursor composition, reactor type and design, discharge density and pressure of buffer gases [66]. High-purity polyhedral graphite particles and multi-walled carbon nanotubes (MWCNTs) were collected from the cathode deposit. In contrast, nano graphite particles, pyrolytic graphite, and MWCNTs can be found in the anode deposit. Consequently, distinct growth methods are applicable for the deposition of these carbon structures on the arc reactor's anode and cathode sites [67]. The energy-intensive

characteristics of arc discharge synthesis and the high accuracy needed for process control may make graphene production less scalable. However, considering the recent advancements, graphene might be produced via arch discharge at a reasonable cost [52].

3. Microwave plasma-based synthesis of graphene under vacuum

Thermal CVD technique requires a catalytic substrate which must be heated to about 1000 °C for a long time to synthesise graphene. When compared to the thermal CVD, this method is more advantageous as it reduces the need for high temperatures and graphene can even be synthesized on a plastic substrate that can withstand temperatures of plasma [68,69]. In a plasma-based CVD system, the electrons undergo inelastic collision with the precursor to form different plasma species. These plasma species have a great role in forming graphene on the substrate. It has been reported that direct nucleation is possible for the synthesis of graphene when microwave plasma is used along with methane precursor as they have high carbon dimer density [70]. Plasma-enhanced chemical vapor deposition (PECVD) has yet another advantage the plasma can control the physical properties like spatial orientation and density that determine the order or pattern of the synthesized nanostructures [71,72]. Plasma enhances the delivery of the precursor forming a chemical potential gradient leading to the growth of film. The temperature decrease in PECVD facilitates the surging of the diffusion coefficient of the atoms into the substrate and also decreases the bonding energy [73]. Moreover, the rapid synthesis and low temperature make this method more convenient [72]. Microwave plasma can be coupled with metal substrates that aid the synthesis of graphene. This can lead to the synthesis of high-quality graphene more easily [74].

The mechanism of graphene formation can be classified into three steps as depicted in Fig. 2. The hydrocarbons dissociate into its components and are absorbed onto the surface [68]. The first step is the graphitic layer formation on the substrate. However, due to internal collisions and plasma temperature, cracks will be formed between the layers [75,76]. The cracks formed will grow like a curl towards an upward direction as the time of growth increases. This is due to the defect and strain on the cracks formed. Secondly, graphene nucleates from the curled cracks and grows vertically. During this step, the direction of the growth of graphene changes to vertical from parallel. In the final step, the carbon radicles will be deposited at the sides of the freestanding graphene. This growth is due to the formation of intermediate species such as carbon atoms or radicals and hexagonal rings which are formed due to the dissociation of the precursor in the microwave plasma. The first two steps occur within 30 min, whereas the third step takes a few minutes. The mechanism of the formation of graphene on the substrate is dependent on the properties of the substrate. An amorphous carbon layer will be formed between the graphite base layer and substrate if the lattice parameters of the substrate and graphite differ. Another possibility is that, if the substrates have any stable carbide, they will be formed first as a buffer layer. This carbide layer formation helps in the strong interaction of graphene flakes into the substrate [68,77].

3.1. Factors affecting the synthesis of graphene

3.1.1. Precursor and plasma gas

The properties of plasma and synthesized graphene are mainly dependent on the precursor or feedstock. In literature, many precursors have been employed for the synthesis of graphene under vacuum using microwave plasma-based chemical vapor deposition (MW-PECVD). One of the most used precursors is methane [78–80]. The precursor is fed into the PECVD system with the help of carrier gases like argon or helium. This not only aids in the plasma excitation but also helps in diluting the precursor reaching the plasma mouth. When the precursor reaches the plasma it starts to interact with it forming carbon radicals leading to the formation of graphene [74].

Large-area graphene was synthesized on non-conductive substrates (glass and quartz) using acetylene (C_2H_2), Ar, H_2 along with CO_2 [81]. Adding CO_2 to the system helped in the smooth graphene film growth by removing the cross-linkers between the graphene flakes. The addition of NH_3 to C_2H_2 in the fabrication of graphene helped in increasing the quality of graphene as well as in the reduction of defects. It was noted that NH_3 assisted in the production of atomic hydrogen easily by thermal degradation at 650–750 °C. However, the addition of H_2 which is more stable than NH_3, which will reduce the amount of hydrogen produced thus compromising the quality of graphene [82].

The effect of gas ratio in graphene synthesis was studied and it was found that the gas ratio determines the nature of the material formed. When the gas ratio of CH_4 and H_2 is 1:4, it exhibited an amorphous character while this was changed to crystalline behavior when the ratio was increased to 1:8. This may be because the precursor interacting with the plasma gets diluted when the rate of carrier gas increases. This helps in forming the crystalline graphene [79]. The effect of gas ratio on the quality of graphene synthesized is illustrated in Fig. 3a. The selection of the optimum gas ratio will enhance the quality of the material. When the gas ratio is 1:8, it exhibits a sharp D peak, G peak and 2D peak when compared to the other gas ratios. Graphene was also synthesized using CO/H_2 in different study and found that the structure and morphology of the graphene will be dependent on the CO/H_2 ratio [83]. This implies that the precursor and the carrier gas determine the quality of graphene formation.

The effect of the rate of flow on the morphology of graphene was examined. A household microwave system was used for the synthesis of 3D cauliflower-shaped graphene clusters from methyl formate ($C_2H_4O_2$) along with Ar and H_2. As the flow rate of $C_2H_4O_2$ decreases and Ar increases, there is a development of porous nanostructures leading to flower-like structures. As described earlier, this may be due to the easy dissociation of the precursor on increasing the Ar flow. Fig. 3b shows the SEM images of graphene in various flow rates of the feed gas [84]. It is apparent that on increasing the Ar flow, the 3D morphology of the material appears prominent.

Polyethylene was another feedstock used in the synthesis of graphene. However, the use of polyethylene imparted greater defects which were evident from the Raman spectrum of the sample. In addition to that, there was a blue shift for the G band due to the thickness and defect

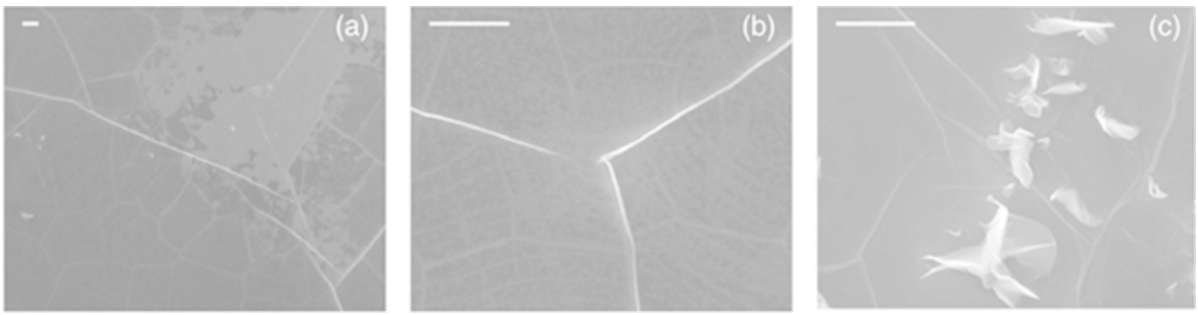

Fig. 2. Three-step mechanism of graphene formation. The scale bar in the figure corresponds to 1 μm [77].

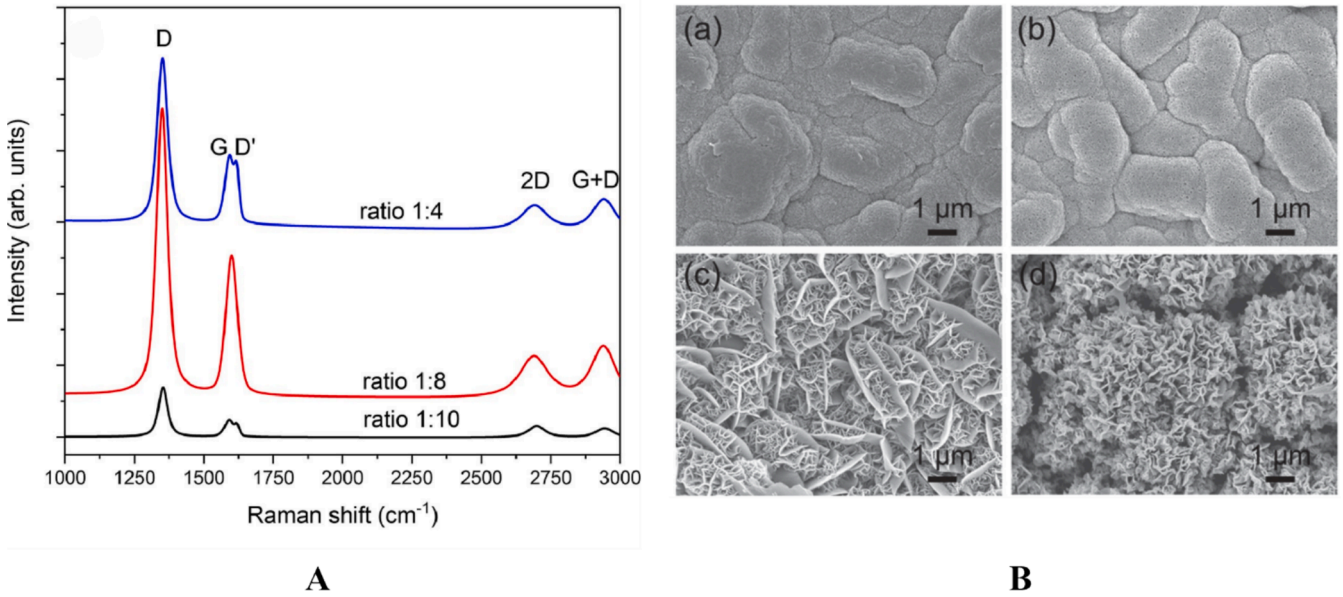

Fig. 3. A) Raman spectra showing the effect of gas ratio in the synthesis of graphene [79], B) SEM image showing the effect of flow rate on the morphology of graphene while decreasing the flow rate of $C_2H_4O_2$ and increasing Ar flow rate [84],

of the sample[85]. Polymethyl methacrylate (PMMA), a flexible polymer, was utilized in the synthesis of single or double-layer graphene on a copper (Cu) substrate. The process involved applying a layer of PMMA onto the Cu surface through spin coating, followed by its exposure to plasma. It was suggested that the graphene formation occurs once the plasma is deactivated. As the temperature drops, carbon particles that had blended into the Cu substrate begin to migrate back to its surface, forming graphene [86]. A sustainable precursor, solid camphor was utilized for the synthesis of few-layer graphene. They utilized solid camphor for the synthesis of few-layer graphene. In low-pressure conditions, solid camphor vaporizes easily as the vapor pressure of camphor is 0.65 mm Hg. They found that plasma can produce graphene by separating the carbon radicals and by dehydrogenation on the surface of the catalyst. The number of layers and the thickness of the graphene can be governed by the amount of the precursor used [87].

3.1.2. *Substrate*

Substrate material has a fundamental role in the synthesis of graphene as the growth mechanism of is dependent on the substrate material. In most of the studies, a metal catalyst is employed for the synthesis of graphene. However, some studies do not rely on the metal catalyst but on a substrate material that can withstand the elevated temperatures of plasma. Therefore, the substrate that is used can be classified as catalytic substrates and arbitrary substrates (semiconducting, dielectric and insulating) [88].

In the case of catalytic substrate, the carbon solubility in the metal substrate affects the synthesis of graphene. At high temperatures, there is bulk diffusion of carbon species inside the metal species like cobalt – a high carbon solubility metal. During cooling, the diffused carbon starts to precipitate back as the solubility of carbon decreases. Therefore, the rate of cooling and substrate thickness is dependent on the number of graphene layers formed. Whereas a stable nucleus is formed for low-solubility carbon metal like copper. Following this, the decomposed species from the precursor attach to this and grow further [78]. Catalytic substrate Ni was also employed for graphene synthesis [89]. The carbon atoms diffuse onto the surface of Ni leading to the formation of graphitic island. After that, it leads to the growth of carbon nanostructures. The carbon atoms are separated based on the grain boundaries of Ni [90]. The graphitic island formed may contain C_2 dimers from which it can nucleate to the formation of graphene.

The Raman spectra of graphene synthesised on both catalytic Cu substrate (Fig. 4a) and arbitrary glass and Si (Fig. 4b) substrates are displayed in Fig. 4. The Raman spectra for graphene synthesised at different temperatures are displayed in Fig. 4a. This leads to the conclusion that higher temperatures were needed to synthesise high-quality graphene, while lower temperatures created graphene with more defects [91]. The Raman spectra for graphene synthesised at different temperatures on Si and glass substrates are shown in Fig. 4b. They both have nearly identical intensity peaks. Graphene that was synthesised at 560 °C, however, showed a more organised graphitic structure [92].

Graphene was also synthesized on various catalytic and non-catalytic substrates like glass, SiO_2 wafer and Cu sheet. They found that wrinkled graphene layers are formed on each substrate of different heights. The synthesis is dependent on the properties of the substrate such as wettability and roughness of the surface. The inter-layer spacing (d) of the graphene also soared as the interaction time increased from 60 s to 180 s as shown in Fig. 5 [93]. The effect of Al foil and Cu foil on the synthesis of graphene was studied. The graphene synthesized in non-catalytic Al foil showed defects and low intensity 2D band of Raman spectra. Whereas the graphene in Cu foil showed less defect and intense 2D band. The usage of surface-wave plasma enabled the synthesis of graphene in both Cu and Al and the catalytic effect of Cu is not anticipated [94].

The effect of quartz, silicon, and platinum substrates in the growth mechanism of graphene was examined. For silicon, carbides are formed at the surface of the substrate before nucleation. This helps in increasing the adhesion of graphene flakes to the surface of the substrate. Both for silicon and quartz, an amorphous carbon layer is formed if there is a disparity in the graphite and the lattice parameters of substrate. For platinum substrate, owing to its good agreement in graphite and lattice parameters, amorphous carbon is not found. In these three cases, as growth time proceeds the spectra does not exhibit any features that are substrate dependent and looks similar [77]. Similar results were also obtained for the study explaining the formation of carbide layers for silicon, an amorphous carbon layer for quartz and direct graphitic base layer formation for platinum substrates. The final properties of the graphene synthesized are the same for all the substrates [95]. Catalyst-free graphene synthesis was also done using Si wafers without extra heating. This helped them in eliminating the additional step of

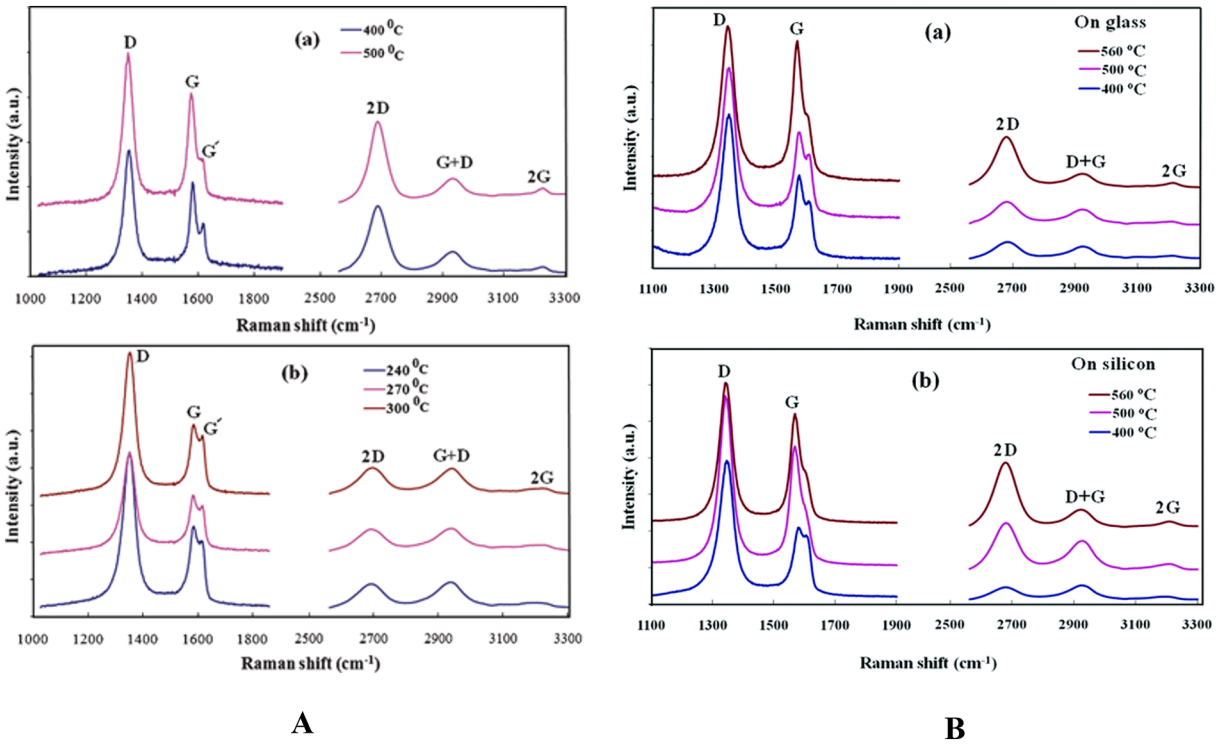

Fig. 4. Raman spectrum of graphene synthesised at A) Cu substrate [91], B) Arbitrary substrates [92].

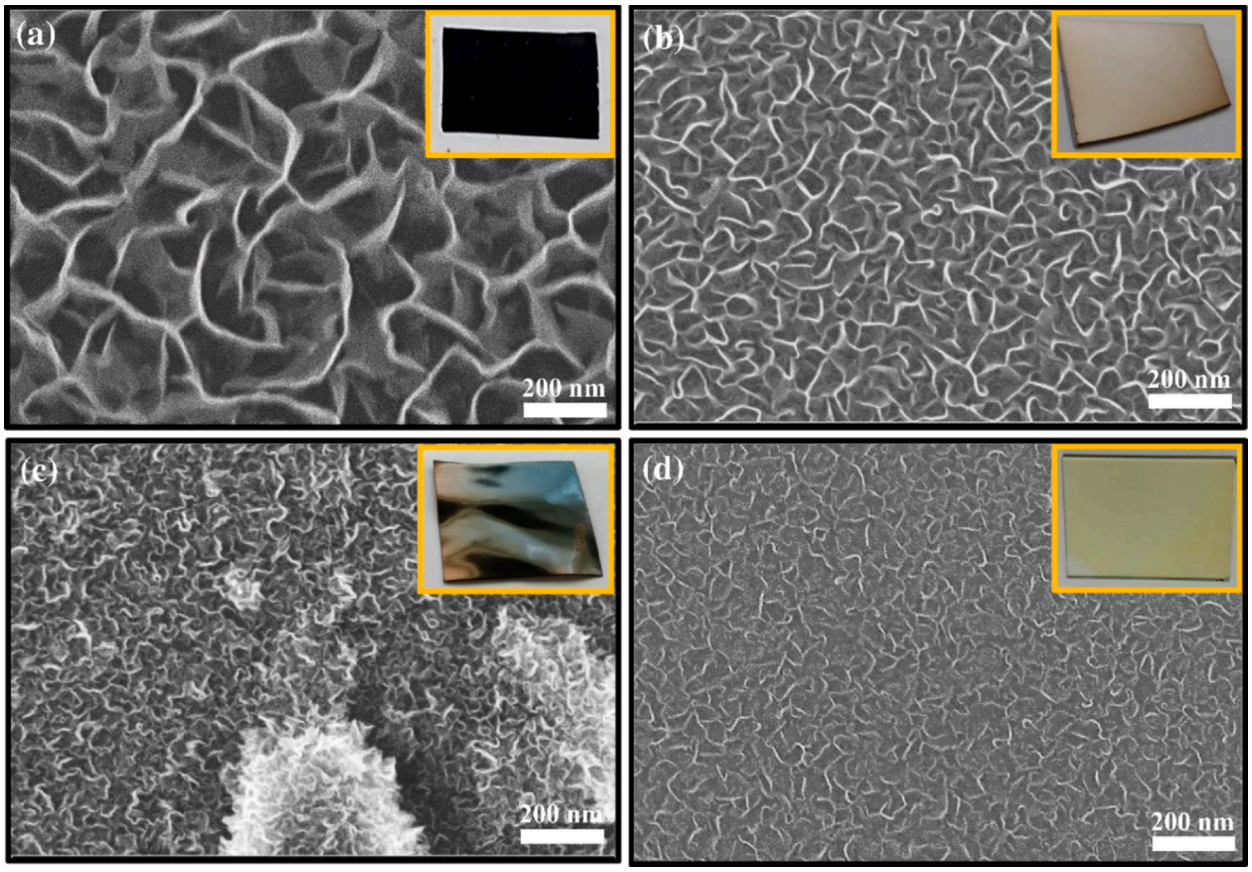

Fig. 5. Graphene synthesised on different substrates; a and b) SiO_2 wafer with interaction time 60 s and 180 s, c) Cu sheet with interaction time 60 s, d) glass with interaction time 10 s [93].

transferring the graphene from the metal catalyst like Cu [79].

3.1.3. Temperature

In the PECVD process, the low-temperature synthesis of graphene is possible. Plasma can produce high-energy electrons that enhance the ionization, excitation and dissociation of the precursor leading to the graphene fabrication at low temperatures. This enables the synthesis of graphene in any other substrates other than metal [68]. The temperature has a role in altering the number of layers formed during the synthesis of graphene. It was also found that a temperature below 600 °C does not support the synthesis of graphene. As temperature increases there is a decrease in the number of layers. The reason is that the rate of desorption of carbon is increased with temperature [96]. Another study also confirms that the minimum temperature requirement for the synthesis of good quality of graphene is above 600 °C. The temperature of the substrate is dependent on the position of the substrate, microwave power and gas temperature [77].

The effect of temperature on the synthesis of graphene was examined [97]. Three different temperatures were studied such as 700 °C, 400 °C and room temperature. At room temperature there was no graphene formation rather it formed amorphous carbon. However, the nucleation of graphene was started as the temperature was increased [97]. In contrast to this, the lowest temperature graphene deposition was possible by Yamada et al. [94]. The surface wave plasma was utilized for the synthesis of graphene. The production of graphene was possible at a substrate temperature of 318 °C which was a very low temperature. The advantage of using this method was that any substrate that can withstand this temperature can be used for the synthesis of graphene. This makes the process more cost-effective.

The temperature of the substrate can be adjusted by adjusting the space between the plasma and the substrate. The distance between the sample and plasma can affect the nature of the material and found that as the distance decreases, the temperature increases. They found that the temperature increases from 275 °C to 336 °C as the gap between the plasma and substrate is changed. The crystallinity of graphene has been improved as the distance was decreased from 200 nm to 180 nm [79]. The quality of graphene can be studied based on the temperature of the substrate. The cooling of the substrate after the plasma exposure has a great role in determining the crystallinity of graphene. It was cooled both at a high rate (50–100 °C/min) and low rate (25 °C/min). The sample that cooled at a lower rate exhibited good crystallinity which is evident from Fig. 6 [86]. The better crystallinity can be attributed to the excellent diffusion that could happen at the low rate of cooling. The sharp peaks in Fig. 6 confirm the formation of crystalline nature of the graphene formed. Thus, it is possible to alter the temperature of the system and the graphene synthesis can be done even below the low temperature of 600 °C. This makes the process more economical and energy efficient.

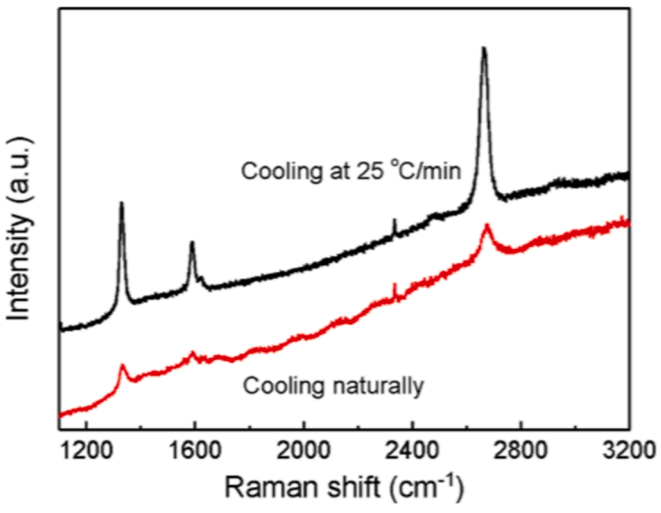

Fig. 6. Raman spectra of graphene which are cooled naturally and at a rate of 25 °C/min [86].

3.1.4. Pressure

Pressure has a role in synthesizing quality graphene as well as in the rate of production. The heavy particles and electrons collide to increase the temperature of the system which has a key role in graphene synthesis. This collision does not happen under atmospheric pressure. Therefore, the chamber is vacuumed. Vacuum conditions also help in reducing the impurities in graphene synthesis and raising their quality [1]. Atmospheric pressure, low pressure and high pressure are used for the synthesis of graphene. Energy transfer between the gas and electrons in the plasma and their collision frequency increases as the pressure increases [78]. The collision rate in the system can be varied by the pressure. High pressure could result in a loss in energy inside the system and the electron density inside the system reduced as a consequence [98]. Table 1 provides with an overview of different parameters used in microwave plasma-based graphene synthesis in vacuum conditions.

4. Microwave plasma-based synthesis of graphene in atmospheric pressure

Microwave plasma for substrate-free graphene synthesis, also called as aerosol-through-plasma technique, provided instantaneous graphene under atmospheric pressure. Earlier, atmospheric pressure microwave plasma reactors were utilized for the synthesis of boron nitride particles and aluminium nanoparticles [102,103]. Subsequently, Dato et al. [104] (2008), for the first time, introduced this method for graphene synthesis. The quantity of precursors, the microwave power, and the carrier gas flux have all been employed to influence the quality of the graphene sheets. The gas temperature at the plasma output gas stream, plasma tuning, and plasma afterglow are the major factors that determine the nucleation and growth of graphene. The synthesized graphene can be collected from the walls of the reaction chamber or membrane filters [104].

Single or bilayer graphene was produced from ethanol in a matter of seconds using microwave plasma reactors. Unlike previous results, the electron diffraction of graphene revealed unique clear spots that resembled the graphene created by micromechanical cleavage. Moreover, graphene was of higher quality than the previously produced graphene using other techniques with a production rate of 2 mg/min [105]. Comparable to that, using an argon microwave plasma system in atmospheric circumstances, stable and highly ordered graphene with few layers was synthesized. Evidence of well-crystallized graphene was seen in the form of ordered lattice fringes. By adjusting the gas temperature in the plasma outlet stream, it was possible to vary the disorder of the sheet [104].

Then, they selectively synthesized high-quality 2D nanostructures such as graphene and nitrogen-doped graphene (N-graphene) with a production rate of 2 mg/min. The sp^2/sp^3 carbon ratio and the control over the amount of oxygen functionalities were achieved by the introduction of IR and UV radiation in the gas phase zone of the reactor. The HR-TEM in Fig. 7a demonstrates that sheet crumbling causes the darkest area to appear, while sheet overlap leads to the less transparent area in a freely suspended graphene. They have succeeded in obtaining graphene with a single to few layers as shown in Fig. 7b and an interlayer spacing of 3.6 Å, greater than that of graphite. The generated graphene's morphology shows that it has a thin, wrinkled structure comparable to paper and is curled or wavy [106].

Experimental and theoretical research was conducted to produce free-standing graphene. They have updated a model that was created previously and provided information on how graphene breaks down. Both theoretical and experimental estimates indicated that carbon monoxide, hydrogen, and solid carbon were the principal products of

Table 1
Different process parameters used in the synthesis of graphene using microwave plasma in vacuum conditions.

Precursor	Plasma gas	Microwave power	Substrate and temperature	Pressure	Reference
Methane	Ar, H_2	2000—2500 W	Si wafer 300 °C	933 Pa	[79]
Methane	Ar, H_2	300–580 W	Cu/Co 700 °C – 980 °C	10 mbar-25 mbar	[78]
Methane	H_2	1300 W	Cu 880 °C	80 torr	[99]
Methane	H_2	1 kW	Cu 950–1030 °C	50–65 mbar	[80]
Acetylene	H_2	500 W	Cu 500 °C	7×10^{-4}	[97]
Methane	H_2	1.2 kW	Fused silica 800 °C	22 mbar	[100]
Methane	H_2	5.5 kW	Cu 650 °C	7 kPa	[101]
Acetylene, Ammonia	H_2	600 W	Al_2O_3, SiO_2 700–750 °C	1×10^{-6}	[82]
Polyethylene	–	700 W	–	–	[85]
Methyl formate	Ar, H_2	–	Ni 450 °C	–	[84]
PMMA	H_2	1300 W	Cu 850 °C	23 torr	[86]
Camphor	Ar	1 kW	Cu 560 °C	45 Pa	[87]

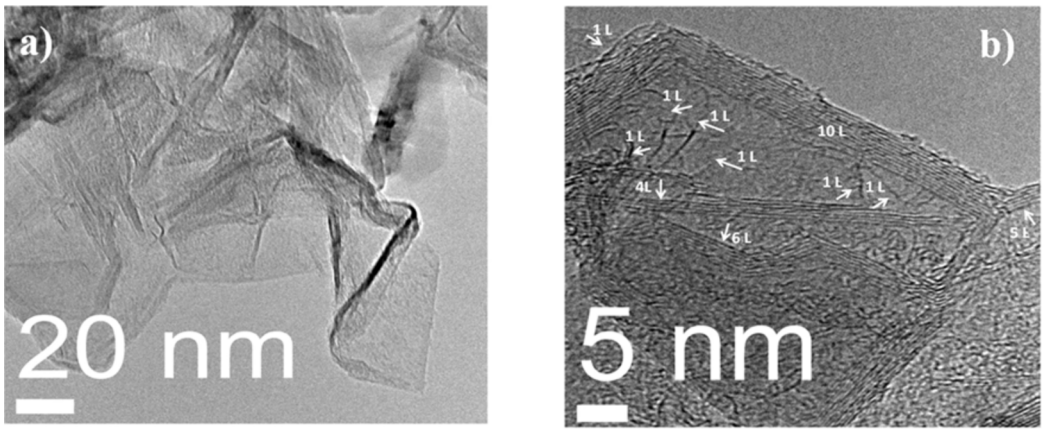

Fig. 7. The HR-TEM images of graphene a) Freely suspended graphene b) Number of graphene layers formed [106].

ethanol disintegration in argon plasma. Along with ethanol and Ar, they also introduced H_2 as a background gas. This helped to produce C_2 radicals two times easier than the C atoms. The production of C_2 radicals and carbon atoms initiated the production of sp^2 carbon and sp^3 carbon respectively [107]. This may be because added H_2 might interact with ethanol and undergo reactions which help in the formation of C_2 radicals which are the precursors to the graphene formation.

Another study also concluded that graphene forms more readily when C_2 radicals are formed, and the production rate was 1.33 mg/min. However, the presence of air may inhibit the production of C_2 radicals while promoting the synthesis of CN species. The fact that the oxidizing agents, such as oxygen and water, create CO_2 and CO near the plasma exit is an additional crisis. The unique glass reactor utilized may alter the ethanol breakdown pathways minimizing plasma contact with the surrounding air. Thus, the issues are avoided when glass reactors are used [108].

Recently the mechanism of graphene synthesis based on their folding and structure in the APMP method was studied. Their research indicates that there are primarily four steps in the mechanism which is given in Fig. 8. The first stage involves using the carbonaceous species to create a two-dimensional, spherical graphene sheet. The circular single-layer graphene sheet must fully develop in the second step. In the third stage, this sheet keeps getting bigger. In the absence of a substrate, step four involves folding the graphene sheets into themselves. There are two possible outcomes from this: either the sheet begins to crumble in random configurations, or graphene folds by itself like an envelope or curls into itself. The first option results in graphene sheets that crumble at random, whereas the second option causes the graphene sheets to curl in on themselves or undergo flat self-folding, which forms a quadrilateral shape [109].

The atmospheric pressure microwave plasma method for synthesizing graphene offers numerous advantages compared to vacuum-based graphene synthesis. This single-step process is catalyst and substrate-free, eliminating the need for specific temperatures or a vacuum environment, making it cost-effective. In addition to that, the synthesised graphene is scalable [110]. Pure and highly ordered, gas phase-synthesised graphene (GSG) has special properties that make it valuable for a diverse application including energy storage, lubrication, sensors, and catalysis. Many factors contribute to the production of atmospheric pressure plasma-based graphene inclusive of microwave power, plasma reactor design, the rate of precursor and gas flow and composition of the precursor [111].

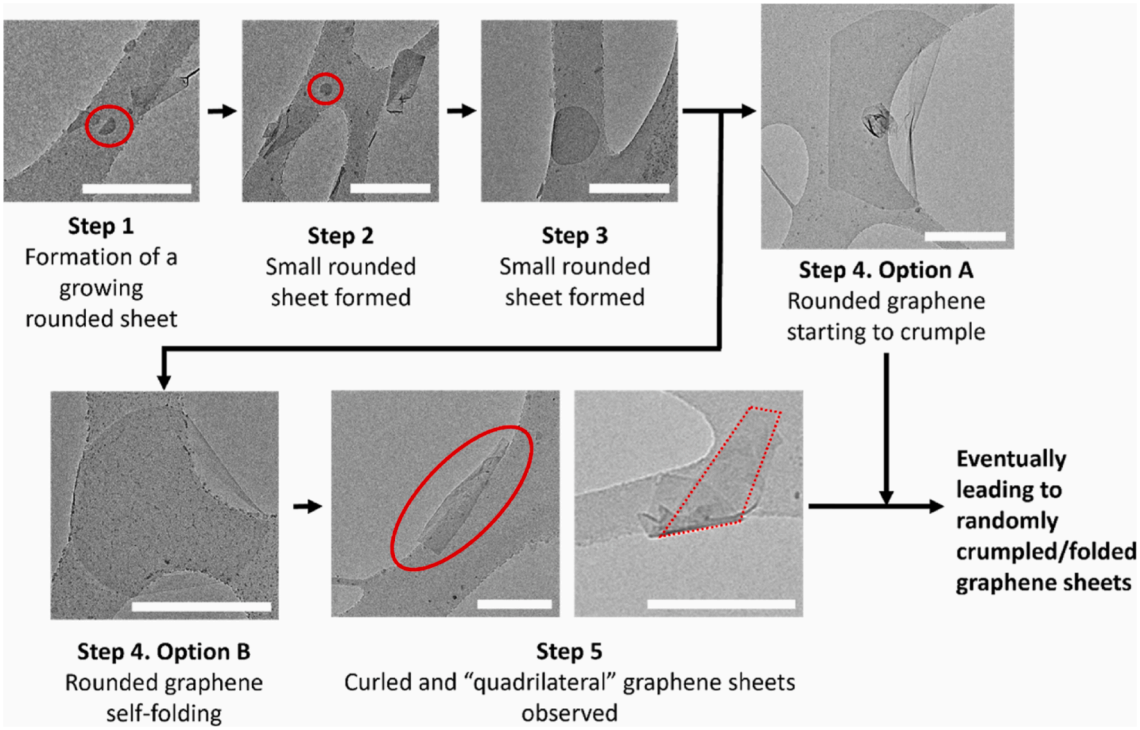

Fig. 8. Mechanism of graphene formation based on their structure [109]. The scale in the figure is 0.5 μm.

4.1. *Factors affecting the synthesis of graphene*

4.1.1. *Plasma reactor and microwave power*

Various types of plasma reactors have been employed in literature to synthesise graphene, despite the similarities in the fundamental system. To the best of our knowledge, five different kinds of plasma reactors are employed. The Fig. 9 summarises the reactors that have been used in graphene fabrication in the literature. Nanodiamonds were synthesised using low-pressure microwave plasma reactors [112]. Successively, Dato et al. [105] employed this method to synthesise graphene after it was discovered that microwave plasma could be used at atmospheric pressure. The reactor is made up of a quartz tube where the Ar plasma forms via a microwave guide, as shown in Fig. 9a. Additionally, a tiny alumina tube is used to transfer ethanol-containing Ar gas (aerosol) into the Ar plasma. In the plasma, ethanol has a resistance time of only 10^{-1} s. Shortly after the graphene is formed, it rapidly cools and gathers on filter membranes.

Surface waves-driven microwave plasmas at atmospheric pressure is another type of plasma reactor that produces graphene as well as other carbon nanostructures as shown in Fig. 9b. This system consists of a

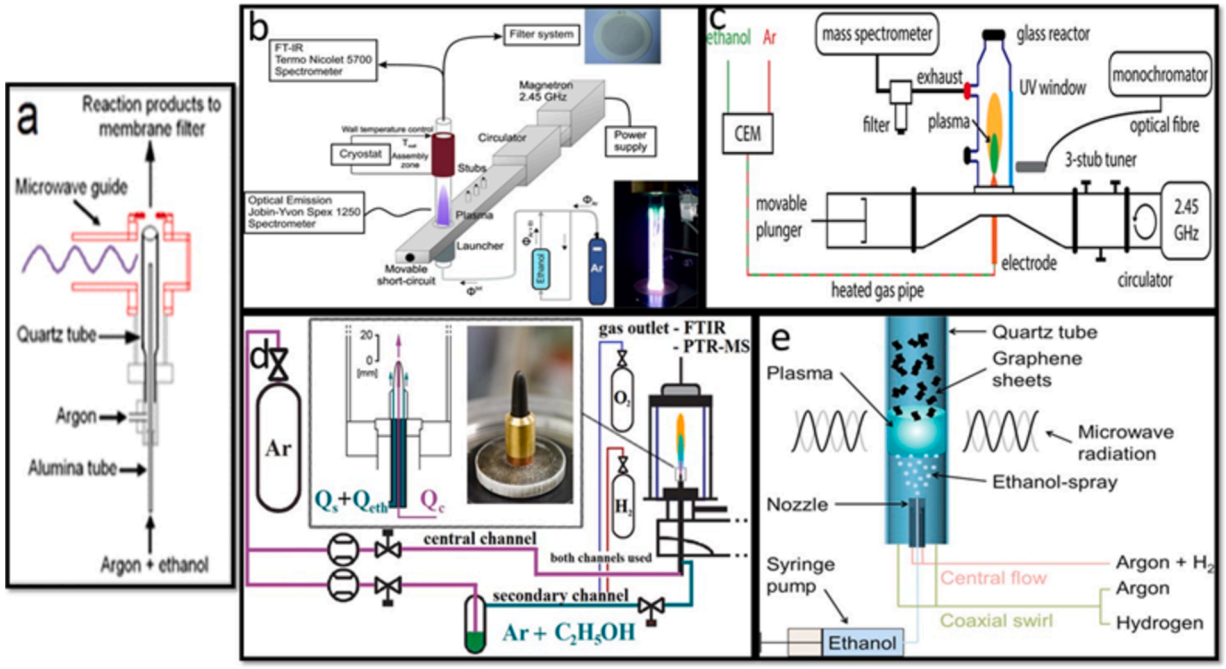

Fig. 9. Different plasma reactors used in the APMP method [105,113–116].

2.45 GHz generator and a surfatron that produces microwave plasma by surface waves. When compared to other reactors, it has two quartz tubes. First quartz tube is where the discharge of plasma happens and the second provides the gaseous precursor to the discharge zone. To control the temperature of the assembly zone, a cryostat and a heat exchanger were introduced as the temperature can impact the final product structure [104,113].

TIAGO (Torche à Injection Axiale Sur Guide d'Ondes) torch is another special microwave plasma torch used for the synthesis of graphene. Fig. 9c depicts that TIAGO consists of a waveguide which has less height and a metallic rod which is hollow cylindrically. The plasma discharge happens as a conical jet flame through the tip as shown in Fig. 9c. A quartz reactor was placed around the metallic rod. The vaporised precursor was obtained by using a controlled evaporator mixer (CEM) which introduced the precursor into the plasma region. The produced graphene will be collected in the inner walls of the reactor eliminating the use of other solvents and extraction methods [108].

Fig. 9d depicts the dual-channel microwave plasma torch that is used for the synthesis of graphene. It consists of a tip/nozzle made of graphite through which the gases are supplied by two channels. The central channel supplied the plasma gas, whereas the Ar-ethanol mixture was introduced through a secondary channel. The possibility of passing oxygen and hydrogen gases to the central and secondary channels makes this reactor an exceptional one. The amount of precursor used can be calculated by the mass loss method. The graphene can be collected from the sides of the reactor, or the Si substrate placed in the holder above the discharge [115,117].

Münzer et al. [116] used a microwave slot antenna system to synthesise graphene as shown in Fig. 9e. The basic components of the system remained the same when compared to Dato et al. [105]. Additionally, a microwave slot antenna was connected to the microwave generator. It also consisted of two nozzles linked to the centre of the quartz tube. For the proper flow of the carrier gases to the reactor, there were two openings for the central flow system and the coaxial swirl. The function of the coaxial system was to stabilize the central flow. Moreover, the precursor was introduced into the system by using a syringe. This enabled them to adjust the rate of ethanol entering the plasma system [116,118].

The microwave plasma reactor can produce a range of microwave power that leads to the formation of graphene. In literature, the lowest power used for the synthesis of graphene by atmospheric pressure microwave plasma method is 60 W [115] and the highest power is 2 kW [106]. Different microwave powers from 60 W to 350 W were examined for graphene synthesis and noted that as the microwave power increases, the geometry of the plasma afterglow was affected. Also, the concentration of byproducts formed by ethanol decomposition, i.e., CO_2 and H_2O are decreased whereas, the concentration of CO is almost stable [115]. Another study investigated how microwave power affected the synthesis of graphene. They discovered that the production of solid carbon increased along with an increase in microwave power, maintaining a constant concentration of the byproducts, H_2 and C_2H_2. This is due to the low amount of final products formed [119].

In an interesting study, Toman et al. [114] proved that microwave power has no effect on the quality of graphene synthesised. However, it can increase the amount of the synthesised graphene. This is evident from the Raman spectra as shown in Fig. 10a. The intensity of the D peak, G peak and 2D peak are the same for the three microwave powers. The I_D/I_G and I_{2D}/I_G ratio in Fig. 10b shows that the graphene synthesised at different powers has almost the same values [114]. Owing to this reason microwave power can be employed as a tool for graphene fabrication on an industrial scale.

4.1.2. Precursor and carrier gas

There are only a few precursors or feedstock used in atmospheric pressure microwave plasma-based synthesis of graphene. Ethanol is the widely studied precursor and the carrier gas used is Ar. The precursor is sent to the plasma in the form of aerosol [105]. The effect of ethanol flow on the morphology of the graphene was examined [117]. The flow rate of the argon carrier gas was varied, and it was found that as the rate of flow increases, there is a steady rise in the dimension and the dense accumulation of the graphene is formed as shown in Fig. 11.

Another set of precursors, methanol, ethanol, isopropyl alcohol, and dimethyl ether were used. The introduction of methanol into plasma resulted in no graphene production. However, the dissociation of ethanol and its isomer dimethyl ether in Ar plasma produced single-layer graphene which was confirmed by TEM and Raman spectroscopy. In the case of isopropyl alcohol, it produced carbonaceous soot, an intermediate between amorphous carbon and graphite. Since methanol is unable to generate many C-C bonds, the nucleation of a sufficient number of aromatic species and their development to solid carbon structures are prevented by the synthesis of a small number of PAHs. In contrast, isopropyl alcohol causes more PAHs to dissociate, which then causes them to collide with other PAHs frequently, forming soot particles. The slower nucleation of PAHs and their rapid development in the atmospheric plasma zone are responsible for the synthesis of graphene from ethanol and dimethyl ether [120].

Graphene and diamond-like nanoparticles were synthesised from methane using a 1 kW microwave power in the presence of Ar gas. Methane and Ar entered the system at flow rates of 2 sccm and 600 sccm, respectively, and graphene was produced. Conversely, diamond

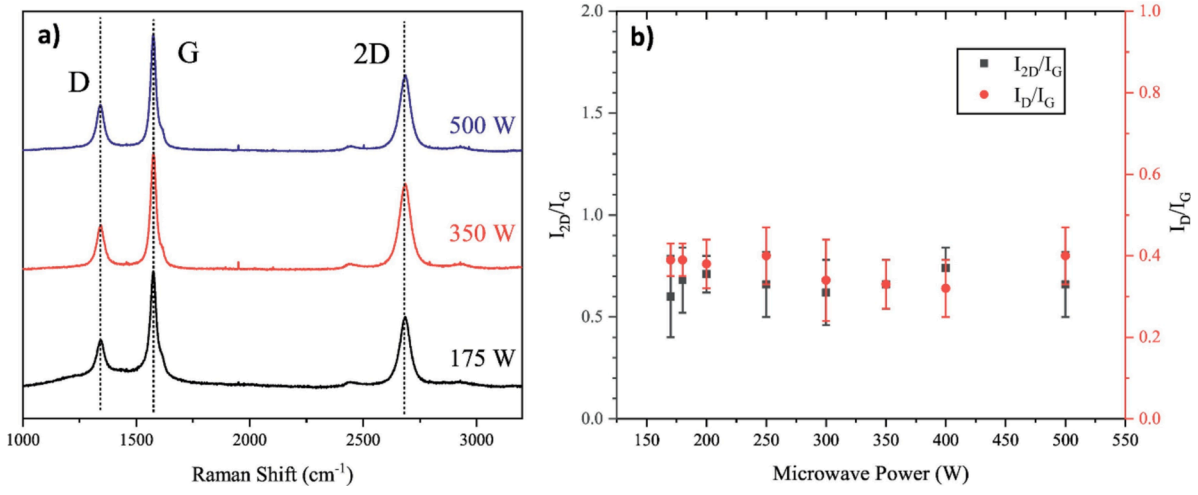

Fig. 10. A) raman spectra of graphene, b) the I_D/I_G and I_{2D}/I_G ratio at 175 W, 350 W and 500 W microwave powers [114].

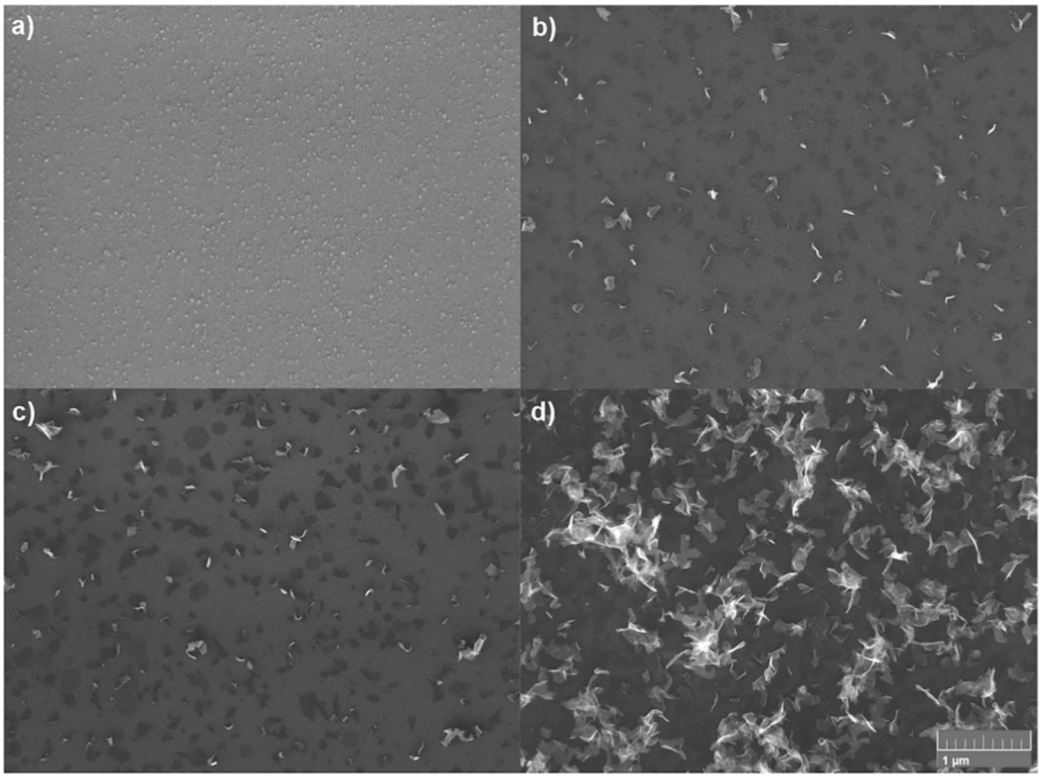

Fig. 11. The effect of flow rate (carrier gas) on the graphene formation; a) 35sccm, b) 70sccm, c) 105sccm and d)140 sccm [117].

nanoparticles formed at larger flow rates but with the same power [119]. Singh et al. [121] also synthesised graphene from methane. However, methane was sent to the reactor along with H_2. The concentration of methane and H_2 was varied in the study which resulted in the few to multilayers of graphene. When compared to the previous studies, they have used more power for producing graphene ranging from 1.2 kW to 1.4 kW. Methane is a single-carbon hydrocarbon. So, the formation of C-C bonds will be challenging. This might have led to the use of high microwave powers for graphene synthesis.

Recently, graphene was synthesised from the essential oil of a sustainable precursor, *Melaleuca Alternifolia* which is also called tea tree oil. The formation of graphene was confirmed by the Raman spectra. In Fig. 12, the high and low-resolution SEM images reveal that there is an aggregation of graphene due to unceasing production and it possesses a curled petal-like morphology. This was the first sustainable precursor used in the atmospheric pressure microwave plasma method for the synthesis of graphene with multilayers. They also have obtained a rate of production of about 1.37 mg/min [122].

The expired tangerine peel oil was another sustainable precursor used in the APMP method. They attained good quality graphene and observed that as the microwave power increases the defect in graphene decreases due to the decreased amount of oxygen groups attaching to the hexagonal structure of graphene [123].

The behaviour of several hydrocarbons, such as methanol, ethanol, ethylene, toluene, i-propanol, and i-butanol, in an atmospheric pressure microwave plasma reactor in the presence of H_2O and Ar was analysed. Their focus was on the function of oxygen in the synthesis of graphene. Regarding alcohol, they contained oxygen. On the other hand, water was added to ethylene to add oxygen. It was shown that ethylene could produce a C/O ratio of 2:1.5 in the presence of water, which was higher

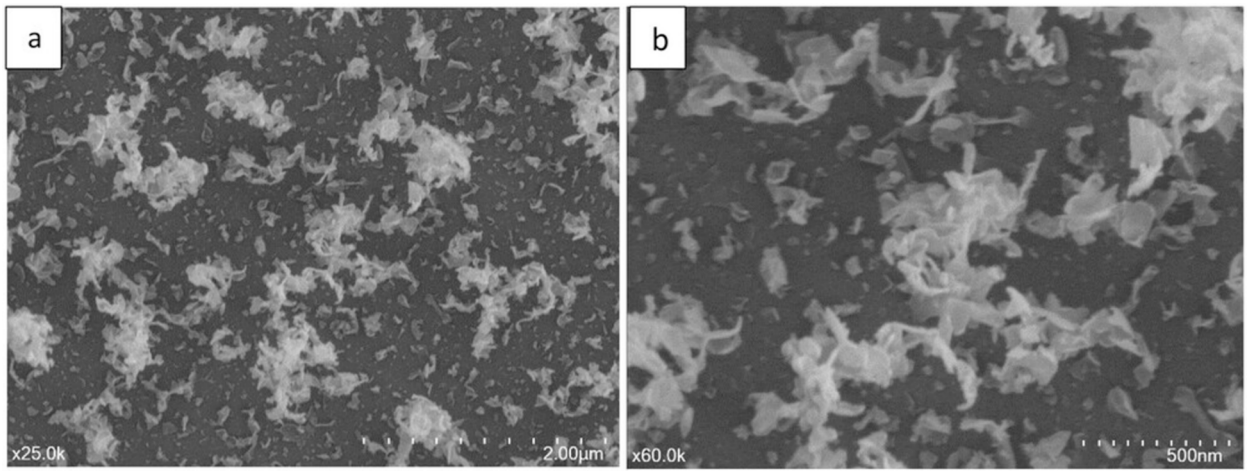

Fig. 12. The SEM image of graphene at 200 W [122].

than ethanol (2:1). In both cases they produced few-layer graphene (FLG). However, methanol did not produce either graphene or soot [124]. Producing graphene from methanol is challenging because it may require higher temperatures or catalysts to break down into C_2 dimers. Additionally, the presence of oxygen complicates the process. While ethanol and other alcohols also contain oxygen, they have more than one carbon atom, making it easier for them to form C_2 dimers compared to methanol. This could explain why graphene formation from methanol is unsuccessful.

N-graphene was synthesised by various research groups by using different precursors. N-graphene was produced using ammonia and ethanol as nitrogen and carbon precursors along with Ar gas. They acquired a nitrogen doping of about 0.4 % with a production rate of 1.3 mg/min [125]. However, Tsyganov et al. [126] synthesised N-graphene using the same carbon precursor and carrier gas, but the nitrogen precursor used was N_2 gas. The low doping levels in the high N_2 flow and the low production yields (0.1 mg/min) are the drawbacks of using N_2 as a precursor. Thus, it was understood that N_2 gas would reduce the doping levels of nitrogen in graphene. This might be due to the large bond dissociation energy of the N_2 molecule. Therefore, it may be difficult to break the triple bond and to form a nitrogen atom which would have doped into the graphene.

Later, they switched out the N_2 gas for NH_3, maintaining the same carbon precursor. Two methods were used to introduce ammonia into the plasma environment: spraying ammonia into the mild (bottom-to-up) and hot (top-to-bottom) plasma zones. It was discovered that the chemical mechanisms of decomposition of ethanol remain unchanged in the presence of ammonia. Nonetheless, it was noted that doping leads to a pyrrolic N structure with higher oxygen content in the hot plasma zone. This yield was extremely low – 0.1 mg/min. On the contrary, when ammonia was given via mild plasma zones, the doping percentage jumped to approximately 1.4 % with the pyridinic N arrangement. In

Table 2
An overview of different process parameters used in the APMP method.

Microwave power	Precursor and its flow rate	Plasma gas and its flow rate	Production rate	References
250 W	Ethanol –	Ar 1.71 L/min	–	[128]
2 kW	Ethanol 1 ml/min	Ar & H2, 5slm,0.5 slm	–	[129]
250 W	Ethanol 4×10^{-4} L/min	Ar, 1.71 L/min	2 mg/min	[130]
250 W	Tea tree oil	Ar 2.5slm	–	[60]
80 W	Aniline, 3 L/min	Ar –	–	[131]
2 kW	Ethanol, methane & methylamine 35, 20 & 6 sccm	Ar 1200 sccm	0.5 mg/min	[132]
175–500 W	Ethanol 2 g/h	Ar 1 L/min	35.3 ± 1.1—111.3 ± 7.1 mg/h	[133]
700–900 W	Ethanol 0.6 sccm	Ar, H2 250 sccm, 1–2.5 sccm	–	[107]
2 kW	Ethanol & Ammonia 50–120 sccm	Ar 1000–1500 sccm	1.3 mg/min	[125]
200–500 W	Ethanol 2–4 g/h	Ar 0.15–1 L/min	1.08 ± 0.07–1.17 ± 0.03 mg/min	[134]
200 W	Ethanol, 0.22 g/h	Ar, 0.75 L/min	–	[135]
400 W-1 kW	Ethanol & Methane 0.6–10 sccm	Ar 250–1500 sccm	–	[136]
500–900 W	Ethanol 0.6–3.5 sccm	Ar 250 sccm	–	[113]
1.2–1.4 kW	Methane	Ar, H2	–	[121]
1 kW	Methane 2–8 sccm	Ar 600–2000 sccm	–	[119]
250–1050 W	Ethanol, methanol, isopropyl alcohol 4.0×10^{-4} L/min	Ar 2.4 lpm	–	[120]
300 W	Ethanol 2 g/h	Ar 1 L/min	1.33 mg/min	[108]
60–350 W	Ethanol 1–34 sccm	Ar 112–700 sccm	232 mg/h	[115]
2 kW	Ethanol 0.1–1.5 ml/min	Ar & H2 5–11 slm, 0.1–0.5 slm	–	[116]
500–2 kW	Ethanol 30 sccm	Ar 1200 sccm	2 mg/min	[137]
250 W	Ethanol 4.0×10^{-4} L/min	Ar 1.71 l/min	2 mg/min	[105]
400–900 W	Ethanol 0.5–3.5 sccm	Ar 250–2000 sccm	2 mg/min	[104]
80–200 W	Aniline 3 L/min	Ar 0.2 L/min	–	[138]
250 W	Methane 2500 sccm	Ar 3000	1.53 mg/min	[110]
2 kW	Ethanol & Ammonia, 35 sccm, 20–100 sccm	Ar 1200 sccm	0.1–0.5 mg/min	[127]
200–600 W	Tea tree oil	Ar 3 slm	1.37 mg/min	[122]
105–455 W	Ethanol 2–19 mg/min	Ar 300–500 sccm	–	[117]

addition to the higher production yield of almost 0.5 mg/min, there was also a lower oxygen content [127]. Table 2 gives a summary of the various process parameters used in the atmospheric pressure microwave plasma method.

5. Structural comparison of graphene in vacuum and atmospheric pressure

There are several differences in the graphene synthesised using microwave plasma in vacuum and atmospheric pressure conditions in terms of its structural characteristics. The surface morphology, crystallinity, defects, and number of layers of graphene are all factors that contribute to the structural quality of graphene. Microwave plasma-based graphene synthesis in vacuum conditions generally synthesises vertical graphene or graphene nanowalls [139]. The synthesis of the vertical graphene depends on several parameters such as microwave power, substrate, temperature and pressure [72]. Continuous and uniform graphene can be obtained using this technique with minimum defects and greater structural quality [140]. Even monolayer graphene can also be synthesised using this method [141].

The graphene synthesised at atmospheric pressure using microwave plasma produces irregular flakes with rough surfaces and less uniformity [131]. This might be due to the uncontrolled precursor and plasma supply in the APMP reactor. The APMP method generally synthesises graphene with multilayers or few layers. However, monolayer graphene was also synthesised using the technique by Dato et al [130]. The defects in graphene produced using this technique are higher than those synthesised in vacuum conditions which is evident from the Raman spectroscopic results. Yet, the structural quality of the graphene can be improved by the use of IR and UV radiations [137].

6. Carbon footprints in graphene synthesis

The total amount of greenhouse gases such as methane, nitrous oxide, and carbon dioxide emitted into the atmosphere by human activity triggers drastic climate change and global warming. The total amount of greenhouse gases emitted into the earth's atmosphere is referred to as carbon footprint [142,143]. Therefore, carbon footprint is a serious issue that is to be addressed as its impact would negatively affect all the inhabitants of the earth. Since graphene can be synthesised using different techniques, each method contributes to carbon footprint differently.

In both graphene synthesis techniques, i.e. in vacuum and atmospheric conditions, different types of feedstocks are used. However, the

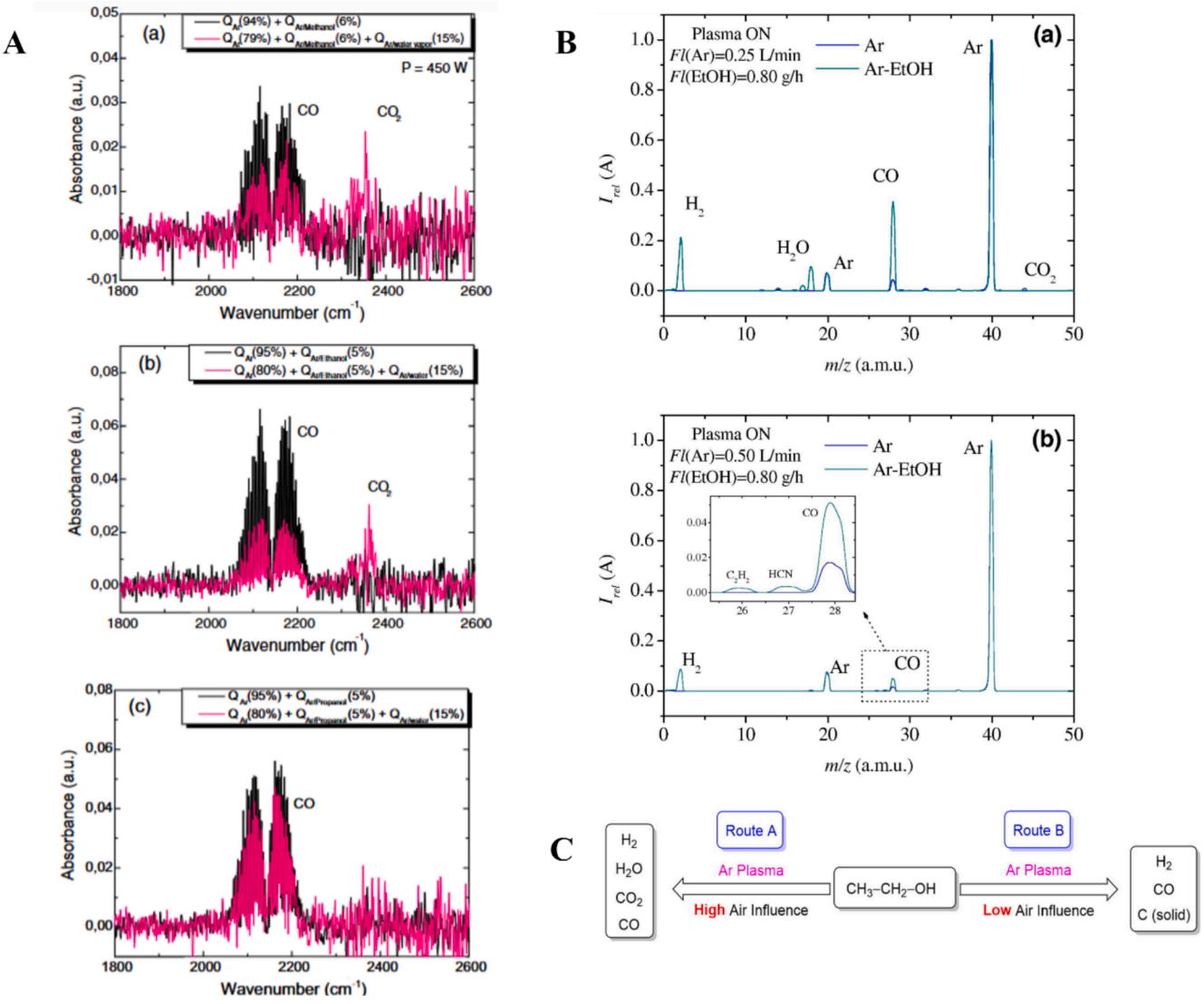

Fig. 13. A) FTIR absorption spectra of methanol, ethanol and propanol in the absence of water and in the presence of water [144], b) Mass spectra showing the effect of Ar flow, c) The effect of air in the ethanol decomposition [145].

amount of greenhouse gases emitted in each method is not given prime importance. Still, some studies discuss the by-products formed in graphene synthesis. It was reported that the main byproduct in graphene formation was CO when CH_3OH, C_2H_5OH and C_3H_7OH were used as feedstock. A very low amount of CO_2 was also found. The addition of water to methanol caused the release of CO_2 which was confirmed by the FTIR absorption spectra which are shown in Fig. 13a. The CO formed here undergoes a water–gas shift reaction that results in the formation of CO_2 both in methanol and ethanol [144]. The CO_2 was not formed in the case of propanol. The CO formed before and after the addition of water was almost the same in the case of propanol whereas, in methanol and ethanol, there was a notable difference in the amount of CO formed which would have led to the formation of CO_2. This suggests that the CO formed after the water addition has led to the CO_2 formation.

In another study, the effect of Ar flow and the presence of air in the formation of the by-products was examined. Fig. 13b shows that the ethanol decomposition resulted in CO and CO_2 emission whereas the amount of CO decreased and there was a disappearance of CO_2 as the Ar flow was increased. It was also noted that the presence of atmospheric air such as N_2 and O_2 along with Ar flow determines the by-products. When the Ar flow is high, less air reaches the plasma discharge and results in CO and H_2 gases (route B) as shown in Fig. 13c. When Ar flow is less, more air interferes in ethanol decomposition leading to the formation of CO_2, CO, H_2O and H_2 (route A) [145]. This indicates that the flow of Ar and the presence of air is a key factor that determines the by-products that are formed. Therefore, from this, it can be concluded that high Ar flow is favoured in ethanol decomposition in atmospheric pressure conditions as the carbon emissions can be reduced.

This proves that a large amount of greenhouse gases is entering into the earth's atmosphere as a result of graphene synthesis. This causes a serious threat to the environment. Thus, a green method and green precursors are advised in the synthesis of graphene which compliments to the carbon neutrality or net zero emissions. A sustainable approach and a green precursor are always preferred in graphene synthesis. A sustainable precursor is a material that is cheap, eco-friendly, ample and a renewable source. While a sustainable method aims at producing a large amount of superior-quality graphene which is scalable with a carbon-negative footprint. The use of both sustainable methods and sustainable precursors will enhance graphene production which effectively leads to net-zero emission goals [146]. Carbon-negative materials are those materials which capture CO_2 from the atmosphere beyond that they emitted. This will effectively lead to a carbon-negative footprint. It is advisable to use carbon-negative materials as the feedstock for the synthesis of graphene.

7. Conclusion

Graphene is an extraordinary material that has exceptional properties and a unique structure. Owing to the properties and the structure of graphene, it is used in a broad spectrum of applications. Microwave plasma-based synthesis of graphene in vacuum and atmospheric conditions are two different techniques that follows the bottom-up method. Both techniques are compared based on their mode of operation, mechanism and process parameters. Each method has its merits as well as demerits.

The synthesis of good-quality graphene is possible with microwave plasma-based synthesis of graphene in vacuum conditions. The use of substrate, whether it is catalytic or arbitrary, helps in the growth mechanism of graphene. The physical properties of graphene such as density and spatial orientation can be controlled by this method. Thus, it provides the opportunity to play with the patterning and ordering of the nanostructures. Large area synthesis with control over layer is another advantage of this technique leading to the high rate of graphene synthesis. Despite these advantages, the use of external temperature and pressure makes it an energy-inefficient method. Additionally, the need for a substrate as well as its pre-cleaning will make it an expensive and time-consuming method which is a challenge in the view of large-scale synthesis. Moreover, post-transfer contamination is also an issue in the plasma-based synthesis of graphene in vacuum conditions. However, the good quality of graphene and its better rate of production makes it a convenient method.

Scalable graphene is the merit of microwave plasma-based synthesis in atmospheric pressure over vacuum conditions. The precursor used has an important role in determining the amount of graphene formed as some precursors such as methanol cannot produce C–C bonds which aids in the synthesis of graphene. As this process eliminates the use of a substrate or catalyst, it avoids the post-transfer contamination and defects that might affect the quality of the graphene. Moreover, graphene can be synthesised within few minutes when compared to the graphene synthesis using microwave plasma-based synthesis of graphene in vacuum conditions. Even though it has various merits, one of the major demerits is the yield. A poor rate of synthesis does not make this process suitable for industrial production.

In a nutshell, microwave plasma-based synthesis of graphene in vacuum and atmospheric pressure conditions varies in a few ways. Microwave plasma-based synthesis of graphene in vacuum conditions needs various conditions to be fulfilled to function such as temperature, pressure and catalyst or substrate. This process is also time consuming since it takes time to cool the system from high temperatures and to vent the system from vacuum conditions. Whereas the plasma-based synthesis of graphene in atmospheric pressure does not require an external temperature, catalyst or substrate and vacuum conditions. They only depend on the microwave power, precursor, plasma gas and their flux which is also governing the other method. Besides, easy fabrication of graphene is possible. Owing to these reasons, microwave plasma-based synthesis of graphene in atmospheric pressure conditions can be used economically as it eliminates the cost of high-temperature furnaces and vacuum systems. The production rate and quality of graphene synthesis are also a great concern in vacuum-based graphene synthesis. When comparing with the APMP method, a better quality and good production rate of graphene is obtained in vacuum-based synthesis. This helps in acquiring graphene that can be used in various realms of day-to-day applications.

8. Outlook

There are certain domains that should be given significant importance in the upcoming research. Plasma-based synthesis in vacuum conditions, requires a substrate for graphene nucleation. Since the mechanism of graphene formation involves the surface, the substrate must be carefully chosen to get a better quality of graphene. Recently insulating substrates are used for graphene synthesis. It helps to avoid the post-treatment such as transfer of graphene which eliminates the defects in graphene transfer. However, the rate of growth, breakdown of precursor and the diffusion process while using insulating substrates are to be addressed. The temperature and pressure of the system must be considered as it is an unavoidable part of the synthesis. Low-temperature synthesis has been employed for graphene production. However, it can affect the quality of graphene produced in terms of its crystallinity and size. Therefore, without compromising the crystallinity and size different methods should be adopted to decrease the temperature used. This will make the process more economical. These changes will make the whole process more reasonable.

In the APMP method, one of the major limitations is the low yield. The product yield must be the primary focus of future research. Even though many studies are advancing using this technique, they all converge to laboratory-scale synthesis. Folding based mechanism of graphene formation is the only mechanism that is available in literature using this method. To the best of our knowledge, the mechanism of graphene formation in terms of the carbon species formation and their nucleation and growth using the APMP method has not been reported yet. So, understanding how graphene formation happens will also help

in increasing the yield of graphene by choosing the appropriate feedstock. Precursors can also be varied in the synthesis of graphene. Other than hydrocarbons and essential oils, different types of precursors that are cheap and sustainable can be explored. Moreover, solid precursors can also be tried for graphene synthesis using the APMP method which sometimes will be beneficial to synthesize graphene with higher quality.

CRediT authorship contribution statement

Rosemary Johnson: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation. **Muhammad Adeel Zafar:** Writing – review & editing, Validation, Supervision, Methodology. **Sabu Thomas:** Writing – review & editing. **Mohan V Jacob:** Writing – review & editing, Validation, Supervision, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

[1] M.A. Zafar, M.V. Jacob, Plasma-based synthesis of graphene and applications: a focused review, Rev. Mod. Plasma Phys. 6 (1) (2022) 37.
[2] S.S. Nasker, P.M. Ajayan, S. Nayak, "Emerging Trends and Future Direction of Graphene Family of Materials as Potential Antimicrobials: A Critical Review,", ACS Mater. Lett. 5 (3) (2023) 673–693.
[3] A. Ibrahim, A. Klopocinska, K. Horvat, Z. Abdel Hamid, Graphene-based nanocomposites: Synthesis, mechanical properties, and characterizations, Polymers 13 (17) (2021) 2869.
[4] D. Shahdeo, A. Roberts, N. Abbineni, and S. Gandhi, "Chapter Eight - Graphene based sensors," *Comprehensive Analytical Chemistry*, C. M. Hussain, ed., pp. 175-199: Elsevier, 2020.
[5] A. Dias, E. Felizardo, N. Bundaleska, M. Abrashev, J. Kissovski, A.M. Ferraria, A. M. Rego, T. Strunskus, P.A. Carvalho, A. Almeida, Plasma-enabled multifunctional platform for gram-scale production of graphene and derivatives, Appl. Mater. Today 36 (2024) 102056.
[6] W. Choi, I. Lahiri, R. Seelaboyina, Y.S. Kang, Synthesis of graphene and its applications: a review, Crit. Rev. Solid State Mater. Sci. 35 (1) (2010) 52–71.
[7] I.-L. Chang, J.-A. Chen, The molecular mechanics study on mechanical properties of graphene and graphite, Appl. Phys. A 119 (2015) 265–274.
[8] J. Wu, H. Lin, D.J. Moss, K.P. Loh, B. Jia, Graphene oxide for photonics, electronics and optoelectronics, Nat. Rev. Chem. 7 (3) (2023) 162–183.
[9] G.F. Smaisim, A.M. Abed, H. Al-Madhhachi, S.K. Hadrawi, H.M.M. Al-Khateeb, E. Kianfar, Graphene-based important carbon structures and nanomaterials for energy storage applications as chemical capacitors and supercapacitor electrodes: A review, BioNanoScience 13 (1) (2023) 219–248.
[10] T.-R. Cui, D. Li, T. Hirtz, W.-C. Shao, Z.-B. Zhou, S.-R. Ji, X. Li, J.-D. Xu, J.-M. Jian, Z.-K. Chen, Laser-Induced Graphene for Multifunctional and Intelligent Wearable Systems: For Health Care and Human–Computer Interaction, Appl. Sci. 13 (8) (2023) 4688.
[11] A. Kausar, I. Rafique, B. Muhammad, Aerospace application of polymer nanocomposite with carbon nanotube, graphite, graphene oxide, and nanoclay, Polym.-Plast. Technol. Eng. 56 (13) (2017) 1438–1456.
[12] H. Korucu, A.I. Mohamed, A. Yartaşı, M. Uğur, The detailed Characterization of graphene oxide, Chem. Pap. 77 (10) (2023) 5787–5806.
[13] J. Blakely, J. Kim, H. Potter, Segregation of carbon to the (100) surface of nickel, J. Appl. Phys. 41 (6) (1970) 2693–2697.
[14] A. Kaniyoor, and S. Ramaprabhu, "A Raman spectroscopic investigation of graphite oxide derived graphene," *Aip Advances,* vol. 2, no. 3, 2012.
[15] D.R. Dreyer, R.S. Ruoff, C.W. Bielawski, From conception to realization: an historial account of graphene and some perspectives for its future, Angew. Chem. Int. Ed. 49 (49) (2010) 9336–9344.
[16] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, "Two-dimensional atomic crystals," *Proc. Natl. Acad. Sci. U S A,* vol. 102, no. 30, pp. 10451-3, Jul 26, 2005.
[17] N. Kumar, R. Salehiyan, V. Chauke, O. Joseph Botlhoko, K. Setshedi, M. Scriba, M. Masukume, S. Sinha Ray, Top-down synthesis of graphene: A comprehensive review, FlatChem 27 (2021) 100224.
[18] A. Kalluri, B. Dharmadhikari, D. Debnath, P. Patra, C.V. Kumar, Advances in Structural Modifications and Properties of Graphene Quantum Dots for Biomedical Applications, ACS Omega 8 (24) (2023) 21358–21376.
[19] M. Yi, Z. Shen, A review on mechanical exfoliation for the scalable production of graphene, J. Mater. Chem. A 3 (22) (2015) 11700–11715.
[20] K.E. Whitener, P.E. Sheehan, Graphene synthesis, Diam. Relat. Mater. 46 (2014) 25–34.
[21] M.G. Sumdani, M.R. Islam, A.N.A. Yahaya, S.I. Safie, Recent advances of the graphite exfoliation processes and structural modification of graphene: a review, J. Nanopart. Res. 23 (11) (2021) 253.
[22] C.S. Park, H. Yoon, O.S. Kwon, Graphene-based nanoelectronic biosensors, J. Ind. Eng. Chem. 38 (2016) 13–22.
[23] L.M. Viculis, J.J. Mack, O.M. Mayer, H.T. Hahn, R.B. Kaner, Intercalation and exfoliation routes to graphite nanoplatelets, J. Mater. Chem. 15 (9) (2005) 974–978.
[24] Y. Yan, F.Z. Nashath, S. Chen, S. Manickam, S.S. Lim, H. Zhao, E. Lester, T. Wu, C. H. Pang, Synthesis of graphene: Potential carbon precursors and approaches, Nanotechnol. Rev. 9 (1) (2020) 1284–1314.
[25] M.S.A. Bhuyan, M.N. Uddin, M.M. Islam, F.A. Bipasha, S.S. Hossain, Synthesis of graphene, International Nano Lett. 6 (2016) 65–83.
[26] L.M. Viculis, J.J. Mack, R.B. Kaner, A chemical route to carbon nanoscrolls, Science 299 (5611) (2003) 1361.
[27] C. Vallés, C. Drummond, H. Saadaoui, C.A. Furtado, M. He, O. Roubeau, L. Ortolani, M. Monthioux, A. Pénicaud, Solutions of negatively charged graphene sheets and ribbons, J. Am. Chem. Soc. 130 (47) (2008) 15802–15804.
[28] A.R. Kamali, D.J. Fray, Molten salt corrosion of graphite as a possible way to make carbon nanostructures, Carbon 56 (2013) 121–131.
[29] N. Liu, P. Kim, J.H. Kim, J.H. Ye, S. Kim, C.J. Lee, Large-area atomically thin MoS2 nanosheets prepared using electrochemical exfoliation, ACS Nano 8 (7) (2014) 6902–6910.
[30] C.-Y. Su, A.-Y. Lu, Y. Xu, F.-R. Chen, A.N. Khlobystov, L.-J. Li, High-quality thin graphene films from fast electrochemical exfoliation, ACS Nano 5 (3) (2011) 2332–2339.
[31] J. Wang, K.K. Manga, Q. Bao, K.P. Loh, High-yield synthesis of few-layer graphene flakes through electrochemical expansion of graphite in propylene carbonate electrolyte, J. Am. Chem. Soc. 133 (23) (2011) 8888–8891.
[32] Y. Zhang, Y. Xu, Simultaneous electrochemical dual-electrode exfoliation of graphite toward scalable production of high-quality graphene, Adv. Funct. Mater. 29 (37) (2019) 1902171.
[33] S. Yang, A.G. Ricciardulli, S. Liu, R. Dong, M.R. Lohe, A. Becker, M.A. Squillaci, P. Samorì, K. Müllen, X. Feng, Ultrafast delamination of graphite into high-quality graphene using alternating currents, Angew. Chem. Int. Ed. 56 (23) (2017) 6669–6675.
[34] Y.L. Zhong, T.M. Swager, Enhanced electrochemical expansion of graphite for in situ electrochemical functionalization, J. Am. Chem. Soc. 134 (43) (2012) 17896–17899.
[35] X. Lu, M. Cai, X. Wu, Y. Zhang, S. Li, S. Liao, X. Lu, Controllable Synthesis of 2D Materials by Electrochemical Exfoliation for Energy Storage and Conversion Application, Small 19 (9) (2023) 2206702.
[36] B.C. Brodie, Sur le poids atomique du graphite, Ann. Chim. Phys. 59 (466) (1860) e472.
[37] L. Staudenmaier, Verfahren zur darstellung der graphitsäure, Ber. Dtsch. Chem. Ges. 31 (2) (1898) 1481–1487.
[38] W.S. Hummers Jr, R.E. Offeman, Preparation of graphitic oxide, J. Am. Chem. Soc. 80 (6) (1958) 1339.
[39] G. Eda, Y.-Y. Lin, S. Miller, C.-W. Chen, W.-F. Su, and M. Chhowalla, "Transparent and conducting electrodes for organic electronics from reduced graphene oxide," *Applied Physics Letters,* vol. 92, no. 23, 2008.
[40] J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, S. Guo, Reduction of graphene oxide via L-ascorbic acid, Chem. Commun. 46 (7) (2010) 1112–1114.
[41] X. Zhou, J. Zhang, H. Wu, H. Yang, J. Zhang, S. Guo, Reducing graphene oxide via hydroxylamine: a simple and efficient route to graphene, J. Phys. Chem. C 115 (24) (2011) 11957–11961.
[42] H.J. Shin, K.K. Kim, A. Benayad, S.M. Yoon, H.K. Park, I.S. Jung, M.H. Jin, H. K. Jeong, J.M. Kim, J.Y. Choi, Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance, Adv. Funct. Mater. 19 (12) (2009) 1987–1992.
[43] A.B. Bourlinos, D. Gournis, D. Petridis, T. Szabó, A. Szeri, I. Dékány, Graphite oxide: chemical reduction to graphite and surface modification with primary aliphatic amines and amino acids, Langmuir 19 (15) (2003) 6050–6055.
[44] A. Adetayo, D. Runsewe, Synthesis and fabrication of graphene and graphene oxide: A review, Open J. Compos. Mater. 9 (02) (2019) 207.
[45] A. Santhiran, P. Iyngaran, P. Abiman, N. Kuganathan, Graphene synthesis and its recent advances in applications—a review, C 7 (4) (2021) 76.
[46] K. Edward, K. Mamun, S. Narayan, M. Assaf, D. Rohindra, and U. Rathnayake, "Review rticle State-of-the-Art Graphene Synthesis Methods and Environmental Concerns," 2023.
[47] Y. Jin, B. Hu, Z. Wei, Z. Luo, D. Wei, Y. Xi, Y. Zhang, Y. Liu, Roles of H 2 in annealing and growth times of graphene CVD synthesis over copper foil, J. Mater. Chem. A 2 (38) (2014) 16208–16216.

[48] M. Bahri, S.H. Gebre, M.A. Elaguech, F.T. Dajan, M.G. Sendeku, C. Tlili, D. Wang, Recent advances in chemical vapour deposition techniques for graphene-based nanoarchitectures: From synthesis to contemporary applications, Coord. Chem. Rev. 475 (2023) 214910.

[49] R. Munoz, C. Gómez-Aleixandre, Review of CVD synthesis of graphene, Chem. Vap. Depos. 19 (10-11-12) (2013) 297–322.

[50] G.R. Yazdi, T. Iakimov, R. Yakimova, Epitaxial graphene on SiC: a review of growth and characterization, Crystals 6 (5) (2016) 53.

[51] Q. Abbas, P.A. Shinde, M.A. Abdelkareem, A.H. Alami, M. Mirzaeian, A. Yadav, A. G. Olabi, Graphene Synthesis Techniques and Environmental Applications, Materials 15 (21) (2022) 7804.

[52] X.J. Lee, B.Y.Z. Hiew, K.C. Lai, L.Y. Lee, S. Gan, S. Thangalazhy-Gopakumar, S. Rigby, Review on graphene and its derivatives: Synthesis methods and potential industrial implementation, J. Taiwan Inst. Chem. Eng. 98 (2019) 163–180.

[53] X. Wan, K. Chen, D. Liu, J. Chen, Q. Miao, J. Xu, High-Quality Large-Area Graphene from Dehydrogenated Polycyclic Aromatic Hydrocarbons, Chem. Mater. 24 (20) (2012) 3906–3915.

[54] H. Ji, Y. Hao, Y. Ren, M. Charlton, W.H. Lee, Q. Wu, H. Li, Y. Zhu, Y. Wu, R. Piner, R.S. Ruoff, Graphene Growth Using a Solid Carbon Feedstock and Hydrogen, ACS Nano 5 (9) (2011) 7656–7661.

[55] M. Shavelkina, R.K. Amirov, D. Kavyrshin, D. Yusupov, Plasma Jet-Assisted Synthesis of Graphene Using a DC Plasma Torch, Plasma Phys. Rep. 45 (2019) 1080–1086.

[56] M. Füner, C. Wild, P. Koidl, Simulation and development of optimized microwave plasma reactors for diamond deposition, Surf. Coat. Technol. 116 (1999) 853–862.

[57] I.V. Antonova, M.B. Shavelkina, A.I. Ivanov, R.A. Soots, P.P. Ivanov, A. N. Bocharov, Graphene flakes for electronic applications: DC plasma jet-assisted synthesis, Nanomaterials 10 (10) (2020) 2050.

[58] I.V. Antonova, M.B. Shavelkina, A.I. Ivanov, N.A. Nebogatikova, R.A. Soots, V. A. Volodin, Engineering of graphene flakes in the process of synthesis in DC plasma jets, PCCP 24 (46) (2022) 28232–28241.

[59] W. Iqbal, and N. Wali, "Synthesis and Structural Analysis of Multilayered Graphene via Microwave Atmospheric Pressure Plasma," *arXiv preprint arXiv: 2403.03813*, 2024.

[60] M.A. Zafar, Y. Liu, S. Allende, M.V. Jacob, Expeditious and Eco-friendly fabrication of Graphene-Ag nanocomposite for methyl paraben sensing, Appl. Surf. Sci. 638 (2023) 158006.

[61] M. Hiramatsu, K. Shiji, H. Amano, M. Hori, Fabrication of vertically aligned carbon nanowalls using capacitively coupled plasma-enhanced chemical vapor deposition assisted by hydrogen radical injection, Appl. Phys. Lett. 84 (23) (2004) 4708–4710.

[62] H. Shi, W. Wu, F. Wei, Q. Chen, Three elements for the preparation of vertical graphene by RF-PECVD method, FlatChem 30 (2021) 100306.

[63] N. Li, Z. Zhen, R. Zhang, R. Mu, Z. Xu, L. He, The nucleation and growth of graphene under a controlled atmosphere during radio frequency-plasma-enhanced chemical vapor deposition, Vacuum 196 (2022) 110750.

[64] K. Yi, D. Liu, X. Chen, J. Yang, D. Wei, Y. Liu, D. Wei, Plasma-enhanced chemical vapor deposition of two-dimensional materials for applications, Acc. Chem. Res. 54 (4) (2021) 1011–1022.

[65] N. Arora, N. Sharma, Arc discharge synthesis of carbon nanotubes: Comprehensive review, Diam. Relat. Mater. 50 (2014) 135–150.

[66] G. Borand, N. Akçamlı, D. Uzunsoy, Structural characterization of graphene nanostructures produced via arc discharge method, Ceram. Int. 47 (6) (2021) 8044–8052.

[67] F. Liang, T. Shimizu, M. Tanaka, S. Choi, T. Watanabe, Selective preparation of polyhedral graphite particles and multi-wall carbon nanotubes by a transferred arc under atmospheric pressure, Diam. Relat. Mater. 30 (2012) 70–76.

[68] M. Li, D. Liu, D. Wei, X. Song, D. Wei, A.T.S. Wee, Controllable synthesis of graphene by plasma-enhanced chemical vapor deposition and its related applications, Adv. Sci. 3 (11) (2016) 1600003.

[69] Y. Okigawa, K. Tsugawa, T. Yamada, M. Ishihara, M. Hasegawa, Electrical characterization of graphene films synthesized by low-temperature microwave plasma chemical vapor deposition, Appl. Phys. Lett. 103 (15) (2013).

[70] S. Hussain, E. Kovacevic, J. Berndt, N.M. Santhosh, C. Pattyn, A. Dias, T. Strunskus, M.-R. Ammar, A. Jagodar, M. Gaillard, Low-temperature low-power PECVD synthesis of vertically aligned graphene, Nanotechnology 31 (39) (2020) 395604.

[71] L. Jiang, T. Yang, F. Liu, J. Dong, Z. Yao, C. Shen, S. Deng, N. Xu, Y. Liu, H.-J. Gao, Controlled synthesis of large-scale, uniform, vertically standing graphene for high-performance field emitters, Adv. Mater. 25 (2) (2013) 250–255.

[72] S. Sahoo, G. Sahoo, S.M. Jeong, C.S. Rout, A review on supercapacitors based on plasma enhanced chemical vapor deposited vertical graphene arrays, J. Storage Mater. 53 (2022) 105212.

[73] J. Zhao, M. Shaygan, J.R. Eckert, M. Meyyappan, M.H. Rümmeli, A growth mechanism for free-standing vertical graphene, Nano Lett. 14 (6) (2014) 3064–3071.

[74] H. Wang, Y. Han, P. Luo, Y. Zhou, Q. Chen, H. Zhu, Y. Yang, B. Zhang, K. Huang, Advances in Microwave-Enhanced Chemical Vapor Deposition for Graphene Synthesis, ChemistrySelect 7 (18) (2022) e202200103.

[75] M. Zhu, J. Wang, B.C. Holloway, R. Outlaw, X. Zhao, K. Hou, V. Shutthanandan, D.M. Manos, A mechanism for carbon nanosheet formation, Carbon 45 (11) (2007) 2229–2234.

[76] A.N. Obraztsov, E.A. Obraztsova, A.V. Tyurnina, A.A. Zolotukhin, Chemical vapor deposition of thin graphite films of nanometer thickness, Carbon 45 (10) (2007) 2017–2021.

[77] A. Malesevic, R. Vitchev, K. Schouteden, A. Volodin, L. Zhang, G. Van Tendeloo, A. Vanhulsel, C. Van Haesendonck, Synthesis of few-layer graphene via microwave plasma-enhanced chemical vapour deposition, Nanotechnology 19 (30) (2008) 305604.

[78] K. Pashova, I. Hinkov, X. Aubert, S. Prasanna, F. Bénédic, S. Farhat, Graphene synthesis by microwave plasma chemical vapor deposition: Analysis of the emission spectra and modeling, Plasma Sources Sci. Technol. 28 (4) (2019) 045001.

[79] J. Kulczyk-Malecka, I.V. dos Santos, M. Betbeder, S.J. Rowley-Neale, Z. Gao, P. J. Kelly, Low-temperature synthesis of vertically aligned graphene through microwave-assisted chemical vapour deposition, Thin Solid Films 733 (2021) 138801.

[80] S. Gottlieb, N. Wöhrl, S. Schulz, V. Buck, Simultaneous synthesis of nanodiamonds and graphene via plasma enhanced chemical vapor deposition (MW PE-CVD) on copper, Springerplus 5 (1) (2016) 1–16.

[81] R. Vishwakarma, R. Zhu, A.A. Abuelwafa, Y. Mabuchi, S. Adhikari, S. Ichimura, T. Soga, M. Umeno, Direct synthesis of large-area graphene on insulating substrates at low temperature using microwave plasma CVD, ACS Omega 4 (6) (2019) 11263–11270.

[82] S. Zheng, G. Zhong, X. Wu, L. D'Arsiè, J. Robertson, Metal-catalyst-free growth of graphene on insulating substrates by ammonia-assisted microwave plasma-enhanced chemical vapor deposition, RSC Adv. 7 (53) (2017) 33185–33193.

[83] S. Mori, T. Ueno, M. Suzuki, Synthesis of carbon nanowalls by plasma-enhanced chemical vapor deposition in a CO/H2 microwave discharge system, Diam. Relat. Mater. 20 (8) (2011) 1129–1132.

[84] J. Wu, S. Feng, X. Wei, J. Shen, W. Lu, H. Shi, K. Tao, S. Lu, T. Sun, L. Yu, Facile synthesis of 3D graphene flowers for ultrasensitive and highly reversible gas sensing, Adv. Funct. Mater. 26 (41) (2016) 7462–7469.

[85] M. Gomaa, G.A. Fattah, Synthesis of graphene and graphene oxide by microwave plasma chemical vapor deposition, J. Am. Sci. 12 (3) (2016) 72–80.

[86] C. Wang, M.F. Yuen, T.W. Ng, S.K. Jha, Z. Lu, S.Y. Kwok, T.L. Wong, X. Yang, C. S. Lee, S.T. Lee, Plasma-assisted growth and nitrogen doping of graphene films, Appl. Phys. Lett. 100 (25) (2012).

[87] G. Kalita, S. Sharma, K. Wakita, M. Umeno, Y. Hayashi, M. Tanemura, Synthesis of graphene by surface wave plasma chemical vapor deposition from camphor, Physica Status Solidi (a) 209 (12) (2012) 2510–2513.

[88] G. Kalita, M. Umeno, Synthesis of graphene and related materials by microwave-excited surface wave plasma CVD methods, Appl. Chem. 2 (3) (2022) 160–184.

[89] Y. Kim, W. Song, S. Lee, C. Jeon, W. Jung, M. Kim, C.-Y. Park, Low-temperature synthesis of graphene on nickel foil by microwave plasma chemical vapor deposition, Appl. Phys. Lett. 98 (26) (2011).

[90] S. Chockalingam, A. Bisht, O. Panwar, A. Kesarwani, B. Singh, J. Chand, V. Singh, Synthesis, structural and field emission properties of multiwall carbon nanotube-graphene-like nanocarbon hybrid films grown by microwave plasma enhanced chemical vapor deposition, Mater. Chem. Phys. 156 (2015) 38–46.

[91] G. Kalita, K. Wakita, M. Umeno, Low temperature growth of graphene film by microwave assisted surface wave plasma CVD for transparent electrode application, RSC Adv. 2 (7) (2012) 2815–2820.

[92] G. Kalita, M.S. Kayastha, H. Uchida, K. Wakita, M. Umeno, Direct growth of nanographene films by surface wave plasma chemical vapor deposition and their application in photovoltaic devices, RSC Adv. 2 (8) (2012) 3225–3230.

[93] H.J. Park, B.W. Ahn, T.Y. Kim, J.W. Lee, Y.H. Jung, Y.S. Choi, Y.I. Song, S.J. Suh, Direct synthesis of multi-layer graphene film on various substrates by microwave plasma at low temperature, Thin Solid Films 587 (2015) 8–13.

[94] T. Yamada, J. Kim, M. Ishihara, M. Hasegawa, Low-temperature graphene synthesis using microwave plasma CVD, J. Phys. D Appl. Phys. 46 (6) (2013) 063001.

[95] R. Vitchev, A. Malesevic, R.H. Petrov, R. Kemps, M. Mertens, A. Vanhulsel, C. Van Haesendonck, Initial stages of few-layer graphene growth by microwave plasma-enhanced chemical vapour deposition, Nanotechnology 21 (9) (2010) 095602.

[96] R. Gudaitis, A. Lazauskas, Š. Jankauskas, Š. Meškinis, Catalyst-less and transfer-less synthesis of graphene on Si (100) using direct microwave plasma enhanced chemical vapor deposition and protective enclosures, Materials 13 (24) (2020) 5630.

[97] R. Thomas, G.M. Rao, Synthesis of 3-dimensional porous graphene nanosheets using electron cyclotron resonance plasma enhanced chemical vapour deposition, RSC Adv. 5 (103) (2015) 84927–84935.

[98] G. Shivkumar, S. Tholeti, M. Alrefae, T. Fisher, A. Alexeenko, Analysis of hydrogen plasma in a microwave plasma chemical vapor deposition reactor, J. Appl. Phys. 119 (11) (2016).

[99] M. Hiramatsu, M. Naito, H. Kondo, M. Hori, Fabrication of graphene-based films using microwave-plasma-enhanced chemical vapor deposition, Jpn. J. Appl. Phys. 52 (1S) (2013), pp. 01AK04.

[100] E. Rajackaitė, D. Peckus, R. Gudaitis, T. Tamulevičius, Š. Meškinis, S. Tamulevičius, The evolution of properties with deposition time of vertical graphene nanosheets produced by microwave plasma-enhanced chemical vapor deposition, Surf. Interfaces 27 (2021) 101529.

[101] L. Fang, W. Yuan, B. Wang, Y. Xiong, Growth of graphene on Cu foils by microwave plasma chemical vapor deposition: The effect of in-situ hydrogen plasma post-treatment, Appl. Surf. Sci. 383 (2016) 28–32.

[102] J.C. Weigle, C.C. Luhrs, C. Chen, W.L. Perry, J.T. Mang, M.B. Nemer, G.P. Lopez, J. Phillips, Generation of aluminum nanoparticles using an atmospheric pressure plasma torch, J. Phys. Chem. B 108 (48) (2004) 18601–18607.

[103] S. Gleiman, C.-K. Chen, A. Datye, J. Phillips, Melting and spheroidization of hexagonal boron nitride in a microwave-powered, atmospheric pressure nitrogen plasma, J. Mater. Sci. 37 (2002) 3429–3440.
[104] E. Tatarova, J. Henriques, C. Luhrs, A. Dias, J. Phillips, M. Abrashev, C. Ferreira, Microwave plasma based single step method for free standing graphene synthesis at atmospheric conditions, Appl. Phys. Lett. 103 (13) (2013).
[105] A. Dato, V. Radmilovic, Z. Lee, J. Phillips, M. Frenklach, Substrate-free gas-phase synthesis of graphene sheets, Nano Lett. 8 (7) (2008) 2012–2016.
[106] E. Tatarova, A. Dias, J. Henriques, M. Abrashev, N. Bundaleska, E. Kovacevic, and B. Goncalves, "Towards large-scale in free-standing graphene and N-graphene sheets Sci," Rep, 2017.
[107] D. Tsyganov, N. Bundaleska, E. Tatarova, A. Dias, J. Henriques, A. Rego, A. Ferraria, M. Abrashev, F. Dias, C.C. Luhrs, On the plasma-based growth of 'flowing'graphene sheets at atmospheric pressure conditions, Plasma Sources Sci. Technol. 25 (1) (2015) 015013.
[108] C. Melero, R. Rincón, J. Muñoz, G. Zhang, S. Sun, A. Perez, O. Royuela, C. González-Gago, M. Calzada, Scalable graphene production from ethanol decomposition by microwave argon plasma torch, Plasma Phys. Controlled Fusion 60 (1) (2017) 014009.
[109] C.-F. López-Cámara, P. Fortugno, M. Heidelmann, H. Wiggers, C. Schulz, Graphene self-folding: Evolution of free-standing few-layer graphene in plasma synthesis, Carbon 218 (2024) 118732.
[110] M.A. Zafar, M.V. Jacob, Synthesis of free-standing graphene in atmospheric pressure microwave plasma for the oil-water separation application, Appl. Surf. Sci. Adv. 11 (2022) 100312.
[111] A. Dato, Graphene synthesized in atmospheric plasmas—A review, J. Mater. Res. 34 (1) (2019) 214–230.
[112] M. Frenklach, R. Kematick, D. Huang, W. Howard, K. Spear, A.W. Phelps, R. Koba, Homogeneous nucleation of diamond powder in the gas phase, J. Appl. Phys. 66 (1) (1989) 395–399.
[113] E. Tatarova, A. Dias, J. Henriques, A.B. do Rego, A. Ferraria, M. Abrashev, C. C. Luhrs, J. Phillips, F. Dias, C. Ferreira, Microwave plasmas applied for the synthesis of free standing graphene sheets, J. Phys. D Appl. Phys. 47 (38) (2014) 385501.
[114] J. Toman, M. Šnírer, R. Rincón, O. Jašek, D. Všianský, A.M. Raya, F.J. Morales-Calero, J. Muñoz, M.D. Calzada, On the gas-phase graphene nanosheet synthesis in atmospheric microwave plasma torch: Upscaling potential and graphene nanosheet-copper nanocomposite oxidation resistance, Fuel Process. Technol. 239 (2023) 107534.
[115] J. Toman, O. Jašek, M. Šnírer, D. Pavliňák, Z. Navrátil, J. Jurmanová, S. Chudják, F. Krčma, V. Kudrle, J. Michalička, On the transition of reaction pathway during microwave plasma gas-phase synthesis of graphene nanosheets: from amorphous to highly crystalline structure, Plasma Processes Polym. 18 (8) (2021) 2100008.
[116] A. Münzer, L. Xiao, Y.H. Sehlleier, C. Schulz, H. Wiggers, All gas-phase synthesis of graphene: Characterization and its utilization for silicon-based lithium-ion batteries, Electrochim. Acta 272 (2018) 52–59.
[117] O. Jašek, J. Toman, J. Jurmanová, M. Šnírer, V. Kudrle, V. Buršíková, Study of graphene layer growth on dielectric substrate in microwave plasma torch at atmospheric pressure, Diam. Relat. Mater. 105 (2020) 107798.
[118] E. Bertin, A. Münzer, S. Reichenberger, R. Streubel, T. Vinnay, H. Wiggers, C. Schulz, S. Barcikowski, G. Marzun, Durability study of platinum nanoparticles supported on gas-phase synthesized graphene in oxygen reduction reaction conditions, Appl. Surf. Sci. 467–468 (2019) 1181–1186.
[119] N. Bundaleska, D. Tsyganov, A. Dias, E. Felizardo, J. Henriques, F. Dias, M. Abrashev, J. Kissovski, E. Tatarova, Microwave plasma enabled synthesis of free standing carbon nanostructures at atmospheric pressure conditions, PCCP 20 (20) (2018) 13810–13824.
[120] A. Dato, M. Frenklach, Substrate-free microwave synthesis of graphene: experimental conditions and hydrocarbon precursors, New J. Phys. 12 (12) (2010) 125013.
[121] M. Singh, A. Sengupta, K. Zeller, G. Skoptsov, and R. L. Vander Wal, "Effect of hydrogen concentration on graphene synthesis using microwave-driven plasma-mediated methane cracking," *Carbon,* vol. 143, pp. 802-813, 2019.
[122] M.A. Zafar, Y. Liu, F.C.R. Hernandez, O.K. Varghese, M.V. Jacob, Plasma-Based Synthesis of Freestanding Graphene from a Natural Resource for Sensing Application, Adv. Mater. Interfaces 10 (11) (2023) 2202399.
[123] M.A. Zafar, Y. Liu, M.V. Jacob, Green synthesis of graphene for targeted recovery of silver from photovoltaic waste, Chemosphere (2024) 142512.
[124] P. Fortugno, S. Musikhin, X. Shi, H. Wang, H. Wiggers, C. Schulz, Synthesis of freestanding few-layer graphene in microwave plasma: The role of oxygen, Carbon 186 (2022) 560–573.
[125] N. Bundaleska, J. Henriques, M. Abrashev, A. Botelho do Rego, A. Ferraria, A. Almeida, F. Dias, E. Valcheva, B. Arnaudov, K. Upadhyay, Large-scale synthesis of free-standing N-doped graphene using microwave plasma, Sci. Rep. 8 (1) (2018) 12595.
[126] D. Tsyganov, N. Bundaleska, J. Henriques, E. Felizardo, A. Dias, M. Abrashev, J. Kissovski, A. Botelho do Rego, A. Ferraria, E. Tatarova, Simultaneous synthesis and nitrogen doping of free-standing graphene applying microwave plasma, Materials 13 (18) (2020) 4213.
[127] D. Tsyganov, N. Bundaleska, A. Dias, J. Henriques, E. Felizardo, M. Abrashev, J. Kissovski, A.B. do Rego, A. Ferraria, E. Tatarova, Microwave plasma-based direct synthesis of free-standing N-graphene, PCCP 22 (8) (2020) 4772–4787.
[128] K. Nakahara, J. Knego, T. Sloop, C. Bisquera, N. Subler, A. Dato, Enhanced mechanical properties of epoxy-matrix nanocomposites reinforced with graphene synthesized in atmospheric plasmas, Plasma Processes Polym. 17 (5) (2020) 1900244.
[129] E. Bertin, A. Münzer, S. Reichenberger, R. Streubel, T. Vinnay, H. Wiggers, C. Schulz, S. Barcikowski, G. Marzun, Durability study of platinum nanoparticles supported on gas-phase synthesized graphene in oxygen reduction reaction conditions, Appl. Surf. Sci. 467 (2019) 1181–1186.
[130] A. Dato, Z. Lee, K.-J. Jeon, R. Erni, V. Radmilovic, T.J. Richardson, M. Frenklach, Clean and highly ordered graphene synthesized in the gas phase, Chem. Commun. 40 (2009) 6095–6097.
[131] M.A. Zafar, Y. Liu, S. Allende, M.V. Jacob, Electrochemical sensing of oxalic acid using silver nanoparticles loaded nitrogen-doped graphene oxide, Carbon Trends 8 (2022) 100188.
[132] N. Bundaleska, A. Dias, N. Bundaleski, E. Felizardo, J. Henriques, D. Tsyganov, M. Abrashev, E. Valcheva, J. Kissovski, A. Ferraria, Prospects for microwave plasma synthesized N-graphene in secondary electron emission mitigation applications, Sci. Rep. 10 (1) (2020) 13013.
[133] J. Toman, M. Šnírer, R. Rincón, O. Jašek, D. Všianský, A. Raya, F. Morales-Calero, J. Munoz, M. Calzada, On the gas-phase graphene nanosheet synthesis in atmospheric microwave plasma torch: Upscaling potential and graphene nanosheet-copper nanocomposite oxidation resistance, Fuel Process. Technol. 239 (2023) 107534.
[134] A. Casanova, R. Rincón, J. Muñoz, C. Ania, M. Calzada, Optimizing high-quality graphene nanoflakes production through organic (bio)-precursor plasma decomposition, Fuel Process. Technol. 212 (2021) 106630.
[135] R. Rincón, C. Melero, M. Jiménez, M. Calzada, Synthesis of multi-layer graphene and multi-wall carbon nanotubes from direct decomposition of ethanol by microwave plasma without using metal catalysts, Plasma Sources Sci. Technol. 24 (3) (2015) 032005.
[136] E. Tatarova, A. Dias, E. Felizardo, N. Bundaleski, M. Abrashev, J. Henriques, Z. Rakocevic, L. Alves, Microwave plasmas applied for synthesis of free-standing carbon nanostructures at atmospheric pressure conditions, J. Magnetohydrodynamics Plasma Res. 21 (2) (2016) 185.
[137] E. Tatarova, A. Dias, J. Henriques, M. Abrashev, N. Bundaleska, E. Kovacevic, N. Bundaleski, U. Cvelbar, E. Valcheva, B. Arnaudov, Towards large-scale in free-standing graphene and N-graphene sheets, Sci. Rep. 7 (1) (2017) 10175.
[138] M.A. Zafar, O.K. Varghese, F.C. Robles Hernandez, Y. Liu, M.V. Jacob, Single-step synthesis of nitrogen-doped graphene oxide from aniline at ambient conditions, ACS Appl. Mater. Interfaces 14 (4) (2022) 5797–5806.
[139] Z. Bo, Y. Yang, J. Chen, K. Yu, J. Yan, K. Cen, Plasma-enhanced chemical vapor deposition synthesis of vertically oriented graphene nanosheets, Nanoscale 5 (12) (2013) 5180–5204.
[140] N. Woehrl, O. Ochedowski, S. Gottlieb, K. Shibasaki, S. Schulz, Plasma-enhanced chemical vapor deposition of graphene on copper substrates, Aip Adv. 4 (4) (2014).
[141] N.-C. Yeh, C.-C. Hsu, J. Bagley, W.-S. Tseng, Single-step growth of graphene and graphene-based nanostructures by plasma-enhanced chemical vapor deposition, Nanotechnology 30 (16) (2019) 162001.
[142] T. Gao, Q. Liu, J. Wang, A comparative study of carbon footprint and assessment standards, Int. J. Low-Carbon Technol. 9 (3) (2014) 237–243.
[143] A.B. Kharissova, O.V. Kharissova, B.I. Kharisov, Y.P. Méndez, Carbon negative footprint materials: A review, Nano-Struct. Nano-Objects 37 (2024) 101100.
[144] E. Tatarova, N. Bundaleska, F. Dias, D. Tsyganov, R. Saavedra, C. Ferreira, Hydrogen production from alcohol reforming in a microwave 'tornado'-type plasma, Plasma Sources Sci. Technol. 22 (6) (2013) 065001.
[145] R. Rincón, A. Marinas, J. Muñoz, C. Melero, M. Calzada, Experimental research on ethanol-chemistry decomposition routes in a microwave plasma torch for hydrogen production, Chem. Eng. J. 284 (2016) 1117–1126.
[146] F.E.C. Othman, N.A.H.M. Nordin, N. Ismail, H.S. Zakria, H. Junoh, M.H.A. Aziz, A review on sustainable graphene production from rice husks: Strategies and key considerations, Chem. Eng. J. 497 (2024) 154408.