Graphene Synthesis Using a CVD Reactor and a Discontinuous Feed of Gas Precursor at Atmospheric Pressure

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1. Introduction

Graphene is a two-dimensional material with sp² hybridization and carbon atoms in a honeycomb arrangement [1, 2]. Nevertheless, it was not until 2004, after its isolation by mechanical exfoliation, that electric properties of a monolayer were published [3], followed by many other studies that showed extremely interesting properties, such as electronic mobility in room temperature higher than 2.105 cm² V⁻¹ S⁻¹, Young’s Modulus of 1 TPa, thermal conductivity above 3000 WmK⁻¹, 2.3% of optical absorption, and the capacity to be functionalized by a wide range of organic groups [4–6]. Hence, graphene is a material with a broad range of applications from mechanical, electrical, and optical applications to medical ones [5, 7]. Several methods have been used to prepare graphene, including graphite micromechanical exfoliation, epitaxial growth over SiC, graphite oxide reduction, and CVD [8] with the unique purpose to obtain large areas and more production [9, 10].

Therefore considering its high productivity, CVD is one of the most promising processes to grow high quality graphene in large areas [11–13]. Accordingly, in recent years a considerable effort has been done to optimize the process, improve the kind of substrate, and control graphene growth [12, 14].

In initial experiments to form graphene, CVD systems with methane as the carbon precursor and hydrogen as a balancing gas were used and are still commonly used today. Thereafter, atmospheric pressure CVD (AP-CVD) or other
Table 1: Overview of CVD processes synthesis.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Annealing</th>
<th>Growth conditions</th>
<th>Temperature (°C)</th>
<th>Total time (min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-p</td>
<td>H₂/Ar</td>
<td>CH₄</td>
<td>5</td>
<td>700</td>
<td>1045</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂/Ar</td>
<td>CH₄/Ar</td>
<td>15</td>
<td>1:1000</td>
<td>1050</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂</td>
<td>CH₄</td>
<td>35</td>
<td>1</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu (111)</td>
<td>H₂</td>
<td>CH₄</td>
<td>5</td>
<td>3.9 × 10⁻²</td>
<td>1000</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂/Ar</td>
<td>CH₄</td>
<td>20</td>
<td>1:20</td>
<td>1000</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂</td>
<td>CH₄/CH₂</td>
<td>50</td>
<td>1:1</td>
<td>1000</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂</td>
<td>CH₄/CH₂</td>
<td>5–20</td>
<td>2:1</td>
<td>1000</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂/Ar</td>
<td>CH₄/CH₂</td>
<td>10</td>
<td>1:8</td>
<td>1000</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂/Ar</td>
<td>CH₄</td>
<td>5</td>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂/Ar</td>
<td>CH₄/Ar</td>
<td>30</td>
<td>1:9</td>
<td>950</td>
</tr>
<tr>
<td>Ni</td>
<td>H₂</td>
<td>C₂H₂/C₂H₃</td>
<td>6–36</td>
<td>2:1</td>
<td>0.99</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂/Ar</td>
<td>C₂H₂/Ar</td>
<td>20</td>
<td>1–12</td>
<td>12:1000</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂</td>
<td>C₂H₂/C₂H₃</td>
<td>40</td>
<td>1:9</td>
<td>1:280</td>
</tr>
<tr>
<td>Cu-p</td>
<td>H₂</td>
<td>C₂H₄</td>
<td>60</td>
<td>1:1</td>
<td>1</td>
</tr>
<tr>
<td>Cu-p</td>
<td>N₂</td>
<td>C₂H₄</td>
<td>20</td>
<td>30</td>
<td>1</td>
</tr>
</tbody>
</table>

Cu-p: copper polycrystalline laboratory grade. *This work. **Standard cubic centimeter per minute. Note: In this table the time cooling and heating is not considered.

Carbon feedstocks have been explored (other gaseous hydrocarbons or carbon containing liquid or solid precursors) [15, 16]. Hydrogen is almost always used to achieve a better control in the synthesis of graphene on Cu. In industry, due to safety and cost issues, the use of pure hydrogen may not be preferred. Although processes using diluted hydrogen and methane have been developed, it should be noted that, in practice, these gases invariably contain trace amounts of oxidative impurities, which may have a significant effect on graphene growth [17].

At the same time, a deeper understanding has been acquired for each role in the synthesis stages [10, 13, 18, 19]. And two main challenges have been identified concerning graphene quality. First, substrates can lose their catalytic activity during permanence time inside the reactor, a process known as “cooking.” The second factor is related to the high temperatures and long growth times needed when monocrystalline cooper (111) is used as a substrate. An important challenge in graphene synthesis is to obtain high production volumes with high structural quality and visualize a methodology for future application on an industrial scale. Even so, the reported experiments still contemplate long synthesis times of up to 27 hrs at continuous gas flowrates [20] and expensive substrates [21] (Table 1). When the above variables are not taken into account, the performance and commercial attractiveness of this material could be decreased or limited [22].

The improvement of each of these aspects enables the control of graphene properties to satisfy the application-oriented needs such as production specifications (e.g., cost, rate). Until now, the commercial use of graphene is still restricted by the lack of standardized techniques for production that guarantee high energy efficiency and high structural quality. The improvement of electronic devices depends strongly on the quality of the graphene obtained [23].

In this paper, a novel and fast CVD method for graphene synthesis is proposed in order to decrease dramatically the usage of gases in a batch process. In addition, Cu (technical grade) polycrystalline substrates are used instead of monocrystalline (111) or laboratory grade (reagent) decreasing the production costs about 80 percent when compared to traditional CVD processes. Finally, the proposed method allowed the production of graphene with a similar quality (∆I_G/2I_G > 2) to that obtained by methods that require high vacuum and a continuous gas flowrate [24, 25].

2. Experimental

2.1. Materials. Polycrystalline copper foils of quality electrolytic industrial (C-1000) with a size of 15 × 30 cm and purity of 99.9% w/w were used as substrates. The copper was washed with plenty of acetone and cleaned with wipes to remove grease and dust. Acetylene gas was used as carbon precursor with 98% concentration. High purity nitrogen gas was used for getting a neutral atmosphere and a high purity 90:10 mixture of N₂ : H₂ gases were used to obtain reducing conditions inside the reactor and before the graphene deposition. A conventional CVD reactor provided with an inverted compressor was used in order to facilitate the gas expulsion.

2.2. Growth Process. The studied parameters were temperature and flow rate of carbon precursor. In brief, a flow...
of N₂ gas was introduced into the reactor for 15 min to remove the present oxygen. Then 1 L/min of N₂/H₂ was introduced to reduce the copper oxides in the surface of the sheet. Afterwards, on the one hand, acetylene was injected to the reactor at constant flow rate for 1 min. The injection was stopped in order to start the graphene growth process with the gas trapped inside reactor at different temperatures (Table 2). The cooling down was carried out under nitrogen atmosphere with a ramp of 8 °C/min.

2.3. Characterization. Graphene layers were analyzed in a high-resolution transmission electron microscope (HRTEM) JEOL-JEM 2200FS equipped with a spherical aberration corrector in the condenser lens and operated at 200 kV. Images were acquired in STEM mode, with bright field (BF) and high angle annular dark field (HAADF) detectors. Also, atomic force microscopy (AFM) was used, Asylum, model MFP3D-SA, using the technique of noncontact mode or AC, with rectangular cantilever model AC240TS-R3 at 2 N/m and a scanning speed of 70 kHz. The Raman spectra of graphene layers on copper substrate were recorded using a Renishaw in Via Raman spectrometer with an electronically cooled (−70 °C) CCD camera and a Leica microscope. The excitation source used was a He-Ne laser with emission at 633 nm; integration time was 10 seconds. A diffraction grating at 1200 lines/mm and objective of 50x magnification with numerical aperture of 0.75 were used.

3. Results and Discussion

3.1. Graphene Synthesis by CVD. Table 1 shows an overview of CVD processes used with different gas precursors and growth conditions. Unlike the conditions mentioned in Table 1, our process allows the graphene synthesis, in a maximum time of 66 min, without making use of vacuum pumps. Note that for similar times of synthesis, pressures of 3–9 × 10⁻² torr are required in most of the processes reported in Table 1 while atmospheric pressure is used in ours. Also in our process N₂ is used as carrier gas instead of using argon, which is more expensive.

The proposed synthesis method is compound by four stages (cleaning, precursor injection, reaction time, and cooling). The temperature and flowrate of carbon precursor were the studied parameters. In Figure 1(a) the traditional process and differences with our process are shown.

In the first stage, the process temperatures 800, 900, and 1000 °C were evaluated as shown in Table 2. The objective was to know the temperature at which amorphous carbon is formed and avoid it in the following tests. A flowrate at 100 sccm of acetylene was used as reference.

In the second stage, acetylene gas flowrate was tested at 100, 80, 30, and 10 sccm as shown in Table 3. The heating temperature was fixed after obtaining the results being 1000 °C, the temperature which avoids the amorphous carbon deposition.

3.2. Proposed Reaction Mechanism. For graphene synthesis by CVD the use of both saturated and unsaturated hydrocarbons is essential [5, 8, 37, 38]. Saturated hydrocarbons are stable and less reactive than unsaturated hydrocarbons. C₂H₂ has a positive Gibbs free energy formation with a value of ∆G = 209 KJ/mol, indicating that reactants are favored in the

![Figure 1: Schematic representation of the graphene synthesis with (a) proposed method at atmosphere pressure using polycrystalline substrate and gas discontinuous flow and (b) traditional process at high vacuum using monocrystalline substrate and gas continuous flow.](image-url)
following reaction: \( 2C_{(s)} + H_{2(g)} = C_{2}H_{2(g)} \) [39, 40]. According to thermodynamics data, \( C_{2}H_{2} \) begins to decompose at 25°C and is highly reactive. Figure 2 shows a comparison of \( \Delta G_f \) between \( C_{2}H_{2} \) and other hydrocarbons that have commonly been used in graphene synthesis [41]. As can be seen in Figure 2, as temperature increases, methane retains more stability when compared with acetylene (\( CH_4 > C_2H_6 > C_2H_4 > C_2H_2 \)). Thus, acetylene presents a positive \( \Delta G_f \) in a wide range of temperatures unlike methane which has a negative \( \Delta G_f \) in temperatures lower than 500°C.

Since acetylene is highly reactive, it might interact within the reactor with hydrogen, generating hydrogenation reactions. Thus other hydrocarbon species can be formed. To gain insight into the possible reactions occurring within the CVD furnace, the following acetylene reactions were analyzed:

\[
\begin{align*}
C_2H_2(g) & = 2C + H_2(g) \quad (1) \\
C_2H_2(g) + H_2(g) & = C_2H_4(g) \quad (2) \\
C_2H_2(g) + 2H_2(g) & = C_2H_6(g) \quad (3) \\
C_2H_2(g) + 3H_2(g) & = 2CH_4(g) \quad (4) \\
CH_4(g) & = C + 2H_2(g) \quad (5)
\end{align*}
\]

The variation of the standard Gibbs free energy change with temperature is

\[
\Delta G = \Delta H^0_f - T \Delta S^0_f, \tag{Ec.1}
\]

where

\[
\Delta S^0_f = \Delta H^0_f/298 + \int_{298}^{T} \Delta C_p \, dT - T \Delta S^0_{298} - T \int_{298}^{T} \Delta C_p \, T \, dT \tag{Ec.2}
\]

[42] and

\[
\Delta C^0_f = -RT \ln K, \tag{Ec.3}
\]

where \( K \) is the equilibrium constant.

The constant \( K \) allows knowing the behavior of a reaction by increasing the temperature; therefore, for \( \log K > 1 \), the reaction favors the products, while for \( \log K < 1 \) the reaction favors the reagents [39]. Figure 3 shows the \( \log K \) for acetylene hydrogenation reactions as well as its dehydrogenation reaction.

3.3. Transmission Electron Microscopy. Figure 4 shows typical micrographs obtained by electron transmission microscopy using dark and bright field illumination mode. By means of this technique, some highlights of the sample are visible which are difficult to observe in normal mode. Basically, transparent parts of the sample are shown in dark while the particles appear bright since they receive and scatter light in different directions. The results show sheets that were pulled up from Cu substrates during sonication. In Figure 4, images that appear at the top show the bright field and the corresponding dark field STEM images appear at the bottom. The acetylene flow was fixed at 100 sccm and images in the left, center and right side correspond to temperatures of 1000, 900, and 800°C, respectively (Table 2). Both images at 1000°C show the presence of few layers of graphene in contrast to the other temperatures (900 and 800°C). In samples obtained at 900°C the presence of graphene layers and carbon agglomerates as brighter areas (bottom) was observed. This effect can be attributed to the stacking of carbon atoms on the nucleation.

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**Table 3: Evaluated acetylene gas flow rates.**

<table>
<thead>
<tr>
<th>Heating ( T ) (°C)</th>
<th>Cleaning Time (min)</th>
<th>Growth conditions Injection ( C_2H_2 \times 1 \min ) (sccm)</th>
<th>Reaction time (min)</th>
<th>Cooling Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>30</td>
<td>100</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>1000</td>
<td>30</td>
<td>80</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>1000</td>
<td>30</td>
<td>30</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>1000</td>
<td>30</td>
<td>10</td>
<td>5</td>
<td>30</td>
</tr>
</tbody>
</table>

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**Figure 2: Stability of hydrocarbon species.**
centers, which avoid the epitaxial growth of graphene sheets. Similarly, in process at 800°C, carbonaceous agglomerates are observed on a graphene sheet (top) confirming the agglomeration hypothesis using low temperatures. Initially, acetylene is decomposed on the copper surface facilitating the growth of a graphene sheet; nonetheless, under the growth conditions studied in this work, carbon precipitations were observed for process with temperatures below 900°C.

Additionally, the effect of acetylene flowrate was studied (see Table 3) maintaining a fixed temperature at 1000°C as a direct consequence of the obtained results. The objective was reducing the amount the amount of graphene layers previously obtained with a flow of 100 sccm. The presence of fairly thin sheets of graphene was achieved with a flow rate of 80 sccm (Figures 5(a) and 5(b)). In Figures 5(c), 5(d), and 5(e), samples where graphene was synthesized using 30 sccm can be seen. However, when acetylene flow rate of 10 sccm (data not shown) was tested, no graphene layers were observed, concluding that the flow rate of 10 sccm is not enough as carbon precursor.

3.4. Raman Spectroscopy. Raman spectroscopy was carried out in order to evaluate the structure of the graphene film growth at different conditions. This spectroscopy technique has been used to probe structural and physical properties of graphitic materials, providing valuable information about the atomic structure of edges, presence of disorder, defects, charges, and strain [43].

Figure 6 shows the characteristic spectra of this kind of carbonaceous materials. The analysis of Raman is focused on the D, G, and 2D bands of the spectrum, which are expected to appear at ∼1350 cm⁻¹, ∼1580 cm⁻¹, and ∼2680 cm⁻¹, respectively [44]. D band corresponds to disordered structure in graphene, especially at the edges of the graphene sheets. The G peak originates from the first-order scattering process due to the double degenerate phonon mode vibrations at the center of Brillouin zone and is related to sp² bonded carbon [45]. Measurement of \( I_D/I_G \) ratio is a well-known method for characterization of disorder [46, 47]. Ferrari et al. [48] showed that it is possible to use the second-order 2D (or \( G' \)) band in the graphene Raman spectra to learn about the number of layers in a graphene sample by using the \( I_{2D}/I_G \) ratio [49].

On one hand, as can be seen in Figure 6(a) (black line), sample obtained at 800°C shows a spectrum with a lot of defects in the structure of the material. Peaks D and G are overlapped by a combination of sp2 and sp3 bonds, corresponding to the presence of structural disorder or defects [47]. Thus, these spectroscopic results and those obtained by using the microscopic technique indicate that 800°C is not an adequate temperature for the synthesis of graphene since different carbon species are obtained.

Samples obtained at 1000 and 900°C (Figure 6(a), blue and red lines, respectively) present spectra with the three principal graphene peaks, which are consistent with the results observed in micrographs from Figure 4. Therefore, both temperatures could be adequate for the synthesis of carbon laminar structures. Nonetheless, for some cases, the \( I_D/I_G \) intensity ratio is high according to Malard et al., indicating that a greater intensity in the D band is attributed to defects such as incomplete carbon–carbon bonds at edges. On the other hand, as shown in Figure 6(c), a \( I_{2D}/I_G \) ratio value lower than two was obtained, which indicates that the synthesized graphene consists of multilayers [31]. At
1000°C an increase in this ratio ($I_{2D}/I_G$) with respect to 800 and 900°C was observed. Thus, 1000°C was chosen as the synthesis temperature for further experiments.

As previously discussed, in order to reduce the number of layers and defects, different acetylene flowrates were tested in the synthesis of graphene. For this case, experiments were carried out by using 100, 80, 30, and 10 sccm of acetylene per minute of synthesis. The Raman spectra indicate that an acetylene flowrate of 30 sccm produces a 2D band two times more intense than the G band (Figure 6(b), blue line). An increase in the intensity of the 2D peak as well as a decrease of the D band may indicate a lower number of layers and fewer defects (Figure 6(d)).

The $I_{2D}/I_G$ ratio obtained by using a gas flowrate of 80 sccm was of 1.3, while the ratio $I_{2D}/I_G$ with a flowrate of 30 sccm was 2.5. In both cases, a reduction in the number of defects was observed (Figure 6(d)); however, its presence is expected due to polycrystallinity in the Cu substrate. It is important to take into account the fact that the Cu grain boundaries and the edges of the graphene domains promote defects in its structure [43]. However the honeycomb shaped arrangement predominates in the entire structure. A ratio of $I_{2D}/I_G > 2$ indicates the presence of graphene near to monolayer [21, 50–52] which indicates the production of a film with high quality (Figure 6(d)) [53].

3.5. Atomic Force Spectroscopy. AFM is one of the most important characterization techniques used to elucidate the amount of graphene layers present in a material. Figure 7 shows micrographs of graphene synthesized at 1000°C and with different acetylene flowrates. Synthesis carried out with 100 sccm (Figure 7(a)) renders plates with a thickness of 5.08 nm. Under these conditions, the 2D peak in Raman was small, but TEM micrographs showed hardly any laminar structures (data not shown). Assuming a distance between layers of approximately 0.34 nm [54], the number of layers could be set at 14. While, at flow rate of 80 sccm, plate thickness was 3.29 nm, corresponding to 8 graphene layers. Finally, injecting acetylene at 30 sccm generated plates of 1.65 nm, corresponding to approximately 4 layers of graphene.
4. Conclusions

The method described in this work offers important advantages such as (1) the number of parameters was simplified; (2) time of synthesis is shorter than those used in traditional methods; (3) it is a low-cost method when compared to those that using a continuous gas flowrates; (4) the proposed process in batch, besides using lower gas consumption, represents a significant reduction of emissions in the environment; (5) besides, the use of electrolytic technical grade copper instead of monocrystalline copper (reagent grade or high
Figure 6: Raman spectra for (a) graphene synthesized at different temperatures with a fixed C$_2$H$_2$ flow rate (100 sccm) and (b) with different C$_2$H$_2$ flow rates at 1000 °C. Schematic representation for $I_D/I_G$ and $I_{2D}/I_G$ ratios at (c) fixed flow rate and (d) fixed temperature.

Purity cooper foil also contributes to reducing costs; (6) finally, the use of a mixture of N$_2$/H$_2$ (90:10) instead of pure H$_2$, decreases the explosive risk by gas accumulation. In general, the synthesized graphene shows a good quality with spectral characteristics very near to the monolayer graphene; therefore, the obtained material with the proposed method represents an attractive option for industrial purposes or graphene mass production.
Figure 7: AFM micrographs of graphene obtained at 1000°C and with different acetylene flow rates: (a) 100 sccm, (b) 80 sccm, and (c) 30 sccm.
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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