

## Chapter

# Chemical Vapor Deposition Synthesis of Graphene on Copper Foil

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## Abstract

Chemical vapor deposition (CVD) represents a viable synthesis route to produce good-quality, large-area graphene films. In simple words, the technique relies on the thermal decomposition of a carbon-rich source and the further deposition of carbon atoms in a honeycomb pattern on top of a metallic catalyst film. Due to the versatility of the method, many alternatives have been explored for the synthesis of this amazing carbon 2D nanomaterial: low pressure, atmospheric pressure, roll-to-roll. Different catalysts have been explored as well; however, copper (Cu) represents the prime choice, being micrometer-thick foils the most commonly used form in CVD experiments. This chapter focuses on the production of graphene *via* the CVD method using copper foils, and it commences by explaining the generalities of the technique and its variants; next, a description of the method for the production of graphene using copper is included as well as the different precursors (gas, liquid, solid) that have been reported for its synthesis; we continue explaining the importance of the other gases involved in the synthesis and the efforts toward production of large-size single crystals; the obliged transfer process is reviewed, and we conclude by analyzing the advantages and the challenges of the technique.

**Keywords:** CVD, graphene, polycrystalline, copper foil, precursor

## 1. Introduction

Graphene belongs to the extensive realm of nanostructured allotropes of carbon. It is a 2D nanomaterial conformed of  $sp^2$ -bonded carbon atoms arranged in a hexagonal pattern, each carbon atom bonds in the plane to other three atoms, forming a chicken-wire network only one-atom thick. This amazing nanomaterial was isolated in 2004 by Novoselov and Geim [1], who later, in 2010, were awarded the Nobel Prize in Physics. Perhaps the most natural way to obtain graphene is by exfoliating a layer from graphite, such was the method used by Novoselov and Geim. This method, however, poses intrinsic disadvantages such as the low yield, the time required to find monocrystals, and the irreproducibility of the shapes of the crystals. Scientists realized that a method to produce graphene in a more controlled, reproducible, and

scalable way was necessary. Among the many techniques available to produce nano-materials, the chemical vapor deposition (CVD) method has proven to be advantageous for the production of carbon nanostructures, it has been used to produce carbon nanotubes, carbon nanospheres, nanoribbons, fullerenes, and in 2009, the production of multilayer graphene (MLG) was reported on top of nickel (Ni) films [2, 3]. Later the same year, the synthesis of large-area graphene films was reported using Cu foils by the group of R.S. Ruoff [4], ever since, most CVD-graphene reports use copper foils as catalysts. The basics of the technique, the roles of the precursor, the catalysts, and the synthesis gases are reviewed in detail in the following paragraphs.

Early reports of CVD-graphene accounted for continuous films with regions of single-layer, bilayer, and few-layer graphene (SLG, BLG, FLG, respectively). Characterization of these films revealed that the BLG and FLG do not respect an AB stacking of the layers, the stacking from highly oriented pyrolytic graphite (HOPG); the orientation between adjacent layers is random in CVD-grown films. Another peculiarity of these graphene films is their polycrystallinity, as will be described below in detail.

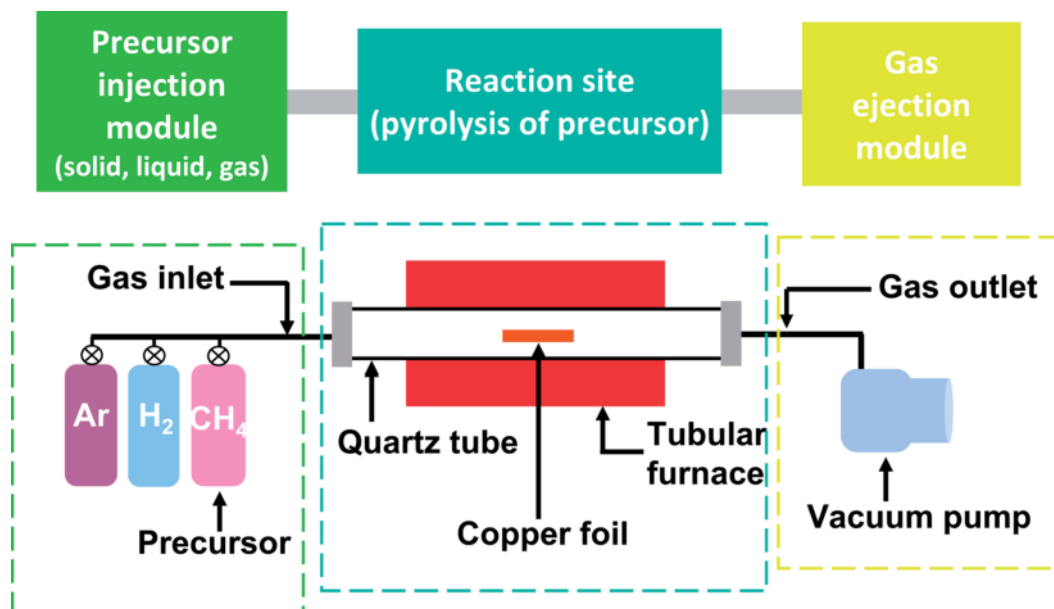
## **2. Chemical vapor deposition**

The chemical vapor deposition technique is based on the chemical thermal decomposition of a precursor (the compound that provides the feedstock for the production of the desired material), so their individual constituents can build up a solid film or nanostructure into a specified substrate. In general, a common CVD equipment is composed of three main modules: 1) a precursor injection module, 2) the reaction site or chamber, and 3) the gas ejection module [5]. Although these three modules can be arranged either vertically or horizontally, the horizontal configuration is the most widely used. The reaction site consists of a region subjected to high temperatures where the thermal decomposition of the precursor can be triggered. A very common setup consists of a tubular furnace with a borosilicate/quartz/alumina tube inside serving as reaction chamber, see **Figure 1**, the nature of the tube would depend on the temperature conditions used in the process. If the process requires a catalyst, it can be placed inside the reaction chamber, such is the case for the CVD synthesis of graphene as will be reviewed in detail below. Depending on the mechanism used for the delivery and the type of precursor, the pressure conditions employed, different CVD configurations can be considered [5]. Each one of these alternatives can undergo the same tasks, but each will use a different approach to fulfill it. In the following sections, some of the most common and popular configurations will be exposed.

### **2.1 APCVD**

The atmospheric pressure chemical vapor deposition (APCVD) is one of the simplest configurations found for a CVD system since it operates in normal conditions (atmospheric pressure), making this option more affordable and easier to implement at laboratories. However, due to these conditions, problems related to the dispersion of the gases within the chamber have been considered as one of its major disadvantages, because the decomposed particles will not cover the substrate homogeneously as expected [6, 7].

For this approach, different precursors can be used. In the case of liquids or solids dissolved in solution, a bubbler or an evaporation system will be required to stimulate the particles to be expelled and consequently be transferred into the chamber by the action of a carrier gas, provoking its decomposition in the reaction site [6].



**Figure 1.** Schematic representation of a horizontal CVD setup, specifying the three constituent modules (top) and diagram of an LPCVD setup for the synthesis of graphene on copper foil and methane as precursor (bottom), dashed rectangles highlight the corresponding modules.

## 2.2 LPCVD

The low-pressure chemical vapor deposition (LPCVD) is based on the use of vacuum for the outgassing of the system to achieve low pressures throughout the deposition process. In comparison with the last approach, with this technique, the dispersion and the deposition are enhanced, making it possible to obtain better coverage within the substrates and a higher quality. The pressures commonly used are between  $10^{-1}$  and  $10^{-2}$  torr and are reached with the use of mechanical and molecular vacuum pumps connected to the gas ejection module [6].

## 2.3 AACVD

The aerosol-assisted chemical vapor deposition (AACVD) is characterized for using fine sub-micrometer-sized aerosol droplets of precursor dispersed throughout a gaseous medium, which eventually are transported into the reaction zone to be decomposed and deposited in the target substrate. The atomization of the liquid precursor can be achieved by different routes, as it could be the use of an ultrasonic aerosol generation, a pneumatic aerosol jet, or *via* an electrostatic atomization. The AACVD possesses the advantage that thermally unstable and nonvolatile precursors can be employed for the synthesis of CVD products at lower cost. In addition, this variant is considered a more flexible option since it can be carried out under low pressure, atmospheric pressure, and in open atmosphere [8].

## 2.4 Roll-to-roll CVD

Roll-to-roll CVD is one of the most recent approaches developed, and it consists of a continuous process that can carry out the deposition of the material on a substrate and its withdrawal or a sequential process such as a further transference into another

suitable substrate (in some cases it is required). This CVD variant is equipped with conveyor belts that are in charge of the transport of the substrates into the reaction site, where a continuous inlet of gases throughout the chamber leads to a constant deposit built up in the incoming substrate without interruption. Subsequently, the conveyor belts either introduce the material into a second stage, where a transfer procedure can be done automatically, or take the substrate out of the system. This CVD configuration can be developed for different process conditions, such as ambient pressure, low pressure, or a plasma-enhanced CVD [9, 10].

## **2.5 Other configurations of CVD (PECVD, UHV-CVD, CW-CVD)**

One of the great advantages of using a CVD system is the wide variety of possible configurations. Above, we have described the most popular ones, but there is still a large catalogue of variants, among which are worth mentioning the plasma-enhanced chemical vapor deposition (PECVD), the ultrahigh-vacuum chemical vapor deposition (UHV-CVD), and the cold-wall chemical vapor deposition (CW-CVD), these alternatives will be briefly discussed in the following lines.

The PECVD variant uses plasma to improve the decomposition of the precursor and its deposition, allowing a reduction in the temperature and the possibility of avoiding the use of a catalytic substrate for the deposit [11]. The UHV-CVD is characterized by the use of more extreme low-pressure conditions ( $\sim 10^{-7}$  torr) to avoid the oxidation of the deposit and to enhance the decomposition of the precursor [12]. Finally, the CW-CVD owes its name to the lack of a heating furnace, and it relies on a Joule heating approach for the decomposition of the precursor, achieving a more selective and controllable reaction site, by locally heating the substrate [13, 14].

## **3. Synthesis of graphene *via* CVD**

Chemical vapor deposition has proven to be a very efficient method for graphene film synthesis [15]. It is possible to obtain films with few defects, good uniformity, and good control in the number of layers, acquiring films between one and few layers [16, 17].

Regardless of the CVD equipment configuration, almost all graphene synthesis procedures share the following requirements: a transition metal sheet that acts as a catalyst for carbon dissociation and as a substrate for graphene growth, which is placed inside the reaction chamber; a carbon-based precursor material [18]; temperatures around 1,000°C capable of decomposing the precursor material and dissociating the carbon [19, 20], at such temperatures a borosilicate tube is not convenient, the regular choice is a quartz tube, its transparency allows direct monitoring of the interior of the reaction chamber; a flow of hydrogen ( $H_2$ ) that provides a reducing atmosphere and influences growth behavior; and a flow of inert or carrier gas, argon (Ar) being the privileged option [18]. A diagram of a typical LPCVD setup for the synthesis of graphene is depicted in **Figure 1**. A characteristic of CVD-produced graphene films is the polycrystalline nature of the atom-thick membrane, as will be detailed below.

### **3.1 Copper foils as substrates**

Although the deposition of graphene on metal substrates by CVD was reported for the first time on other metals such as Ni and platinum (Pt), Cu is currently the most widely used metal as a catalyst substrate for the growth of graphene by CVD [16].

This preference can be explained by the growth mechanism of graphene on these substrates. The difference in mechanisms was elucidated by the group of R.S. Ruoff in 2009 [21] using carbon isotope labeling and Raman spectroscopy mapping of graphene films grown on Ni and Cu. The difference is due to the carbon solubility of each metal. For metals with high solubility (9,000 ppm at 900°C in Ni, and 11,000 ppm at 1,000°C in Pt) [22], carbon atoms infiltrate the metal matrix at high temperatures, and this solubility tends to increase with temperature. When the temperature drops, the solute is precipitated from the matrix, leading to the formation of graphene. This saturation and precipitation process results in the formation of MLG regions [17, 22]. In contrast, for metals with low carbon solubility (7.4 ppm at 1,020°C in Cu) [22], the solubility is relatively low despite high temperatures. Therefore, the process of carbon saturation and precipitation does not occur. Graphene is formed on the surface of Cu, limited to it; hence, the size of the graphene films will be correlated with the copper films in the reaction chamber. This process promotes the formation of SLG [17, 22]. Common Cu foil thicknesses for the growth of graphene films are 25 and 50 micrometers; moreover, the purity of the foil varies among commercial suppliers.

### *3.1.1 Growth mechanism*

In general, the growth mechanism of graphene by CVD on a copper substrate can be divided into three stages: (1) The precursor molecules collide with the surface of the Cu substrate. As a result, they can be absorbed on the surface, disperse back to the gas phase, or go to the next reaction step. (2) The molecules dehydrogenate totally or partially, or eliminate any element other than carbon (denitrogenation, deoxygenation), and active carbon species are formed. (3) The active species diffuse over the surface, cluster, generate nucleation sites, and begin to grow on graphene islands on the Cu substrate [15, 23]. These graphene islands are grains of honeycomb arranged carbons, they possess a particular orientation with respect to each other, when the grains are large enough and meet carbon atoms from a nearby grain, they coalesce, forming a grain boundary where the mismatch orientation is overcome by the presence of 5-, 6-, 7-, and 8-membered rings [24].

### *3.1.2 Annealing*

An important step prior to the CVD synthesis of graphene is the thermal treatment of the micrometer-thick Cu foils. Cu substrates undergo an annealing process that consists of heating them at high temperatures close to the Cu melting point, but lower than it (<1,085°C) for a certain period of time [25]. The surface of copper has some roughness, grain boundaries, surface defects, and impurity particles. This process is carried out in order to smooth the copper surface, reduce surface oxides, remove volatile impurities and surface contaminants, and favor the formation of graphene on the surface [26]. In addition, a reorganization of the copper atoms on the surface is promoted, which produces a release of internal stresses and an increase in the size of the Cu microcrystalline structure [25].

Regarding graphene nucleation, flat Cu regions, or terraces, favor the growth of SLG or BLG domains. In contrast, slope regions on the Cu surface, or ledges, promote MLG growth. Additionally, grain boundaries, impurities, and surface defects contribute to the formation of MLG domains [26].

### **3.2 Precursors**

The synthesis of graphene using the CVD technique can be carried out with a large catalogue of carbon-based compounds used as precursors. These precursors can be categorized by their physical state or by their chemical structure. By physical state, they can be classified as gaseous, liquid, and solid. While based on its chemical structure, they are separated as aliphatic and aromatic compounds. The use of an appropriate precursor with the right conditions can improve the efficiency of the production process and the quality of the final product [15].

#### *3.2.1 Gases*

Gaseous carbon precursors are the main source used for graphene synthesis by CVD. The most used are hydrocarbons such as methane ( $\text{CH}_4$ ) and acetylene ( $\text{C}_2\text{H}_2$ ), followed by ethylene ( $\text{C}_2\text{H}_4$ ) [27–29]. A gaseous precursor occupies less space than a liquid or solid one, because they can be stored in certain specialized containers. Some precursors are produced as a by-product of industrial processes, such as biogas, which is constituted essentially of methane and carbon dioxide [15].

#### *3.2.2 Liquids*

Liquid carbon precursors are less commonly used in CVD methods. The most common precursors used in CVD are hexane ( $\text{C}_6\text{H}_{14}$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), and benzene ( $\text{C}_6\text{H}_6$ ) [30–32]. These liquid carbon precursors are easy to use and relatively inexpensive compared with gaseous ones [15, 32].

In contrast to the use of gaseous materials, when the precursor used is in a liquid state, a previous stage is needed to transform the precursor from its liquid form to a vapor in order to be deposited on the metal substrate. Various CVD configurations have been used to work with liquid precursors. An approach constitutes the use of an external source of heat to vaporize liquids with high boiling points. Ultrasonic baths can be used to form aerosols from the liquids [15]. Unlike gaseous precursors that have a certain flow, an external constant gas flow is needed to carry the post-treatment precursor to the reaction chamber [15, 16]. Some of these precursors could be harmful to human health, since some may be volatile organic compounds or carcinogenic in nature [15].

#### *3.2.3 Solids*

Solid carbon precursors are equally rarely used. They are more complex in terms of chemical and biological structure. Any organic material that works as a carbon source can be used, including plant waste, plastics, animal waste, insect parts, even food. Therefore, solid precursors occupy more space in the reaction chamber than gaseous or liquid precursors [15, 33].

As with liquid precursors, prior to the synthesis process, an extra step is required to convert the solid material into a gas phase before acting on the metal catalyst. More energy is required to carry out the process, which can increase costs. Solid carbon precursors can be placed directly on top of the catalyst metal so that graphene forms on the back of the catalyst. Polymers have been spin coated directly on copper foils and used as carbon precursor [34]. Most of the precursors used are solid wastes or biomass; using these products to form graphene would positively impact waste

recycling for the production of a high-value product and may reduce the overall cost of synthesis [15].

**Table 1** presents different carbon precursors that have been used for the synthesis of graphene, divided by their previously discussed physical states, along with a detailed example of the synthesis process using one of those precursors.

Physical state	Compounds	Example
Gas	Methane [27], acetylene [28], ethylene [29], propene [35], biogas [36]	Acetylene was used as a precursor gas in a LPCVD to fabricate SLG and BLG at 1,035°C with a flow of H <sub>2</sub> [28].
Liquid	Ethanol [32], hexane [30], benzene [31], methanol [37], pyridine [38], 1-propanol [37], 2-phenylethanol [39], palm oil [40]	SLG, BLG and tri-layer graphene (TLG) was synthesized with APCVD using two alcohols as precursors: 2-phenylethanol and ethanol at 980 or 990°C using a Ar-H <sub>2</sub> mixture [32].
Solid	PMMA [34], hexabenzocoronene [39], highly oriented pyrolytic graphite [41], cookie [33], cockroach leg [33], grass [33], camphor [42]	APCVD was used to produce SLG and BLG graphene sheets with solid camphor that was evaporated in a first furnace at 200°C, and pyrolyzed in a second furnace at 1,020°C using H <sub>2</sub> as carrier gas [42].

**Table 1.**

*Carbon precursors used for the synthesis of graphene organized by their physical state. An example of the synthesis performed is shown in each case.*

### 3.2.4 Aliphatic compounds

To decompose aliphatic precursors, high temperatures are needed to promote the partial or total dehydrogenation of carbon compounds, as well as the removal of other elements that could be previously linked to the chains, such as nitrogen and oxygen. Subsequently, it is necessary to promote the breaking of the carbon-carbon bonds between the chains. This favors the deposition of active carbon species on the metal substrate, the subsequent formation of graphene growth nuclei in sp<sup>2</sup> formation, and the capture of active carbon for the growth of the graphene islands [15].

### 3.2.5 Aromatic compounds

Aromatic compounds require a lower growth temperature, and graphene growth using benzene at around 300°C has been reported by Jang and coworkers [43]. Processes of dehydrogenation and possible denitrogenation and deoxygenation of the aromatic species take place at lower temperatures. Active aromatic ring species are deposited on the substrate forming graphene growth nuclei and capture the active carbon species for island growth. The low energy needed is related to the basic structure of aromatic compounds, which is analogous to the hexagonal honeycomb packaging of graphene [15].

### 3.2.6 Greener options

In order to develop ecological and environmentally friendly CVD methods, green and bio-renewable carbon sources that are easily obtained at low cost are sought [40, 42, 44].

With the implementation of these precursors, it is attempted to reduce the use of greenhouse gases, the exploitation of toxic materials, and the development of ecological and sustainable technologies [44].

It has been possible to synthesize graphene using various ecological precursors such as foods, for example, cookies, chocolate, honey, sugar, butter, milk, cheese; waste such as plastics, grass, bones, eggshells, dog and cow feces, wood, leaf, bagasse, fruit, tea tree extracts; and derivatives of insects [44].

In particular, the use of solid botanical camphor ( $C_{10}H_{16}O$ ) for the synthesis of SLG and BLG graphene sheets has been studied. Camphor is a natural solid botanical hydrocarbon source, which is regenerative, low-cost, and environmentally friendly [42]. Similarly, the use of palm oil as a carbon precursor for the synthesis of MLG has been studied. Palm oil is a natural oil source that has a unique chemical composition with long-chain carbon. It has high potential as a green and renewable carbon precursor in the large-scale production of graphene [40].

### 3.3 Gases

Molecular hydrogen has a fundamental role in the synthesis of graphene by CVD since it acts as an activating gas. It acts by cleaning the surface of the substrate, reducing impurities and defects during the annealing process, as well as reducing surface oxides [17, 23]. It behaves as a co-catalyst, along with the substrate, promoting the growth of graphene, as well as an etchant to control the growth and its properties [23, 45]. It controls the adsorption, stability, thickness or number of layers, the population on the catalyst surface, the configuration of the edges, and the morphology of the domains of the grown graphene [17, 23, 45].

The flow of  $H_2$  has been considered as an important factor for the quality of graphene during synthesis. By using a gaseous precursor, the radius of  $H_2$  with respect to the precursor gas can be studied [17]. It has been observed that when the  $H_2/CH_4$  volume ratio in a process is greater than 0.5, the graphene remains in small separate islands and does not coalesce to form a large film. This may happen because excess  $H_2$  can limit graphene growth by removing weak carbon-carbon bonds despite acting as a co-catalyst [46]. If the ratio of  $H_2$  to  $CH_4$  is too high, the etching of carbon species becomes much faster than the formation of graphene layers [47], destroying the integrity of the network and reducing the quality of graphene [17].

Regarding the flow of the precursor gas, it has been reported that, for methane, the number of layers does not depend on the  $CH_4$  flow rate, although an increase in defects was observed with the increase in flow [17].

Similarly, the use of an inert gas can help the synthesis process. The inert gas can be used to dilute the carbon feedstock to achieve high  $H_2$  to precursor ratios, to increase the total pressure of the reaction chamber, or to dilute flammable or explosive material below its lower explosive limit [18, 46]. The concentration of each gas can range between 0 and 100%. The explosive limits of  $H_2$  in air range between 18 and 60%, and the flammable limits between 4 and 75%. Pure  $H_2$  and  $H_2$  mixture beyond the flammable limit are dangerous [46]. Furthermore, it can be used as a carrier gas for precursor molecules in certain cases [16]. Gases such as Ar and nitrogen ( $N_2$ ) have been used to fulfill this function [16, 18, 46]. Ar is chemically inert under the conditions used during the synthesis [18, 46].  $N_2$  is inert as well, although more abundant and cheaper than Ar. Since it exists as a diatomic molecule, there is a risk that  $N_2$  will dissociate during synthesis. The dissociation product could act as a substituent in the graphene film, causing a doping or interruption of the network. However, the triple



bond present has a very large binding energy, so the rate of N<sub>2</sub> dissociation should be extremely small at the temperatures used. Furthermore, Cu is an inefficient catalyst for the dissociation of N<sub>2</sub> [18].

#### 4. Large-area single-crystal graphene

Using a CVD system, large-area SLG can be synthesized with high yields; however, its crystallinity can represent an important disadvantage for its application. The polycrystalline nature of the Cu substrate and the presence of impurities within its surface lead to a high density of nucleation sites and adlayers, resulting in a polycrystalline material that will present diminished mechanical and electrical properties than the ideal product.

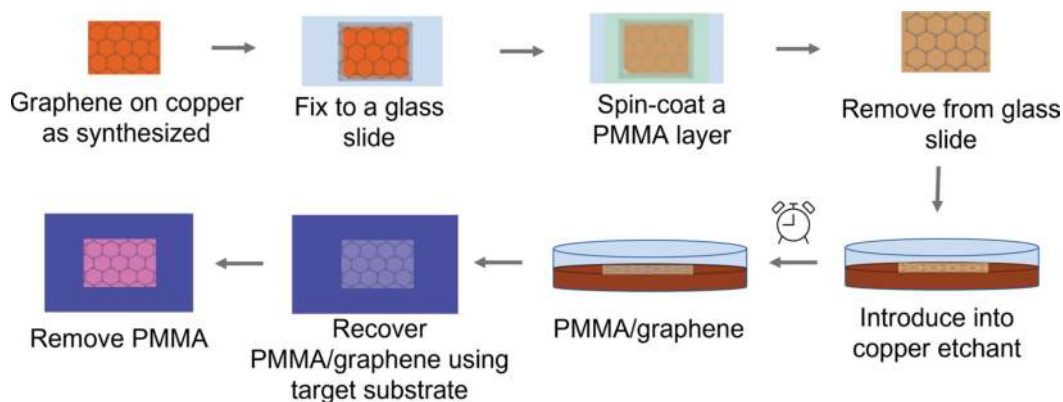
For this reason, in recent years, different alternatives have been proposed to solve this important factor. Li *et al.* and Yang *et al.* presented a methodology to reduce the nucleation sites during the growth, based on the use of Cu foil enclosures (folded as little pockets) that have the purpose to reduce the partial pressure of the precursor and undesired species inside the cavity of the enclosure, such as SiO<sub>2</sub> particles proceeding from the decomposition of the quartz reaction tube, commonly found as contaminants in the graphene surface [48, 49], achieving single crystals in the size range of several hundreds of microns. On the other hand, other research groups have used other alternatives, such as Weatherup *et al.* and Huang *et al.* employed metal catalyst alloys (e.g., Au, Cu/Ni(III)) to grow high-quality single-crystal graphene, also by reducing the nucleation density [50, 51]. In addition, the action of oxygen (O<sub>2</sub>) as a reducer of nucleation has been also studied. Hao and coworkers found in 2013 that O<sub>2</sub> can act as a passivation agent for the nucleation sites, reducing in consequence the density of the adlayers produced. They also concluded that O<sub>2</sub> can be provided by an external source or even by segregation within the Cu substrate, such as a Cu oxide [52]. Now, millimeter-sized single crystals have been achieved [53], this holds promise for the scalable and affordable production of graphene for electronic devices.

#### 5. Transfer procedures

Once graphene has been synthesized on Cu foils, its transfer to more suitable substrates for its study or to be used in different applications is necessary. There are several procedures that have been developed for this transfer step, having as purposes: a) to separate the graphene film from the original metal substrate where it was deposited and b) to protect the graphene after the transference [54]. In general, these procedures can be classified in two groups, the wet chemical methods and the dry chemical methods.

##### 5.1 Wet chemical methods

These methods are based generally on the coating of a protective polymeric layer over the graphene film (e.g., PDMS or PMMA), followed by the immerse in an etching solvent (e.g., FeCl<sub>3</sub>, HCl, HNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, CuCl<sub>2</sub>) to remove the metal substrate, so the graphene can be positioned then in another substrate (e.g., SiO<sub>2</sub>) [55]. **Figure 2** depicts a flowchart of the transfer process using PMMA. Despite the good results that could be obtained with this general technique, in recent years, new variants have been developed to overcome its disadvantages (i.e., the presence of impurities and the formation



**Figure 2.**  
Schematic representation of the wet transfer process using spin-coated PMMA.

of cracks in the material). Such is the case of An and collaborators, who developed a reverse transfer technique by locating the graphene/PMMA bilayer into a flexible substrate (e.g., PET), reducing the density of cracks and the presence of impurities [56]. Lin and coworkers found a way to avoid the use of the polymeric layer, achieving better quality of transferred graphene (free of organic residues). They used isopropyl alcohol (IPA) and ammonium persulfate solution ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) as the etchant agent, which was later substituted with DI water and IPA to reduce the surface tension and ease the transference to the desired substrate [57]. Furthermore, the need of the etching step has been also avoided in some techniques, such as Chandrashekar *et al.* reported a method to separate the Cu foil by oxidizing it in hot water, modifying its nature from hydrophobic to hydrophilic, easing its delamination from graphene [58].

## 5.2 Dry chemical methods

The dry chemical methods are based on the same principle as the wet ones, but with the difference that these ones are performed under dry conditions. Several methodologies have been proposed as well, such as Yang *et al.* reported an electrochemical procedure for the etching of the Cu substrate to reduce the contamination in graphene [59]. Martins' group developed a transference methodology *via* lamination into flexible substrates, using a direct transfer procedure without intermediates [60].

## 6. Conclusions

The chemical vapor deposition method provides graphene films of good quality and large area, the many variants of the method allow versatility in a number of parameters such as: precursor used, temperature, and pressure. From its first reports more than 10 years ago, CVD has remained as reliable technique to produce graphene films, many advances have been reported since, and understanding of the role of every parameter in the synthesis has been achieved. CVD graphene is polycrystalline by nature, and when more than one layer is produced, the mismatch or stacking of layers is not controlled, and these characteristics might condition its performance at the mechanical and electrical level. Applications that require continuous, conductive, transparent films can be tackled using CVD graphene; however, the transfer process remains a challenge to overcome.


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