Strategies for Scalable Gas-Phase Preparation of Free-Standing Graphene

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The preparation of graphene with high quality serves as a prerequisite for its usage. Traditional methods of graphene production, represented by liquid-phase exfoliation and chemical vapor deposition, either sacrifice the quality and purity of graphene or are limited by the substrate and catalyst. Developing simple and scalable preparation methods of high-quality and high-purity graphene remains a big challenge. Herein, we have reviewed the gas-phase methods including carbonization, combustion, arc discharge, and atmospheric plasma for scalable preparation of free-standing graphene, which are catalyst-, substrate-, solvent-free, and without the need for complex post-treatment methods. The obtained graphene exhibits characteristics of high quality and high purity. Moreover, applications of free-standing graphene were also summarized. Finally, perspectives on opportunities and challenges of free-standing graphene have been discussed.

Keywords: scalable production, gas-phase growth, free-standing graphene, high-quality graphene, atmospheric plasma

Introduction

As an allotrope of carbon, intrinsic graphene has unparalleled electrical, thermal, mechanical properties and good biocompatibility, enabling wide applicability of graphene in the fields of high-performance sensors, energy storage, heat dissipation, mechanical enhancement, biomedical applications, and so on. The upstream preparation of the raw materials of graphene directly determines the downstream applications. Therefore, the first and foremost target is to realize the scalable preparation of high-quality and high-purity graphene.
Since the initial preparation of graphene by mechanical exfoliation in 2004, numerous technologies have been developed, which can be roughly divided into two approaches. Top-down methods, such as Hummers' method and liquid-phase exfoliation, are based on the exfoliation from graphite to graphene powder. This types of methods can greatly improve the yield but sacrifice graphene quality with significant contamination and defects, which puts forward higher requirements for the posttreatment of graphene. On the contrary, a bottom-up strategy represented by catalyst-assisted chemical vapor deposition realizes graphene synthesis via the assembly of carbon atoms. Such methods obtain high-quality graphene films through complex parameter adjustment, but the transfer of graphene from catalysts or substrates has always been one of the bottlenecks. It seems that these two types of technologies have their own pros and cons. Is there a possibility that we can achieve scalable production of high-quality and high-purity graphene but get rid of the dependence of catalysts or substrates at the same time? It has been inferred that to obtain high-quality graphene, the bottom-up growth strategy should be adopted, but the introduction of substrate or catalyst is undesirable. Therefore, graphene should be nucleated in the gas phase, where high temperature is required. Hence, if the temperature is high enough to allow graphene to nucleate in the gas phase, then it is likely to achieve graphene growth in the gas phase, which should meet the previous requirements.

Herein, we have summarized the current scalable gas-phase preparation methods of graphene (Figure 1), including carbonization, combustion, arc discharge, and atmospheric plasma. In arc discharge methods, some related parameters, such as type of buffer gas, temperature, and pressure, have been elaborated. Corona discharge, radio frequency-induced thermal plasma, and surface wave-induced microwave plasma have been emphasized in the atmospheric plasma method. Based on the obtained free-standing graphene, we have also reviewed its related applications. Finally, the preparation and applications of free-standing graphene are prospected.

Figure 1 | Preparation of free-standing graphene in the gas phase and related applications. Reproduced with permission from Ref. 21. Copyright 2018, Wiley-VCH. Reproduced with permission from Ref. 22. Copyright 2020, Wiley-VCH.

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Scalable gas-phase preparation of free-standing graphene

Gas-phase preparation of free-standing graphene is a catalyst- and substrate-free way to synthesize graphene without the introduction of solvent. The four associated methods based on carbonization, combustion, arc discharge, and atmospheric plasma are reviewed here.

Carbonization

Carbon-containing precursors can be transformed into graphene when dehydration and carbonization are conducted at high temperature in the absence of air. Both graphene films and graphene powder have been synthesized in this way. It should be mentioned that the mechanisms vary depending on different carbonization processes.

As for graphene films, in addition to being synthesized on the substrate surface,9,20 they can also be fabricated in a substrate-free gas phase, which was reported by Liu et al.23 By heating the volatile camphor at 180 °C, followed by carbonization at a relatively high temperature (800–850 °C) in a furnace, graphene films were deposited on the quartz tube wall, which were easily peeled off (Figure 2a). The graphene films exhibit a regular shape with inner angles of adjacent edges approaching 120° or 105° (Figure 2b). It was speculated that hexagonal or pentagonal carbon rings were formed during pyrolysis of the camphor molecule, and then the carbon rings were cross-linked with each other and stacked in the [0001] direction. As a new method for growing graphene films, the layers and quality of the graphene need to be improved further.

Different from the growth of thin films, carbonization is often used to prepare graphene powder. A method of sugar-blowing was developed to prepare three-dimensionally strutted graphene, which was reported by Wang et al.24 They introduced volatile salts to make pores via pyrolysis. Similar to fermentation, the decomposition of NH4Cl at a relatively low temperature of 250 °C creates bubbles. Then glucose is pyrolyzed at a very high temperature (up to 1350 °C) to obtain 1–6 layers of strutted graphene (Figure 2c). Raman spectra indicates that this graphene exhibits $I_D/I_G>1$ and $I_{2D}/I_G\sim0.9$. In addition to glucose, polymers,25 coal,26 and so on can also be used to produce graphene. Zhang et al. reported a catalytic pyrolysis to obtain high-quality graphene powder. They used FeCl3 as a catalyst in the process of pyrolyzing glucose and found that the quality of the graphene was improved with increasing pyrolysis temperature. The addition of FeCl3 also significantly improved the quality of graphene but can be seen that $I_D/I_G$ was reduced from ~1.1 to ~0.4, while $I_{2D}/I_G$ was increased from ~0.1 to ~0.7, but it is inevitable that the introduction of heterogeneous elements will reduce graphene purity, and, therefore, post-treatments are often necessary.

High temperature makes it easier to regularize the arrangement of carbon atoms, that is, to improve crystallinity. Very recently, Luong et al.27 proposed the use of Joule heating of inexpensive carbon sources to obtain graphene in less than 1 s. This graphene is called flash graphene (FG). They have calculated that the energy consumption per gram of FG is only 7.2 kJ. As shown in Figure 2d, an extremely high temperature of greater than 3000 K was realized within 100 ms, causing an $I_{2D}/I_G$ as high as 17 to appear in some regions (Figure 2e). Additionally, the temperature generated by this Joule heat can be adjusted by changing the applied voltage, directly affecting the quality of FG. Simulations reveal that temperature has a great impact on the formation process of graphene, which is greatly accelerated at higher temperature (even 5000 K). This method provides further possibilities for waste recycling, but the obtained FG is often small in size, ranging from 5 to 30 nm.

Carbonization of carbon sources can easily achieve scalable production of graphene powder, and gram-level graphene can be obtained in one batch from various solid or liquid carbon sources, which is an obvious advantage of this method. The quality of graphene is much related to the pyrolysis temperature. Generally speaking, long-term high-temperature carbonization will polish graphene well, but usually requires great energy consumption by traditional heating methods. Developing new types of carbonization methods, such as Joule heat, will be critical for scalable production of high-quality graphene.

Combustion

Combustion is a self-propagating, high-temperature synthesis technology.28 Generally, solid graphene is obtained by either incomplete combustion of carbon sources with oxygen or reactions of active metals with carbon-containing oxides where the enthalpy change is less than 0, therefore the system can release heat to provide high temperature. Such high temperature may contribute to the formation of free radicals during the combustion of carbon-containing species, which helps the formation of aromatic molecules and ultimately promotes graphene preparation.30 The liberated heat can be the driving force for spontaneous propagation in the form of a combustion wave.30,31 enabling a quick reaction, so that a large amount of graphene can be synthesized in a short time.

Nepal et al.22 reported a way to prepare graphene by combustion of the mixture of C2H2 and O2. It was found that combustion of different molar ratios of O2/C2H2 generated high temperatures, bringing about diverse effects on the obtained graphene (Figures 2f–2h).
In particular, a molar ratio of \( \text{O}_2/\text{C}_2\text{H}_2 \) of 0.6 reached 4200 ± 200 K in the system. Based on this method, a production rate of 300 g/h of graphene was achieved.

Another simpler method for preparing graphene by combustion was studied by Chakrabarti et al., who reacted Mg with \( \text{CO}_2 \) [2\( \text{Mg(s)} + \text{CO}_2(g) \rightarrow 2\text{MgO(s)} + \text{C(s)} \)]. Characterizations, such as Raman spectroscopy

Figure 2 | Production of graphene by carbonization and combustion. (a and b) Schematic diagram of gas-phase preparation of graphene films and the corresponding SEM image. Reproduced with permission from Ref. 23. Copyright 2010, Elsevier Ltd. (c) Growth process for strutted graphene by sugar-blowing. Reproduced with permission from Ref. 24. Copyright 2013, Macmillan Publishers Ltd. (d and e) Schematic diagram of flash Joule heating process and Raman spectra of graphene. Reproduced with permission from Ref. 27. Copyright 2020, Springer Nature Ltd. (f–h) Basic characterizations of graphene by combustion of the mixture of \( \text{C}_2\text{H}_2 \) and \( \text{O}_2 \). Reproduced with permission from Ref. 32. Copyright 2013, IOP Publishing Ltd.
and transmission electron microscopy (TEM), also indicated that the materials were graphene, but the by-products, such as MgO, must be removed with acid at the same time and, typically, oxygen impurities remain in the graphene. Li et al.31 also prepared graphene with the same strategy, but used electricity in the reaction chamber to provide the initial thermal stimulus. Low oxygen content of \(\sim 1.2\%\) and high specific surface area (SSA) of \(\sim 709\) m\(^2\)/g of graphene were realized in a few seconds but was accompanied with a low \(I_{2D}/I_G\) of 0.22. Other metals, such Ca and Li, can also react with CO\(_2\) to produce graphene with similar parameters.34,35

Combustion is an economical and eco-friendly way to produce graphene. Compared with carbonization, the temperature of combustion is higher, where the latter is more conducive to topological defect removal for the regularization of the graphene structure. However, depending on the type of combustion, oxidants (such as O\(_2\)) or active metals (such as Mg) will participate in the graphene preparation, resulting in a certain amount of oxygen contained in the product or the necessary post-treatment process.

Arc discharge

Arc discharge has played an important role in the discovery of carbon nanomaterials. Fullerenes,36 carbon nanotubes,37 carbon nanohorns,38 and so on were originally prepared using this method. In 2009, Subrahmanyan et al.39 reported the idea for preparing graphene by arc discharge for the first time. In this section, we will discuss some important parameters and analyze their respective effects during the synthesis of graphene by arc discharge.

**Equipment and growth mechanism**

A general setup of arc discharge for fabrication of graphene is shown in Figure 3a, where the system is maintained at low pressure and filled with buffer gases.40 Two carbon rods, serving as electrodes and carbon sources, are used to generate arcs when direct current (DC) or alternating current (AC) are applied. To accelerate the heat dissipation, the steel chamber is always cooled by water. Graphene powder is deposited on the surface of the electrodes or chamber.

Other feedstock gases, such as methane (CH\(_4\)), ethylene (C\(_2\)H\(_4\)), and acetylene (C\(_2\)H\(_2\)), can also be used to prepare graphene under arc discharge, in which another setup shown in Figure 3b is employed.41 Gases are inputted from the outside, and the graphene is synthesized through the arc generated by the hollow cylindrical anode and rod cathode, which are made of graphite as well.

There are two possible reasons why graphene can be obtained by arc discharge. Generally speaking, the gasification temperature of graphite is above 4000 K, much lower than the temperature in the core region of the arc, which usually reaches above 5000 K or even 10,000 K.43 Such a high temperature will cause the graphite on the electrode to be gasified to volatile carbon atoms. After the temperature in the near region is slightly lowered, carbon atoms will combine with each other to form carbon fragments, such as C\(_2\), C\(_3\), and so on, followed by nucleation.44 Pristavita et al.45 reported that the nucleation temperature of graphene is 3000–5000 K, while 2500 K is obtained by Chen et al.46 through dynamic simulation. When the temperature further away from the central area of the arc is lower, graphene will continue to grow under the attack of carbon fragments and will form

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**Figure 3** Schematic diagram of equipment and growth mechanism of arc discharge. (a) Schematic diagram of conventional equipment of arc discharge. Reproduced with permission from Ref. 40. Copyright 2010, Elsevier Ltd. (b) Schematic diagram of equipment of arc discharge using other feedstock gases, such as CH\(_4\), C\(_2\)H\(_4\), and C\(_2\)H\(_2\), as carbon sources. Reproduced with permission from Ref. 41. Copyright 2019, Elsevier Ltd. (c–e) Schematic diagram of the growth mechanism of arc discharge. Reproduced with permission from Ref. 47. Copyright 2016, Royal Society of Chemistry.

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graphene flakes in the end. Besides, high temperature is an important factor affecting the growth of graphene. Li et al. believed that arc force is another important factor, which acts as the driving force for sending buffer gas molecules into the arc area and promoting the movement of ionized species to ambient space (Figures 3c–3e). Apart from this mechanism, it is widely accepted that the exfoliation of graphite electrodes during the arc discharge process is another possible mechanism that contributes to graphene deposition on the wall of the chamber.

**Type of buffer gas**

Buffer gases in the arc discharge have a certain effect on the quality, number of layers of graphene, or whether graphene can be synthesized. In the process of fabricating fullerenes by arc discharge, helium (He) is often used as a buffer gas, but is not suitable for graphene alone. Subrahmanyam et al. used the mixture of H2 and He during DC arc discharge and found that graphene flakes with 2–4 layers on the inner wall of the chamber were formed, which were ascribed to the effects of terminating the dangling bonds and preventing the formation of closed structures of graphene by H2. Shen et al. conducted further research on the effect of H2 in DC arc discharge. They explored different buffer gases, such as H2, N2, air, He, H2–He, and H2–N2, and H2–N2–He when maintaining the same pressure. It seemed that the effect on graphene was found to be the same in the cases of pure He, N2, or air, where only carbon nanospheres and caky graphite flakes were found. However, graphene sheets could only be obtained in the presence of H2. Further, they found that graphene exhibited smaller I0/I0’ (~0.31) in a H2–N2 atmosphere than H2–He and H2–N2–He, indicating that graphene had the best crystallinity in this case. Similar results were also reported by Chen et al., who found that graphene in the H2–N2 atmosphere showed higher thermal stability than in H2–Ar and H2–He. Zhang et al. determined the effects of H2 by comparing it with Ar and N2 through experimentation (Figures 4a–4e). They believed that C–X clusters (X is a carbon atom or heteroatom) were important during the formation of graphene. Figure 4a shows three possible mechanisms where carbon atoms cannot bond with Ar, thus random bonds between carbon clusters are formed into amorphous carbon in Ar (Figure 4b), while carbon nanohorns appear in N2 because of the formation of C–N bonds causing the graphite sheet to bend (Figure 4c), and only graphene sheets were obtained by eliminating the dangling bonds in H2 (Figure 4d and 4e).

Chen et al. explored the role of H2 in preparing graphene using other gases instead of graphite rods as carbon sources during arc discharge. The setup is shown in Figure 3b, where they chose C2H2 as the carbon source with the assistance of Ar and H2. By controlling different ratios of H/C, they found that when increasing H content, the proportion of carbon nanospheres continued to decrease while graphene nanoflakes increased, which shows a similar principle to the graphene growth described earlier.

In addition, other gases, such as CO2 and O2, have the same effects. Wu et al. reported the usage of a mixture of CO2 and He for graphene production during DC arc discharge. Graphene with a size of 100–300 nm and 4–5 layers were obtained in such cases. X-Ray photoelectron spectroscopy (XPS) revealed that functional groups such as C–O and O–C=O existed, which were attributed to the weak oxidation of CO2. Research conducted by Qin et al. confirmed the role of active molecules, such as O2, in the formation of graphene. They believed that molecules such as H2, O2, and CO2 affected the graphene edges by either oxidation by O2 and CO2 or reduction by H2, thus terminating carbon-centered radicals and preventing graphene curling. This research further confirmed that carbon volatilization and then nucleation was a possible mechanism for graphene formation.

**Temperature**

Temperature plays an important role in graphene quality, which is usually very high in arc discharge and contributes to the good crystallinity of graphene. Wang et al. changed the temperature by alternating the current. The higher the current is, the higher the temperature of arc will be, making it possible for the pyrolysis products to be transformed from spherical carbon nanoparticles to graphene sheets. Chen et al. used C2H2 as the carbon source to grow graphene during arc discharge and found that graphene quality was related to temperature in the range of 3200–3600 K, that is, the higher the temperature, the higher the quality of graphene. The temperature gradient also affects the arc discharge-derived graphene. Li et al. explored the effect of cooling rate on graphene in He/H2 arc discharge. By building a fan in the chamber, the cooling rate was adjusted by regulating the fan speed. Based on the design, they found that the quality of the graphene increased as the cooling rate increased (Figure 4g). A low I0/I0’ of ~0.206 of graphene was realized when the fan speed reached 11500 rpm. It was interesting that the layers of graphene were also continuously reduced in this case. This was ascribed to the high cooling rate, which was conducive to accelerating the migration of carbon clusters out of the high-temperature region, and the excess carbon atoms were reduced (Figure 4f).

**Pressure**

During arc discharge, buffer gas pressure is another essential factor. Low pressure is typically used in arc discharge because it facilitates gas ionization for arc
Wang et al. explored the effects of pressure during air arc discharge and found a dependence between product and pressure. They found that higher air pressure (from 400 to 1000 torr) yielded more components of the graphene sheets. Conversely, carbon nanohorns or carbon nanospheres were obtained at low air pressure. They speculated that the reasons may be associated with the mechanism of active molecules acting on the graphene edges. Kumar et al. performed the experiment in Ar. It was found that the (002) peak of graphene in X-ray diffraction (XRD) weakened with increasing Ar pressure within 300–500 torr, indicating the graphene layers had decreased. The same trend of decreasing $I_D/I_G$ in the Raman spectra confirmed the increased graphene crystallinity. However, further increases in Ar pressure increased the layers and reduced the graphene quality. Zhang et al. conducted the experiment in different buffer gases at different pressures. It was found that worse crystallinity of aggregated amorphous carbon or carbon nanohorns was obtained in pure Ar or N$_2$ with increasing pressure, respectively, while better crystallinity of graphene sheets was realized in H$_2$ at higher pressures from 40 to 70 kPa (Figure 4h).

**Magnetically enhanced arc discharge**

Magnetically enhanced arc discharge was first invented by Levchenko et al. It is possible to obtain a nonuniform magnetic field by installing a permanent magnet in a nonmagnetic vacuum chamber (Figure 3a). The induction of a magnetic field not only condenses the arc but also enables electron magnetization to promote ionization and increase the plasma density, resulting in an increase in the temperature of the arc and enhancing the

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**Figure 4** | Influencing factors in arc discharge. (a–e) Effects of buffer gases and the corresponding TEM images of obtained carbon nanomaterials in Ar (b), N$_2$ (c), and H$_2$ (d–e) during arc discharge. Reproduced with permission from Ref. 51. Copyright 2018, Elsevier Ltd. (f and g) Effects of cooling rate on graphene during arc discharge. Reproduced with permission from Ref. 54. Copyright 2013, Elsevier Ltd. (h) Effects of pressure on graphene during arc discharge. Reproduced with permission from Ref. 51. Copyright 2018, Elsevier Ltd. (i) Effects of magnetic field on graphene in arc discharge. Reproduced with permission from Ref. 41. Copyright 2019, Elsevier Ltd.
mixture of the buffer gas and the thermal plasma.41,57 Wang et al.41 designed magnetic field-assisted arc discharge for continuous graphene preparation. The magnetic coil provides an axial magnetic field within 0–0.15 T. Assisted by the magnetic field, the arc rotates counterclockwise around the cathode at a high speed (Figure 4i). The introduction of the magnetic field significantly reduced the contents of spherical carbon nanoparticles and increased graphene crystallinity, exhibiting a decrease in I$_D$/I$_G$ from ~1.05 (O T) to ~0.45 (0.09 T), but the effect on the layers of graphene was small. However, in follow-up studies, impurities, such as carbon tubes, were still found in the product, which is a main problem of arc discharge when preparing graphene.58

During the process of arc discharge, a suitable buffer gas must be selected to facilitate the success of graphene production based on the principle of avoiding graphene edge curling. Appropriate temperature and pressure windows are also of great necessity. By adjusting the relevant parameters, quantitative preparation of graphene can be achieved. The temperature of the arc discharge is indeed very high, which helps to create high-quality graphene with very good crystallinity, but makes it easy to obtain impurities such as carbon nanotubes due to interactions with built-in electrodes or the stainless chamber, which is difficult to avoid. Besides, the high nucleation density and sufficient cracking of graphene usually limit the size of graphene to several nanometers.

**Atmospheric plasma**

In contrast with arc discharge, plasma discharge is a method that depends on the gas discharge behavior. Drawbacks of the interference of the built-in electrodes and by-products are greatly avoided, leading to high purity of the prepared graphene. In this section, we will review the current research progress in the preparation of graphene by atmospheric plasma.

**Mechanism**

Plasma is an ionized gas composed of free electrons, atoms, and freely moving positive or negative ions. There are two kinds of temperatures expressed in plasma, which is because the energy transfer of electrons to atoms or ions is not very effective, enabling a deviation from the thermodynamic equilibrium.59,60 One is the electron temperature ($T_e$) estimated based on the kinetic energy of the electrons. During plasma discharge, the electrons affect the excited kinetic energy by either direct collision or the intermediate states.59 The other is the gas temperature ($T_{gas}$) derived from the kinetic energy of heavy particles, such as atoms or ions. A higher gas temperature reflects an enhanced ability of plasma to atomize molecules, which can be calculated based on nonintrusive emission spectra techniques, such as in situ optical emission spectroscopy (OES).61,62 For thermal plasma, the energy loss due to radiation is far less than the energy exchange caused by collision, and the equilibrium state is close to the thermodynamic equilibrium, therefore $T_e$ is close to $T_{gas}$ in this case.63 which is known as local thermodynamic equilibrium.59

In surface wave-driven plasma, electrons absorb surface waves and then transfer energy to atoms or ions by collision, generating a high $T_e$ greater than 10,000 K and a high $T_{gas}$ above 3000 K.59,61,64 therefore, radicals and excited species can be adequately generated.65 The gas temperature changes with input power, location, and radial distribution.66 Graphene produced by plasma discharge in the gas phase is usually performed at atmospheric or low pressure, and torch-like plasma is obtained (Figure 5a).67 Figure 5b is a schematic diagram of the main process for preparing graphene using ethanol (EtOH) as the carbon source by atmospheric plasma, where multiple reactions occur in the hot plasma and assembly zones.66 The stages of cracking of carbon sources, nucleation, and subsequent growth also appear during graphene synthesis. Tsyganov et al.66 explored the mechanism of growing free-standing graphene in an Ar/EtOH/H$_2$ system by atmospheric plasma. It is seen from the simplified equilibrium diagram (Figure 5c) that the temperature can be divided into four regions. The main species in the regions of above 3500, 2000–3500, 1000–2000, and below 1000 K are atomic H and C, H$_2$ molecules, solid carbon or graphene, and CH$_4$ molecules, respectively. The cracking of EtOH starts in the hot plasma zone at a distance of ~0.5 cm (Figure 5d). The boundary temperature of graphene nucleation is ~1800 K, which is lower than that of graphene using methane as carbon source, where the latter is approximately 1.4 times of the former, ranging from 2200 to 2500 K.66

Therefore, in the process of preparing graphene by atmospheric plasma, the carbon sources will be cracked in the hot plasma zone with a very high temperature, then nucleate in the colder zone, and grow at a lower temperature afterwards, during which the migration rate of carbon species in the gas phase will be a key factor affecting graphene growth.

**Corona discharge**

Corona discharge is one of the most common forms of gas discharge, where the local electric field strength exceeds the ionization field strength of the gas near the tip with a small radius of curvature, causing the gas to be ionized and excited.69 Sun et al.21 modified a household microwave oven by penetrating a quartz tube through the interior. Corona discharge was generated by exposing dielectrics, such as silicon wafers, to microwaves, which was used for gaseous cracking of carbon sources.
nucleation, and graphene growth (Figure 6a). This process of synthesizing graphene was realized in the gas phase without any catalysts or substrate, which was similar to “snowing.” Different dielectrics and carbon sources can be employed for graphene production with features of high crystallinity, few layers (<10), and small size (100–200 nm) performed at 1 atm and 700 W (Figures 6b–6e). Corona discharge can obtain high $T_e$ of $\sim$6030 K and enable fully cracked carbon sources, but requires the built-in dielectric, which will be partially damaged after many cycles.

Radio frequency-induced thermal plasma

Gas-phase preparation of graphene by radio frequency (RF)-induced thermal plasma was developed by Zhang et al. from Tsinghua University, who constructed the setup with a power of 10 kW and excitation frequency of 8–13 MHz, as shown in Figure 7a. CH$_4$ was used as the carbon source to prepare graphene with a SSA of 140–152 m$^2$/g and a size of $\sim$200 nm at 1 atm (Figures 7b–7d).

Similar to RF, inductively coupled plasma (ICP) can be used for free-standing graphene production with higher power under a pressure below 1 atm. Mohanta et al. carried out the study in inductively coupled Ar/H$_2$ plasma at a power of 15 kW and a pressure of 400 mbar and found that the temperature of pure Ar plasma reached 6050 K, while the temperature of the plasma dropped to $\sim$4210 K after H$_2$ introduction (Figures 7e and 7f). This was attributed to the inhibition of vibrationally excited H$_2$ molecules to the ionization of Ar, which was also reported by Sun et al. Legrand et al. also used ICP to prepare graphene using CH$_4$ under 20–25 kW and 13–56 kPa, in which the temperature was 6500–7500 K. It was found that the layers of graphene were 5–20 with a $I_D/I_G$ ranging from 0.3 to 0.4.

It can be concluded that both RF and ICP plasmas are electrodeless discharge methods, so that impurities can be effectively avoided. However, high energy input is usually necessary, in general.

Surface wave-induced microwave plasma

Microwave plasma is one of the most important approaches to graphene production in the gas phase, which is generated by the transfer of microwave energy...
to electrons through elastic collisions with heavy particles, such as atoms and ions, or through inelastic collisions with molecules and atoms, causing excitation during discharge. Different equipment has been developed for preparing graphene in the gas phase, which generally contains a high-voltage power supply, magnetron, circulator, stubs, launcher, and movable short-circuit. In general, a magnetron generates microwaves with a frequency of 2.45 GHz and adjustable power under the modulation of a high-voltage power supply, and then the microwaves are transmitted to the launcher through waveguides. Stubs and movable short-circuit work together to make the plasma located in the quartz tube in the reaction chamber normally and

![Figure 6](image)

**Figure 6** | Growth of graphene by corona discharge. (a) Schematic diagram of producing graphene in the gas phase by corona discharge. (b–e) Characterizations of graphene. Reproduced with permission from Ref. 21. Copyright 2018, Wiley-VCH.

![Figure 7](image)

**Figure 7** | Growth of graphene by RF and ICP plasmas. (a–d) Schematic diagram of RF plasma and the corresponding TEM images of graphene. Reproduced with permission from Ref. 70. Copyright 2015 Elsevier Ltd. (e and f) OES of inductively coupled Ar plasma with or without the feeding of H₂. Reproduced with permission from Ref. 71. Copyright 2017, AIP Publishing.
efficiently. Water cooling systems are always utilized to avoid overheating. The launcher is designable, and gas- or liquid-phase carbon sources can be chosen. The obtained graphene is generally deposited on the inner wall of the quartz tube or collected by the filter membrane with gas flowing out.

Dato et al. reported the preparation of graphene using the microwave plasma torch at atmospheric pressure for the first time. In their work, an aluminum (Al) tube with an internal diameter of 3 mm was placed in the center of a reaction quartz tube (21 mm of internal diameter) to transport Ar and EtOH droplets into the Ar plasma to obtain graphene powder. An estimated yield of 2 mg/min of graphene was realized with a carbon input of 164 mg/min. Perfect structure of sixfold symmetry of graphene revealed the high quality of graphene, showing a small $I_D/I_G$ of ∼0.45 in Raman spectra and a high carbon content as high as 98.9%. Different parameters, such as microwave power, types of carbon source precursors, gas flow, and so on, have also been systematically researched in further studies. It showed that graphene can be fabricated over a large power range (250–1050 W), but lower power increases the possibility of preparing carbon particles. In addition, different carbon sources with diverse C/H ratios, such as EtOH and diethyl ether, can also work. Studies have found that EtOH and diethyl ether with a C/H ratio of 0.333 can produce graphene. However, isopropanol with a C/H ratio of 0.375 mainly obtained carbon nanoparticles, while no graphene was obtained by methanol with a C/H ratio of 0.250. However, other follow-up studies found that C/H may not be the only factor as CH$_4$ with the same C/H ratio of 0.250 can also produce graphene, which indicates that the presence of oxygen may also be significant. Besides, the influence on the gas flow rate or the amount of carbon sources can be summarized that a slower flow rate and a larger amount of carbon sources contribute to a larger density of graphene nucleation as well as serious stacking of layered graphene. Therefore, a small amount of carbon input would be favorable for synthesizing few layer graphene.

Tatarova et al. also reported the process of preparing graphene using surface wave-induced microwave plasma. The launcher was a downstream type. Ar was utilized as a carrier gas to stimulate plasma for pyrolysis of EtOH. In situ OES revealed that C$_2$ species were generated in the plasma, and CO and H$_2$ were detected in the exhaust gas by mass spectrometry and infrared spectroscopy. This method has also been extended to the gas-phase preparation of N-doped graphene with a yield of 1.3 mg/min.

Bundaleska et al. used CH$_4$ as the carbon source to prepare graphene (Figure 8a) and found that the gas temperature at a distance of 3–6.5 cm from the launcher...
remained basically constant of $\sim 3000$ K. This high temperature helps CH$_4$ to be cracked in the gas phase and form graphene, resulting in $I_D/I_G$ of $\sim 0.62$ and $I_{2D}/I_G$ of $\sim 0.8$ in the Raman spectra of graphene. A Torche à Injection Axiale sur Guide d’Ondes (TIAGO), as shown in Figures 8b and 8c, with a hollow metal rod perpendicular to the waveguide for plasma ignition, was also utilized to prepare graphene at atmospheric pressure. Studies have shown that the prepared graphene has a high quality of $I_D/I_G$ of 0.2-0.3 and $I_{2D}/I_G$ of 1.4-1.6 together with a yield of 1.38 mg when inputting 33 mg of EtOH. It is obvious that the obtained graphene is deposited on the wall of the glass reactor.

Sun et al. developed a “pulse-etched” microwave-induced “snowing” (PEMIS) process for continuously growth of graphene in the gas phase using CH$_4$. By introduction of O$_2$ in a pulsed manner, the interference of wrapped graphene remaining on the inner wall of the reaction chamber can be greatly avoided. The obtained graphene exhibited high crystallinity with a small $I_D/I_G$ of $<0.3$ and a large $I_{2D}/I_G$ of $>1$, high purity of $\sim 100\%$ carbon content, and ultralow oxygen content lower than 0.6% (Figures 9a-9c). SSA of the obtained small-size graphene was further adjusted by changing the CH$_4$ concentration, indicating that the layers of graphene were adjustable (Figures 9d-9f). Namely, a high yield reaching $\sim 10.46\%$ of high-quality graphene realized in this way indicates promising prospects.

The use of microwave plasma for gas-phase preparation of free-standing graphene is particularly promising. Numerous studies have shown that prepared graphene is of high crystallinity and purity. Future work must focus on the scalable preparation of graphene demanded by industry. In the meanwhile, the adjustment of various parameters during the graphene growth process also requires more detailed work to achieve controlled preparation.

In the process of preparing free-standing graphene by atmospheric plasma, usually high-quality and high-purity graphene with low oxygen content can be produced. This graphene is closer to the intrinsic state to some extent. Corona discharge requires a built-in dielectric, which can be avoided in the plasma induced by RF or surface wave. It is more economic for the plasma induced by microwave rather than RF. The energy consumption may differ by orders of magnitude. Nevertheless, the production of graphene based on atmospheric plasma is slightly disadvantageous in yield because the introduction of gaseous carbon sources will greatly affect the state of the plasma, which must be further improved.
| Method                        | Preparation parameters                                                                 | Type     | Size          | $I_D/I_G$ | $I_{2D}/I_G$ | Number of layers | C/O     | Others            | Refs. | Remarks                                      |
|------------------------------|----------------------------------------------------------------------------------------|----------|---------------|-----------|--------------|------------------|---------|--------------------|-------|---------------------------------------------|
| Carbonization                | Carbonization of evaporated camphor, 800–850 °C                                        | Film     | ~1 cm         | 0.4       | 0.7          | ~                    | —       | —                  | [23]  |                              |
| Carbonization                | Carbonization of sugar bubbles, 1350 °C                                                | Foam     | ~186 μm       | >1        | 0.9          | 1–6               | —       | 1005 m$^2$/g       | [24]  |                              |
| Carbonization                | Carbonization of glucose and FeCl$_3$ mixture at 700 °C                                | Powder   | ~1 μm         | 0.4–1.1   | 0.1–0.7      | Thick             | —       | Fe residue          | [84]  |                              |
| Flash Joule heating of       | inexpensive carbon sources                                                              | Nanodots | 5–30 nm       | 0.1–1.4   | 0.3–0.8      | Several           | —       | 295 m$^2$/g         | [27]  |                              |
| Combustion                   | Combustion of C$_2$H$_2$ with O$_2$                                                     | Flake    | 35–250 nm     | 0.28–1.33 | ~0.7         | Several           | 49      | —                  | [32]  |                              |
| Burning Mg metal in CO$_2$   |                                                                                       | Cubic flake | 50–300 nm     | ~0.6      | ~0.9         | 7–10              | 12.4    | Mg residue          | [33]  |                              |
| Electricity assisted reaction| between Mg and CO$_2$                                                                    | Flake    | >1 μm         | ~12       | ~0.22        | 20–30             | 82      | 709 m$^2$/g         | [31]  |                              |
| Arc discharge                | H$_2$/He arc, 500–700 torr, graphite rod                                              | Flake    | 100–200 nm    | ~1        | ~0.5         | Few               | —       | 270–680 m$^2$/g    | [39]  |                              |
|                                                                 | CO$_2$/He arc, >1270 torr, graphite rod                                                | Flake    | 100–300 nm    | ~0.7      | ~0.97        | ~6                 | 37.6    | —                  | [52]  |                              |
| Graphite rod in water        |                                                                                       | Flake    | ~10 μm        | 0.1–0.6   | 0.4–0.9      | <10               | 2.78–6.98| —                  | [85]  |                              |
| Graphite rod in toluene/water|                                                                                       | Spherical | 200–1000 nm   | ~0.13     | 0.3–0.4     | ~                 | ~0.85   | —                  | [86]  |                              |
| H$_2$/He arc, rapid cooling, |                                                                                       | Flake    | 100–200 nm    | 0.2–0.4   | 0.5–0.8      | 5–8               | —       | —                  | [54]  |                              |
| <100 kPa                     |                                                                                       | Flake    | 50–300 nm     | 0.4–0.5   | ~0.6         | 2–5               | —       | 270–306 m$^2$/g,   | [41]  | With carbon tubes            |
| Atmospheric Plasma           | Corona discharge, 1 atm                                                                  | Flake    | 50–200 nm     | ~0.36     | ~0.75        | 1–10              | 41.8    | —                  | [21]  |                              |
| Radio frequency, CH$_4$      |                                                                                       | Flake    | 200–500 nm    | 0.68–1.68 | ~             | ~                 | —       | 142–152 m$^2$/g    | [70]  |                              |
| ICP$^a$                      |                                                                                       | Flake    | 100–200 nm    | ~0.3      | ~1.15        | ~                 | —       | —                  | [71]  |                              |
| DC thermal plasma torch      |                                                                                       | Flake    | 100–150 nm    | ~               | ~               | ~                 | ~       | 41.5–48.4 m$^2$/g  | [43]  |                              |
| Microwave plasma-CH$_4$      |                                                                                       | Flake    | 15–200 nm     | ~0.8      | >1           | Few               | 18.4    | —                  | [80]  |                              |
| Microwave plasma-CH$_4$      |                                                                                       | Flake    | 40–200 nm     | ~           | ~             | ~                 | ~       | 74–125 m$^2$/g,    | [78]  | With carbon particles           |
| Dual-channel microwave       |                                                                                       | Flake    | <500 nm       | 0.37–0.8  | 0.35–0.90    | Few               | ~8.5    | —                  | [87]  |                              |
| plasma torch                 |                                                                                       | Flake    | 100–200 nm    | 0.2–0.3   | 1.3–1.7      | Few               | ~66     | —                  | [65]  |                              |
| TIAGO torch                  |                                                                                       | Flake    | 80–400 nm     | <0.3      | >1           | Few               | >165    | 266–323 m$^2$/g    | [22]  |                              |
| “Pulse-Etched”               |                                                                                       | Flake    | 80–400 nm     | <0.3      | >1           | Few               | >165    | 266–323 m$^2$/g    | [22]  |                              |
| Microwave-Induced            |                                                                                       | Flake    | 80–400 nm     | <0.3      | >1           | Few               | >165    | 266–323 m$^2$/g    | [22]  |                              |
| “Snowing”                    |                                                                                       | Flake    | 80–400 nm     | <0.3      | >1           | Few               | >165    | 266–323 m$^2$/g    | [22]  |                              |

$^a$ ICP is usually performed at a pressure below 1 atm.
The gas-phase preparation of free-standing graphene is a catalyst-, substrate-, solvent-free method without the need for complex post-treatment. We have discussed the four main types of methods for synthesizing free-standing graphene in the gas phase, including carbonization, combustion, arc discharge, and atmospheric plasma, associated with the introduction of the related equipment and mechanisms. Table 1 lists the methods and corresponding parameters for free-standing graphene. It should be mentioned that the quality of free-standing graphene is an important parameter, which generally depends on the temperature provided. The temperature of carbonization is usually \(~1000 \, ^\circ\text{C}\), while some special processes, such as Joule heating,\textsuperscript{27} can obtain temperatures of \(~3000 \, ^\circ\text{K}\). Combustion utilizes a violent exothermic reaction in a short time and further obtains a temperature of \(~4000 \, ^\circ\text{K}\). The gas temperature of arc discharge and atmospheric plasma can reach a high temperature above \(3000 \, ^\circ\text{K}\), while an ultrahigh electron temperature exceeding \(10,000 \, ^\circ\text{K}\) can be acquired in atmospheric plasma. As the temperature increases, it is conducive to standardizing the arrangement of carbon atoms and eliminating defects of graphene, making it easier to obtain higher quality graphene. Compared with the graphene prepared by Hummers’ method and liquid-phase exfoliation,\textsuperscript{88} the quality of graphene prepared in the gas phase has been greatly improved, which is a great advantage.

Applications of high-quality free-standing graphene

The gas phase-prepared free-standing graphene, especially synthesized by atmospheric plasma, usually exhibits characteristics of high quality, low oxygen content, high purity, small size, and few layers. Based on the intrinsic characteristics of graphene, fields such as mechanical sensors, energy storage,\textsuperscript{29} support film in TEM,\textsuperscript{90} inkjet printing,\textsuperscript{21} reinforcements,\textsuperscript{27} and hyperthermia\textsuperscript{22} have been explored.

Mechanical sensors

Strain sensors and pressure sensors are two kinds of mechanical sensors that convert external forces into electrical signals, such as resistance or capacitance changes.\textsuperscript{96} Free-standing graphene used in mechanical sensors is mainly prepared by carbonization and some is derived from atmospheric plasma.

By carbonization of silk fabrics (CSFs) followed by encapsulation by polydimethylsiloxane (PDMS), Wang et al.\textsuperscript{92} prepared CSFs-based strain sensors for achieving a wide sensing range (\(~0-500\%\)), fast response (<70 ms), and high durability (10,000 cycles), which were attributed to the plain-weave structures of silk fabric by further studies. Later, Zhang et al.\textsuperscript{93} annealed the cotton fabric (CF) to serve as conductive material for fabricating the CF-based strain sensors. Due to the hierarchical network structure, a strain as low as 0.02\% can also be detected. Besides, Sun et al. conducted “snowing” graphene on the downstream PDMS film during corona discharge to form a fluffy three-dimensional graphene network due to electrostatic repulsion and \(\pi-\pi\) interactions of graphene (Figure 10a).\textsuperscript{21} The prepared graphene-based resistive-type strain sensor exhibited characteristics of a large workable range with high sensitivity. High gauge factors of 24.6, 141.27, and 473.6 were realized in the range of 0–60\%, 60–80\%, and 80–110\%, respectively, which was caused by nonhomogeneous deformation of the graphene assembly structure during stretching (Figure 10b).

In addition, free-standing graphene was also employed in a pressure sensor. Wang et al. developed a carbonized silk nanofiber membrane (CSNM)-based pressure sensor by using CSNM as the active material and PDMS as the substrate. This pressure sensor showed a remarkably high sensitivity (34.47 kPa\(^{-1}\)) and ultralow detectable pressure limit (0.8 Pa).\textsuperscript{94}

Energy storage

Münzer et al. realized the production of free-standing graphene and silicon nanoparticles by using EtOH and SiH\(_4\) through surface wave-induced microwave plasma, respectively. The sizes of the graphene and silicon nanoparticles were in the range of 100–200 nm and 50–100 nm. Graphene-silicon nanocomposites were prepared by surface modification (Figure 10c), where graphene accounted for \(~24\%\) by weight. It was found to exhibit an initial specific capacity up to 2200 mAh/g when applied to lithium-ion batteries. Moreover, a capacity retention of 53\% was realized after 500 cycles at a rate of 1.25 A/g with a Coulombic efficiency as high as 99.89\%. However, the compared reduced graphene oxide-based nanocomposites only achieved a low capacity retention of 30\% under the same conditions, showing advantages of this graphene in the field of energy storage (Figure 10d).\textsuperscript{89} The free-standing graphene was also suitable for flexible and rechargeable Zn–air batteries. Wang et al. pyrolyzed silk fibroin with porous Ketjenblack to form active materials with a large surface area and abundant active sites, which was shown to work well in liquid and solid Zn–air batteries. Notably, a power density of 32.3 mW/cm\(^2\) higher than Pt/C + IrO\(_2\) catalyst (26.7 mW/cm\(^2\)) was obtained when applied in an all-solid state Zn–air battery. Wei et al. prepared cauliflower-fungus-like graphene by reacting metal Li with CO\(_2\). When demonstrated as a counter electrode in a dye-sensitized solar cell, a high efficiency of \(~8.1\%\) was achieved.\textsuperscript{35}

Besides, Li et al. reacted Mg with CO\(_2\) to obtain graphene, which was applied to supercapacitors.\textsuperscript{31} It was
found that high energy storage and high power output can be achieved simultaneously. Moreover, ∼90% capacitance retention was maintained even after one million cycles.

Support film

Due to the thin layers of free-standing graphene, it is suitable to serve as a support layer for TEM imaging. Lee et al. applied graphene prepared by microwave plasma as the support layer instead of conventional ultrathin amorphous carbon. When performing TEM characterization by dropping citrate-capped gold nanoparticles, it was found that this free-standing graphene film showed low contrast variation. By masking graphene reflections, obvious gold nanoparticles and citrate molecules were observed with clear interfaces, as shown in Figure 10e.

Furthermore, a filtered image of the citrate molecule was obtained by masking the reflections of gold nanoparticles and graphene (Figure 10f).90 This indicated that high-purity, high-quality, and free-standing graphene is a promising candidate for the support layer in observing soft-hard interfaces in TEM.

Inkjet printing

The obtained free-standing graphene was also used in inkjet printing (Figure 10g), which was achieved by Sun et al., who dispersed graphene in ethanol/terpineol solution containing ethyl cellulose, achieving good graphene dispersion. The concentration of this graphene dispersion can be larger than 2 mg/mL. Graphene patterns were printed on different substrate surfaces and showed a decrease in resistance of the printed lines from

Figure 10 | Applications of high-quality free-standing graphene. (a and b) Schematic diagram of graphene-based strain sensor and tensile test. Reproduced with permission from Ref. 21. Copyright 2018, Wiley-VCH. (c and d) XRD and cycling performance of graphene–silicon nanocomposites. Reproduced with permission from Ref. 89. Copyright 2018, Elsevier Ltd. (e and f) Free-standing-based support film in TEM for imaging citrate-capped gold nanoparticles. Reproduced with permission from Ref. 90. Copyright 2009, American Chemical Society. (g and h) Schematic diagram of graphene-based inkjet printing and the bending performance of graphene patterns. Reproduced with permission from Ref. 21. Copyright 2018, Wiley-VCH. (i–l) Schematic diagram of free-standing graphene-based reinforcement and microwave thermal therapy together with basic characterizations. Reproduced with permission from Ref. 22. Copyright 2020, Wiley-VCH.

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As high as 86.7%.

Chemotherapy was achieved with a tumor treatment rate in mice, a combination of microwave thermal therapy and graphene. Sun et al. used graphene prepared by Joule heating of inexpensive carbon sources to enhance the mechanical strength of cement. By adding 0.1% graphene, the compressive strength and tensile strength of cement were increased by ~35 and ~19%, respectively. An increase of ~250% of the compressive strength of PDMS was also achieved at the same mass fraction. Sun et al. realized the increase in Young’s modulus and flexural modulus of high-density polyethylene by ~22.7% and ~43.3% with the addition of 1% in mass fraction of graphene obtained by the PEMIS process (Figure 10i), the similar effect was also realized by Ahmad et al.

Hyperthermia

Because of its high crystallinity, small size, high purity, and most importantly, microwave responsiveness, free-standing graphene was used in the field of microwave thermal therapy (Figure 10k). Sun et al. found that this graphene exhibited characteristics of wave-absorbing properties at low frequencies mainly based on dielectric loss, therefore, the PEGylated phospholipid (DSPE-PEG2000) functionalized graphene–saline suspension was prepared and able to achieve a temperature increase of 8.2 °C at a concentration of 10 mg/mL than pure saline solution under microwave radiation (450 MHz, 1.8 W) for 5 min (Figure 10l). Afterward, by loading liposoluble drugs such as Apatinib onto graphene followed by injection into mice, a combination of microwave thermal therapy and chemotherapy was achieved with a tumor treatment rate as high as 86.7%.

Conclusions and Future Outlook

Here, we have reviewed methods of graphene prepared in the gas phase including carbonization, combustion, arc discharge, and atmospheric plasma. These methods provide new ideas for the scalable preparation of high-quality graphene. However, quality is not a single-evaluation index of graphene. The pursuits of few layers, low oxygen content, and high-purity graphene are also important goals. Solid carbon sources are typically used in carbonization, which can obtain graphene at large scale, but the large nucleation density will yield thick layers or very small sizes of graphene. Combustion requires the participation of oxygen, so that the obtained graphene contains a relatively high oxygen content. In addition, the rapid volume expansion during the reaction puts forward higher requirements for the equipment. The current output of 300 g/h of graphene realized by combustion is still quite attractive. Graphene production by arc discharge is usually performed at low pressure with high current input, and the equipment is relatively expensive. Moreover, the as-prepared graphene can be a few layers and usually contains some impurities, which poses great challenges for subsequent separation and purification. Atmospheric plasma is conducted under normal pressure, and the equipment is simple and easy to maintain. The obtained graphene has characteristics of high quality, adjustable layer numbers, low oxygen content, and high purity, which is very promising. However, there are some problems that still need to be solved in preparing graphene by atmospheric plasma methods:

- Further understanding of the reaction mechanism. The reaction mechanism can fundamentally guide the experiment, which is the basis for the preparation of graphene. Therefore, it is necessary to dig deeper into the reaction mechanism.
- Further increasing the efficiency and yield. At present, the efficiency and yield of graphene prepared by atmospheric plasma are relatively low. Although some research groups have solved the problem of continuous preparation of graphene and can achieve an efficiency higher than 10%, and other research groups can realize a graphene production rate of 2 mg/min, it is still far from meeting the needs of real industrial scalable preparation. A high flow rate of carbon source input is generally required to ensure the yield, but the high nucleation density is unfavorable for the reduction of the number of layers of graphene. Factors, such as types of carbon sources, sample injection method, power used, and reaction chamber design, are all important. Of course, the increase in yield and efficiency is inseparable from the growth mechanism of graphene production.
- Controlling the number of layers and sizes of graphene. It can be seen that the SSA of currently prepared free-standing graphene in Table 1 is not high, which reflects that the overall number of layers of graphene is quite large. Being able to increase the percentage of single-layer graphene and control the number of layers evoke higher requirements for graphene production. Moreover, the size of graphene prepared in the gas phase is generally around 200 nm. Direct adjustment of the graphene size is also a major difficulty to be considered.
- Design of more suitable instruments. The design of more suitable instruments is of vital importance for graphene from laboratory to industry. For atmospheric plasma, the design of the reaction chamber counts most. Different reaction chambers have different utilization rates for supplied energy and affect the yield and
efficiency for producing graphene. It is of great necessity to design instruments more rationally, delicately, and even more intelligently.

In addition, applications of free-standing small-size graphene have also been reviewed. High-quality graphene shows great application prospects in the fields of mechanical sensors, energy storage, support films in TEM, inkjet printing, mechanical enhancement, and biology, which are associated with the intrinsic properties of graphene. Application fields in mechanical sensors, energy storage, and inkjet printing are more based on the conductive properties of this free-standing graphene itself. However, the size of the free-standing graphene is usually small (<400 nm) in most cases, resulting in large contact resistance. It is foreseen that the conductive properties of this free-standing graphene have no obvious advantages over liquid-phase exfoliation or chemically reduced graphene. Moreover, the few-layer free-standing graphene shows application possibilities as a support film in TEM, while graphene film prepared by chemical vapor deposition is a strong candidate, and there has been some progress in related fields.\textsuperscript{96,97} Considering the characteristics of high crystallinity, high purity, low oxygen content, and small size of few-layer graphene (especially prepared by atmospheric plasma methods), it can be considered that it is closer to intrinsic graphene. For one thing, the mechanical properties of the free-standing graphene are maintained, and the graphene shows excellent dispersive performance in polymers, which indicates that the graphene may be a very good mechanically-enhanced filler. Future work should focus on further improvements of mechanical properties of free-standing graphene-based nanocomposites. For another, the application of graphene in the field of microwave hyperthermia can be regarded as a targeted application that starts from its own properties, and it may shine in biological fields in the future. Overall, there is still a need for more detailed and targeted exploration of free-standing graphene-based applications.

The gas-phase preparation of graphene has a long way to go and must be considered from both the preparation and application levels. At present, the scalable preparation of graphene on the laboratory level is still far from meeting the needs of the market. The scalable preparation technologies of high-quality and high-purity graphene are still in the early stages, where more attention should be paid. Further exploration of scalable methods of intrinsic graphene is urgent and pinpointing the most important applications of graphene is of great necessity.

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Conflict of Interest

The authors declare no conflict of interest.

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