Reviews Article

Synthesis of carbon nanostructures using the chemical vapor deposition technique: An overview

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ABSTRACT

The boom in nanotechnology over the last three decades is undeniable. Responsible for this interest in nanomaterials are mainly the nanostructured forms of carbon, since historically they were the ones that inaugurated the study of nanomaterials with the discovery of fullerenes in 1985 and carbon nanotubes in 1991. Although a variety of techniques exist to produce these materials, chemical vapor deposition (CVD) is particularly valuable as it allows the production of a wide variety of carbon nanostructures, is versatile, scalable, easy to implement and relatively low cost. This review article highlights the importance of CVD and details its principles, operating conditions and parameters, as well as its main variants. A description of the technique used to produce fullerenes, nano-ceramics, carbon nanotubes, nanospheres, graphene and others is made, emphasizing the specific parameters for each synthesis.
Keywords: Chemical Vapor Deposition, Carbon Nanostructures, Synthesis

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1. Introduction

The discovery of C_{60} (buckminsterfullerene) in 1985[1], triggered a wave of research on allotropic nano-sized forms of carbon. This event triggered the discovery of other nanostructured forms of carbon such as: single- and multi-walled nanotubes[2,3], nano-onions[4], nanolistones[5], nano-horns, nano-diamond, carbon dots[6], nanospheres[7]) and recently graphene[8]. Various nanofabrication methods are involved in the synthesis of these nanostructures such as: laser ablation, arc discharge, chemical vapor deposition and more recently hydrothermal or wet chemical methods such as sol-gel.

Of particular importance is the chemical vapor deposition (CVD) method due to its versatility, ease of implementation, low cost, scalability, among other advantages. **Figure 1** illustrates models of carbon nanostructures that can be produced by the CVD technique, most of these materials are made of carbon atoms with sp^2 hybridization. Fullerenes are a family of spherical molecules that can contain 60 atoms or more (even numbers), achieving giant fullerene structures of up to hundreds of atoms. Structurally, the fullerene or C_{60} is a spherical cage (similar to a soccer ball) made up of exactly 60 carbon atoms, in this structure are the carbons with sp^2 hybridization, each attached to 3 neighboring atoms, the introduction of pentagons is essential to form the curvature needed to close[1]. Related to fullerenes are nano-onions, which consist of concentric fullerenes inside each other, generating an onion-like structure. Graphene is a sheet of carbon atoms with sp^2

hybridization configured in a hexagonal arrangement, it is a two-dimensional nanomaterial, graphite is formed by stacking graphene sheets one on top of the other. Starting from a graphene sheet, by rolling it up, carbon nanotubes can be obtained[2,3].

These nanostructures motivated further research in the 1990s and the first decade of the 2000s, their amazing mechanical and electrical properties have led to technological applications in the market and in development. Undoubtedly, the nanostructure that receives more attention is graphene, for its isolation was awarded the Nobel Prize in Physics to Novoselov and Geim in 2010[9]; increasing the number of research and technological innovation projects in order to enhance the amazing properties of this material. The aforementioned nanostructures, and others, are produced by the CVD method. This review article aims to introduce the reader to the principles, parameters and variants of CVD for the synthesis of carbon nanostructures, in addition to listing the most common carbon nanomaterials that are produced by this technique and their synthesis conditions.

2. CVD technique

2.1 Generalities

The chemical vapor deposition technique consists of promoting chemical reactions in the gaseous state from precursors, which trigger the formation of nanomaterials of interest. These chemical reactions generally take place inside a reaction chamber and are activated by high temperatures. The reaction precursors can be in liquid, solid or gaseous state and are brought into the reaction chamber where their decomposition is promoted by the high temperatures involved in the process, generally temperatures for the synthesis of carbon nanomaterials range between 800 °C and 1,000 °C. The reaction chamber must have an evacuation route for the gases that did not participate in the reaction or the vapors containing the products that have not been deposited.

Normally at the exit of the reaction chamber a gas washing or evacuation system is located by means of mechanical systems (vacuum pumps)[10,11]. A CVD setup can be presented in horizontal or vertical configuration, the most common configuration being horizontal at the research laboratory level, however, on the industrial scale there are equipment in vertical format. For the reaction chamber a material is required that resists exposure to high temperatures, which at the same time is inert and does not participate in the reactions of the process; the most common is to use quartz or alumina.
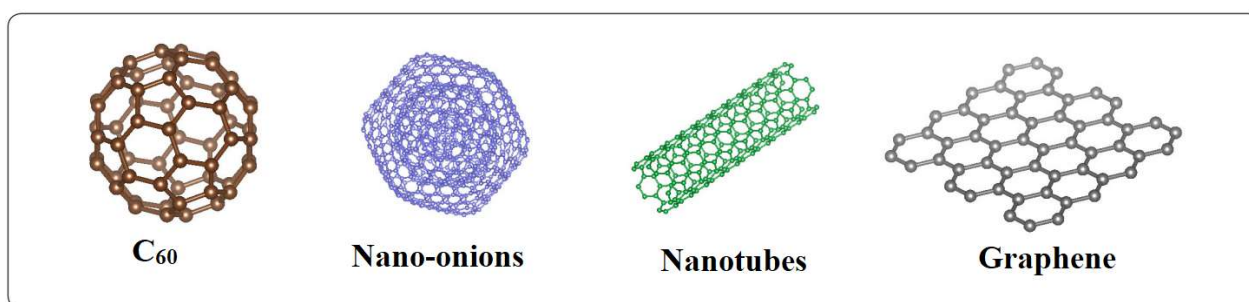

Figure 1. Models of the most representative carbon nanostructures[12–16].

Although there are various configurations, the most used is to place a quartz tube inside an electric tubular furnace, as exemplified in **Figure 2**. The region of the quartz tube inside the furnace is considered the reaction chamber, and at the ends of the tube, at the inlet and outlet, borosilicate glass gaskets are placed to allow the coupling of the pipes for the delivery of the precursors through the flow of a carrier gas[17]. The obvious choice of carrier gas is argon gas, as it is inert and easily accessible, although some groups choose nitrogen (N_2) as the gas in the system; hydrogen (H_2), which is important in the decomposition of precursors, is also used in some processes. Substrates with specific properties can be introduced into the reaction chamber and promote the deposition of the nanomaterials on its

surface, although generally, the quartz tube walls themselves serve as substrates for the deposition of the reaction products, except in cases where the synthesis requires a catalyst and this is not present among the precursors, as will be detailed later[18].

The most common precursors for the synthesis of carbon nanostructures are hydrocarbons, although it has been shown that thermal decomposition of any carbon source can be successful in the production of carbon nanostructures. Specifically for graphene, its synthesis using CVD from insects or cookies has been demonstrated[19].
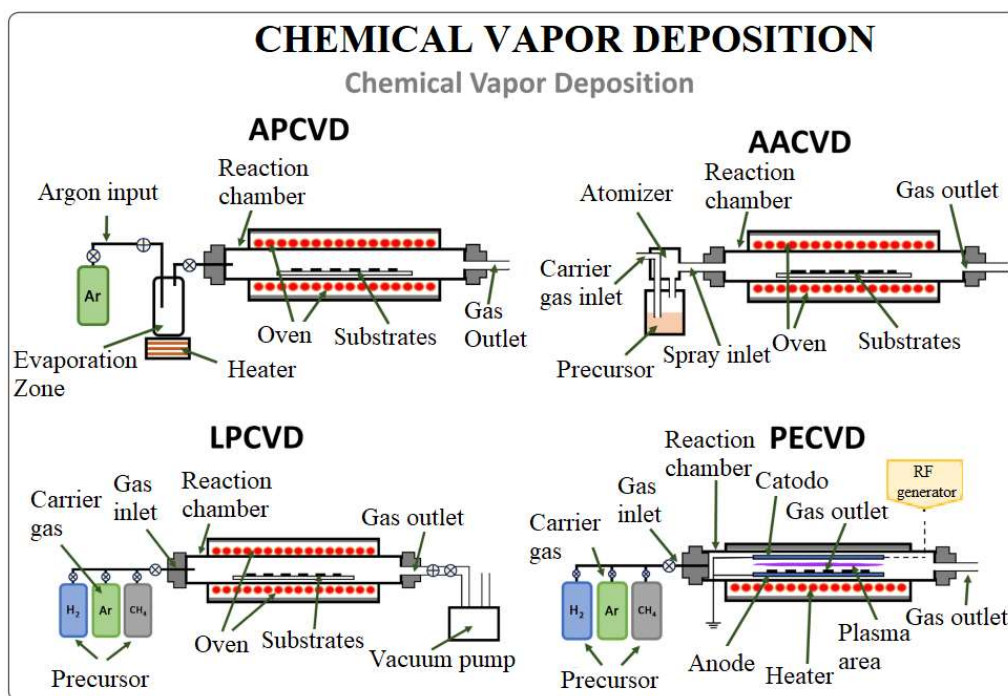

Figure 2. Detailed diagrams of the different CVD variants. APCVD: atmospheric pressure CVD, AACVD: aerosol assisted CVD[21], LPCVD: low pressure CVD[22] and PECVD: plasma enhanced CVD[23,24].

The synthesis of some carbon nanostructures, such as nanotubes, requires the presence of catalysts. The catalysts normally used are metals such as iron, cobalt or nickel. A successful way to provide such elements to the system is by organometallic molecules (ferrocene, cobaltocene, nickelocene) that are mixed with the carbon precursor.

There are two ways of providing the catalysts to the system, the first is called "floating catalyst" and the second "seeded catalyst" (*floating catalyst and seeded catalyst*, respectively), illustrated in **Figure 3**.

The floating catalyst process is characterized by the use of gaseous or solution catalysts mixed with the carbon precursor, which "float" into the reaction chamber. These catalysts are used to favor the decomposition reactions of the precursor, lowering the temperature required for the process. In this technique in particular, as the catalyst is floating, it interacts favorably with the precursor gas, favoring easier and faster decomposition[25].

In the seeded catalyst mode, solid catalysts "seeded" or attached to the substrate where the nanomaterials will be deposited, serve as nucleation points and the substrate is placed inside the reaction chamber. As the precursor decomposes into individual particles or atoms, they will be placed around or on the catalysts to form the final carbon nanostructure. This procedure is widely used in the synthesis of carbon nanotubes since from this "seed" the tubes can be elongated vertically[26]; it also allows the growth of nanotubes on the substrates, obeying specific patterns, since in areas without a seeded catalyst growth is not favored.

2.2 Variants

There are variants in the CVD process, some of them are: atmospheric pressure chemical vapor deposition (APCVD), low pressure chemical vapor deposition (LPCVD), aerosol assisted chemical va-

por deposition (AACVD), plasma activated chemical vapor deposition (PECVD) and microwave assisted chemical vapor deposition and plasma activation (MW-PECVD), described in the following lines and illustrated in **Figure 2**.

2.3 Ambient Pressure Chemical Vapor Deposition (APCVD)

This is the most common form, described above, and is operated at a pressure of 1 atm (ambient pressure). A vacuum pump is not used to regulate the pressure. The precursor is usually a liquid or a dissolved solid, so it is heated to sufficiently high temperatures so that it begins to evaporate and a vapor cloud is generated. The carrier gas is responsible for pushing the precursor vapor into the tube and through the furnace (reaction chamber) to the outlet[27].

2.4 Low Pressure Chemical Vapor Deposition (LPCVD)

It consists of a CVD process using a vacuum pump connected to the tube outlet that regulates the internal pressure of the equipment to pressures close to vacuum (approximately 10^{-1} to 10^{-2} torr). For this process, a fully gaseous precursor is used, which travels through the tube to the outlet along with the carrier gas. Due to the low pressures, the decomposed atoms are better dispersed in the substrate[27].
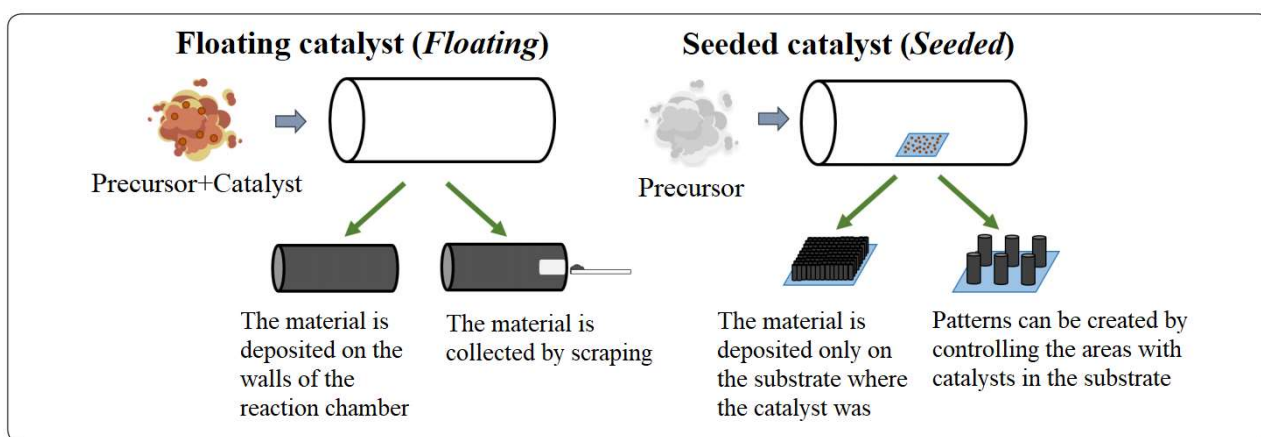

Figure 3. Schematic representation of the types of catalysts used in a CVD process for the synthesis of carbon nanotubes. On the left, floating catalyst, which is introduced into the reaction chamber along with the precursor; on the right, seeded catalyst, which is deposited on a substrate inside the reaction chamber and is activated when the precursor is introduced. Personal elaboration.

2.5 Aerosol-Assisted Chemical Vapor Deposition (AACVD)

In this method, a liquid precursor is used for the synthesis, which is transported to the reaction chamber in the form of an aerosol. Usually an ultrasonic bath is used, which generates ultrasound that propagates throughout the precursor to agitate its particles until aerosol droplets appear. The carrier gas transports the aerosol through the system to react and deposit on the substrate[28].

2.6 Plasma Activated Chemical Vapor Deposition (PECVD)

This method is classified as a variant of LPCVD, very low pressures are used for the decomposition of the precursor, however, in this method much lower temperatures are used due to the use of a plasma, which "activates" the precursor, facilitating its decomposition. The plasma is a gaseous state where reactive radicals coexist in the form of electrons, ions, neutral atoms and other highly energetic particles. This plasma is produced through the acceleration of electrons in an electric field, generated by means of two electrodes connected to a voltage source[29]. In this method, gaseous precursors are used, which with the help of a carrier gas pass through the plasma zone, where the decomposition and deposition reaction takes place on the substrate.

2.7 Microwave Assisted Chemical Vapor Deposition and Plasma Activation (MW-PECVD)

This methodology is a sub-variant of PECVD,

a plasma is also produced for the decomposition of the precursor, but this is produced by microwave action, which is a low energy electromagnetic radiation. A source of approximately 2.45 GHz is introduced through a dielectric window, which will excite the gases producing the characteristic luminescent plasma that will carry out the decomposition reaction. It is characterized by being able to operate at higher pressures than PECVD[30].

3. Carbon nanostructures produced by CVD

3.1 Fullerenes

As mentioned, in 1985, the synthesis of C_{60} fullerene was reported for the first time by the laser ablation method, a technique used to date to obtain the nanomaterial, where the vaporization of graphite is carried out by laser irradiation[1]. Since then, other methods such as chemical vapor deposition, pyrolytic routes[31], arc discharge, and combustion processes have been employed in search of better yields. Combustion processes are emerging as the most favorable for the industrial production of fullerenes due to the high efficiencies reported[32].

Regarding chemical vapor deposition for the synthesis of C_{60} and C_{70}, it should be noted that the technique has been less prominent due to the low yields obtained; however, the formation of these fullerenes as by-products of diamond synthesis by the hot filament chemical vapor deposition method and microwave-assisted chemical vapor deposition has been reported[33].

The microwave-assisted chemical vapor deposition used for the synthesis of diamond and fullerenes consists of a quartz tube as a reaction chamber, inside which an excitation source from a generator (100 W, 2.45 GHz) is incident[34], responsible for the generation of the plasma precursor of the nanostructure. The gases used in this method are argon, hydrogen and acetylene, the latter being the carbon source. The process is subjected to pressures between 1 and 10 torr, but experiments with pressures above 25 torr and below 10 torr are also reported[34].

With regard to hot filament chemical vapor deposition[34], it consists of a stainless steel chamber, inside which is a tungsten filament, hanging vertically, with one of its terminals fixed and the other connected to a braided copper wire to avoid tension on the filament. Generally, the filament has a diameter of 0.75 mm and a length of 8 cm. The gases used for the synthesis are methane as a carbon source (0.4 sccm) and hydrogen (99.6 sccm). Likewise, a stainless-steel substrate support is used for the deposition of the diamond film and, consequently, for obtaining C_{60} and C_{70} fullerenes. Generally, the filament currents are between 50 and 60 A, and filament temperatures are 2,000 to 2,200 °C. Typical substrate temperatures are between 950 and 1,000 °C.

3.2 Nano-onions

Other nanostructures belonging to the family of fullerenes are known as nano-onions. Nano-onions were discovered in 1992 and are multiple layers of carbon that form encapsulated structures[35]. Their first synthesis method was by irradiation of an electron beam to a carbon nanotube sample, however, other methods such as nanodiamond heat treatment, arc discharge, chemical vapor deposition or implantation of carbon ions into metal particles[33].

With respect to chemical vapor deposition, some synthesis routes are based on the use of catalysts or plasma handling as an upgrading method. The catalysts employed are generally iron-containing alloys or compounds and the resulting nanostructures possess a core of this catalyst[36]. An example is using methane as a carbon source and stainless steel as a substrate at 800 °C[37] or the use of a nickel-iron alloy as a catalyst at 850 °C[38].

Plasma assisted chemical vapor deposition is a process generally carried out at pressures ranging from millitorr to a few torr. Inside the chamber there are two electrodes subjected to a small discharge, which generates a plasma from the gases between them, the plasma is generally produced by radiofrequency or direct current. When this process is carried out by radiofrequency, the gases most frequently handled are methane, as a

carbon source, and hydrogen. This synthesis method is very favorable due to the formation of pentagonal carbon rings, which are indispensable for the formation of the concentric spheres[39].

Unlike other methods, nano- onions produced by radiofrequency plasma-assisted chemical vapor deposition do not generate other types of products, such as carbon nanotubes[39]. Structures up to 50 nm in diameter with wave-like behavior in the layers due to the formation of pentagonal, hexagonal and heptagonal carbon rings have been reported[39]. In addition to not obtaining carbon nanotubes by this synthesis, the nano-beads present a unique behavior because during the growth mechanism they do not encapsulate the catalyst used as had been reported in other synthesis methods[39] and the result is a product with fewer impurities.

3.3 Nanotubes

The field of research on carbon nanotubes began in 1991, when they were experimentally observed by Transmission Electron Microscopy (TEM), and the conditions for the synthesis of large quantities of nanotubes were subsequently reported, early work was carried out on multi-wall carbon nanotubes (MWCNTs), which later led to the discovery of smaller diameter single-wall carbon nanotubes (SWCNTs) in 1993[40].

The synthesis of nanotubes can be carried out by different methods that have been reported in recent years, however, the most important is chemical vapor deposition (CVD), with which MWCNTs can be obtained, with the presence of a floating catalyst, by carrying out a pyrolytic decomposition of a feed solution (benzene-ferrocene, for example) in a furnace, by flowing argon through a reaction chamber, with temperatures of about 750 °C in the growth zone and 120 °C at the feedstock injection point[41]. The latter is placed in an alumina crucible and vaporized so that the argon flow transports the vapor to the growth zone and the carbon nanotubes are deposited on the substrate. The AACVD variant has also been used for the synthesis of carbon nanotubes.

The same technique can be carried out at atmospheric pressure using metal nanoparticles (NPs) on a substrate as a seeded catalyst, obtaining SWCNT. By heating the catalyst to elevated temperatures, the NPs become liquid or semi-liquid and hydrocarbon decomposition occurs on the surface of these metal droplets, producing carbon. Carbon precipitates on the outer layer of the catalysts upon reaching its required saturation level, starting to precipitate on its outer layer, forming tubular carbon solids with sp^2 structure, resulting in the growth of carbon nanotubes[42].

3.4 Graphene

Graphene is a two-dimensional (2D) material composed of a layer of carbon atoms densely packed in a hexagonal arrangement of sp^2 carbons bonded in a benzene ring structure[43,44]. The term "graphene", first used in 1987 by Sylvie Mouras, refers to a single atom-thick layer of carbon[45]).

Graphene films were first isolated by the method of mechanical exfoliation of a piece of highly oriented pyrolytic graphite[8]. In this method, graphene sheets stacked on graphite, weakly bound by van der Waals forces, are separated using adhesive tape, obtaining small films of varying thickness[43]. Unfortunately, apart from variations in thickness, they have irregular shapes and there is no control in their orientation[10]. Because of this, the most commonly used synthesis method today is chemical vapor deposition, which consists of the decomposition of a frequently gaseous hydrocarbon (solid and liquid precursors are also possible), usually by means of high temperatures (~1,000 °C), and its deposition on a copper surface[10]. Carbon atoms are provided by the precursor hydrocarbon, deposited on the nucleation sites of the metal substrate and dispersed on its surface aided by low pressures ($\sim 10^{-3}$–10^{-4} atm) forming graphene layers. This technique allows producing continuous graphene films of high purity over large areas[8].

In recent years this material has been extensively studied, due to the belief that graphene could replace many of the existing materials on the market, since it possesses unique properties such as: high mechanical strength and elasticity, high elec-

trical and thermal conductivity, transparency and impermeability. For the reader who wishes to delve into the study of graphene, it is recommended to consult the review by Soldano and collaborators on its production and properties[46].

3.5 Nanospheres

For the synthesis of carbon nanospheres by the ambient pressure chemical vapor deposition (APCVD) method, solid, liquid and gaseous carbon precursors are used.

For liquid precursors, various delivery systems are applied such as the use of bubblers[47], injection pumps or syringes (Direct Liquid Injection)[47], capillary tubes, as well as aerosol assisted pyrolysis mechanisms [48] from the precursor solution (toluene, naphthalene, etc.). For gaseous precursors different types of gas injectors are generally used[49] to regulate the amount of precursor that will enter the system. Finally, for solid precursors, sublimation methods[50] or bubblers[51] are applied. These systems transport the precursors to a previously heated oven where the temperature range varies between 800 °C and 1,100 °C[52], the synthesis time is variable, at the end of the reaction the oven is programmed to return to room temperature. Subsequently, the product is recovered for analysis. It should be noted that the temperature of the synthesis plays an important role in the particle size obtained, the higher the temperature the smaller the diameter[52], and depending on the size, these structures can have a larger or smaller surface area. Due to this property, it is also believed that they can be used as adsorbents[53], or additives for different nanocomposites[54] with a wide range of applications. As the nanostructure is carbon in nature, it is likely to avoid damage to the environment and the human body; moreover, due to its low toxicity, it is considered for use in the biomedical area[55,56].

3.6 Nanolistones

Another carbon nanostructure that has been produced by CVD is the graphitic nanoliston. Nanolistons are one-dimensional structures with lengths in the millimeter range, widths of 100–200 nm and thicknesses of ~20 nm[5]. The synthesis is carried out in an AACVD system, pyrolyzing at 950 °C a precursor solution containing ethanol (CH_3CH_2OH), ferrocene ($FeCp_2$) and a small concentration of thiophene (C_4H_4S). These nanolayers are made up of graphene layers stacked along the ribbon axis. The structure has been confirmed by X-ray diffraction and TEM. The morphology of the nanolayers guarantees a large surface area and the edges of the graphene sheets represent potential sites for binding molecules that will allow them to have varied applications. It has been studied that when subjected to high temperatures, the contiguous layers of graphene in the nanolayers tend to join together, forming bonds, to reduce the action of the highly reactive edges[5].

3.7 Other nanostructures

On the other hand, the CVD technique is not limited to the individual synthesis of nanomaterials, but can also be used as a means to obtain complex structures. Using a two-step procedure, a hybrid carbon nanostructure consisting of double-walled carbon nanotubes (DWCNTs) with graphene nanosheets has been synthesized by this technique. The first step consists of the synthesis of the DWCNTs by CVD with a floating catalyst. The process starts with the flow of argon into the system (500 sccm) until reaching 1,300 °C, at which time the flow of H_2 as carrier gas (1,000 sccm) is started and a solution of ferrocene and thiophene dissolved in ethanol (0.04 mL/min for 20 min) is pumped at ambient pressure. After being purified, the obtained DWCNTs are introduced into the reaction zone to produce the graphene nanosheets by CVD. A flow of argon (500 sccm) is initiated until reaching 1,300 °C and effecting the injection of ethanol (0.04 mL/min) as carbon source, employing H_2 as carrier gas (1,000 sccm). The result of the process is the growth of structures with sharp edges, resembling petals, along the walls of DWCNTs but maintaining the one-dimensional nanotube structure[58].

Another type of nanostructures that are synthesized by the chemical deposition method are nanowalls (NW's), where the plasma-assisted method (PECVD) is used. These are anchored to the surface of a substrate as elemental silicon wafers, without the need for metal catalysts, the structures

are grown by using a copper or tantalum cube located in the center of the substrate holder and a power of 500 W is applied to the system, two plasma treatments are made: one of hydrogen and the other of a combination of ammonia-acetylene. The degree of graphitization and growth rate depend mainly on the amount of ammonia used and the wall thickness depends on the anchorage to the substrate[59]. The utility of this nanostructure would be in electrochemical applications such as batteries and fuel cells, research has also been conducted for its use as a backlighting material for liquid crystal displays[60].

Finally, another nanostructure obtained by CVD is graphene quantum dots (graphene quantum dots, GQD's). These structures are obtained when the growth rate of graphene in the initial stage is suppressed well below the nucleation rate[61]. These conditions are obtained with a low precursor flow rate (2 mL/min) and at a relatively low temperature (1,000 °C), the product is deposited on copper substrates[61]. These structures possess a large number of vents such as biocompatability, low toxicity, good solubility and large surface area[62], so they can have a wide range of applications.

4. Conclusions

The chemical vapor deposition technique is a widely used bottom-up nanofabrication method for the synthesis of nanomaterials. Its versatility and easy implementation make it a highly popular technique for the production of carbon nanostructures. The adjustment of parameters such as temperature, flow, nature of precursors, pressure and synthesis time allows the synthesis of zero-dimensional nanostructures (fullerenes, nano-onions, nanospheres), one-dimensional (nanotubes, nanoribbons), two-dimensional (graphene) and three-dimensional. dimensional (hybrid nanomaterials). This review aims to make known the usefulness of the CVD technique and to introduce some nanostructured allotropes of carbon.

Acknowledgments

Conflict of interest

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