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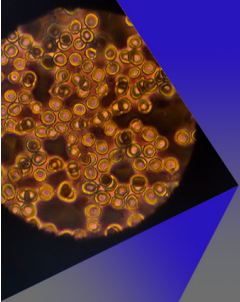
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Single step vacuum-free and hydrogen-free synthesis of graphene

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We report a modified method to grow graphene in a single-step process. It is based on chemical vapor deposition and considers the use of methane under extremely adverse synthesis conditions, namely in an open chamber without requiring the addition of gaseous hydrogen in any of the synthesis stages. The synthesis occurs between two parallel Cu plates, heated up via electromagnetic induction. The inductive heating yields a strong thermal gradient between the catalytic substrates and the surrounding environment, promoting the enrichment of hydrogen generated as fragments of the methane molecules within the volume confined by the Cu foils. This induced density gradient is due to thermo-diffusion, also known as the Soret effect. Hydrogen and other low mass molecular fractions produced during the process inhibit oxidative effects and simultaneously reduce the native oxide on the Cu surface. As a result, high quality graphene is obtained on the inner surfaces of the Cu sheets as confirmed by Raman spectroscopy. © *2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4985751]

INTRODUCTION

Graphene was originally isolated through mechanical exfoliation from graphite,[1] which allowed the separation of high quality crystal flakes with characteristic dimensions in the μm^2 range. These sizes are adequate for scientific research but are not suitable for many technological applications. Therefore, alternative methods have been developed to overcome this difficulty. The most promising approach for graphene production, in large scale applications, is chemical vapor deposition (CVD).[2,3] S. Bae et al. demonstrated the potential of this method by growing square meter scale polycrystalline graphene films, on thin copper foils.[4,5]

A typical CVD synthesis involves the adsorption, dissociation and diffusion of carbon species derived from hydrocarbon gases on the surface of a transition metal. Graphene nucleation occurs when active carbon species at the catalyst surface reach a critical concentration. The growth dynamics profoundly depends on the control parameters such as pressure and temperature but it is primarily governed by the nature of the substrate.[6] Copper is among the most popular metal substrates for graphene growth due to the low carbon solubility, which limits the number of graphene layers produced during synthesis.

There are reports regarding CVD graphene growth under different pressure conditions: AP-CVD (CVD at atmospheric pressure); HV-CVD (CVD in a high vacuum environment) and LP-CVD (CVD at a moderately reduced pressure).[7,8] It has not been elucidated so far which one of these methods produces the best quality graphene.[8] However in terms of production of large area graphene, AP-CVD is indeed economically attractive. In the AP-CVD class, a sub-category can be defined for

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systems that do not require either vacuum systems or pumps. If proper care is taken to prevent ambient contamination, such as oxygen molecules or humidity, high quality graphene can be obtained through these techniques.[9] Typically, in standard AP-CVD, graphene is grown over copper. A Cu foil is loaded into a reaction chamber, which is cleansed from unwanted residual gas molecules by an inert gas purge. In a subsequent step, the temperature of the system is raised up to 1000 °C and the Cu substrate is annealed in a H_2/Ar reducing atmosphere, in order to remove the native oxide layer and increase Cu grain sizes.[10] In the following stage, a carbon gaseous source, in most cases methane, is added to the reaction chamber,[11] diluted in a mixture of argon and H_2. This reducing atmosphere protects the growing graphene against the detrimental action of oxidative species that are often present in the reaction chamber. In the final step, the graphene covered copper foil is cooled down to room temperature, under a constant flow of a hydrogen and argon gas mixture.[9]

Recent publications have emphasized the role of hydrogen in CVD graphene growth.[10–13] In addition to preventing the oxidation of the substrate surface during the growth, hydrogen acts as a co-catalyst that aids the reaction by producing thermodynamically active hydrocarbon species. These gaseous fragments contribute favorably to the adsorption of graphitic forms of carbon on top of the copper foils.[12] According to S. Chen et al,[14] the presence of H_2 during synthesis also changes the primary reaction pathway of methane pyrolysis by increasing CH_4 dissociation. The absence of H_2 does not necessarily prohibit the dissociation of CH_4, although it severely reduces the rate at which this reaction occurs.[14]

Oxygen can be present during synthesis by being: in the gas atmosphere, in the form Cu oxide on the Cu surface or by being dissolved in the Cu bulk. It can affect every step of graphene synthesis in a way that is highly dependent on its concentration. In the case of large amounts of oxidizing impurities, as could be the case in atmospheric pressure synthesis, the synthesis products take mostly the form of oxidized and amorphous carbon clusters instead of graphene.[9] For small amounts of oxygen, on the other hand, there are reports describing the beneficial aspects of its presence on the Cu surface during synthesis. Oxygen can greatly increase graphene domain size by changing the growth kinetics, from edge-attachment–limited to diffusion-limited growth. It also improves the condition of the substrate, by flattening and cleaning of the Cu surface, which in turn favors subsequent graphene growth.[15] Nonetheless, when the oxygen content is too high, hydrogen becomes strictly necessary to counterbalance the etching effect of the former. Under these conditions, the presence of H_2 limits the availability of oxygen species increasing the likelihood of graphene formation after the decomposition of the carbonaceous source. A recent study[16] suggests that when the oxygen content is sufficiently low, graphene can be grown on Cu, from CH_4 without the addition of H_2, which is consistent with the results presented in this report. Under this condition, CH_4 acts both as carbon precursor and also as a source of hydrogen counterbalancing the etching induced by oxygen.

There are indeed several reports of graphene preparation in which hydrogen has been removed from the growth stage during synthesis.[6,17–20] As is expected, the characteristics of the final products vary slightly depending on the particular synthesis conditions. It does remain as a technical challenge the design of a reproducible synthesis method, which is simultaneously vacuum-free and hydrogen free, in all its stages. This is a hard constraint to overcome, considering the need of adding hydrogen during the pretreatment of the Cu sheets, to reduce the native oxide, as well as during synthesis and cooling, to minimize the etching effects, which are more likely to be present during ambient pressure synthesis. See for example Ref. 9.

In the present report a modified method for graphene growth on copper foils is presented. It is based in a modification of AP-CVD procedures, using methane as the carbon source and copper as the catalytic substrate. Graphene is synthesized in a one-step process, inside a chamber opened to air and without the addition of gaseous hydrogen at any stage. The growth reaction occurs between two Cu sheets slightly displaced from each other, which are directly heated up to temperatures close to 1000 °C via electromagnetic induction.[21] There is little drag in the volume between the Cu sheets, so the molecular fragments produced by the decomposition of methane, hydrogen and other intermediate hydrocarbon species, are almost confined within this small reactor. These synthesis fragments inhibit the action of oxygen, reduce the surface oxide and promote carbon adsorption on Cu. Consequently single layer graphene (SLG) growth is achieved on the inner surfaces of the parallel Cu sheets.

EXPERIMENTAL PROCEDURE

The synthesis method, which could be described as: open to air-atmospheric pressure-chemical vapor deposition- (OA-AP-CVD). The experimental apparatus consists of a cylindrical glass chamber (Pyrex glass), 40 mm in diameter, closed at the top and fully opened at its lower end (see Figure 1). In this inverted vase, two circular copper foils 30 mm in diameter, are held in place with the surface normal oriented parallel to the axis of the cylindrical chamber, both Cu foils are slightly separated and supported by three ceramic pillars. The copper foils are heated up by a home-made inductive heater (250 kHz). The central temperature is continuously monitored by a radiation pyrometer (IMPAC, model IS 8). Using the setup just described, monolayer and bilayer graphene were grown on the copper foils (30mm in diameter; 125 μm thick, purity: 99.98%). The foils were previously treated with acetic acid for 2 minutes and rinsed with ethanol, following a standard cleaning procedure.[22] They were later located inside the reaction chamber and exposed to a flux of argon (1 L/min) and methane (0.1 L/min) for 2 min. While keeping the gas flux constant, the inductive heater is energized with sufficient power (∼150W) to raise the Cu foils temperature up to 1000 °C in less than 2 min. Synthesis proceeds for 10 to 15 min. Power is turned off keeping the same flux rates, until the foils reach room temperature. This setup allows a rapid cooling rate, from a 970 °C down to 600 °C in just 10s.

The present design of the reactor was found through successive improvements, implemented in the course of searching for new methods to synthesize graphene under ambient conditions. The original idea was to explore the use of an inverted open flame[23] over a Cu substrate as a mean to produce large area graphene covered electrodes for applications in the mining industry. The stoichiometry of the flame (Ar, O_2, CH_4) was a key parameter to assure both temperature control of the substrate and a good quality flame. Traces of graphene were obtained over copper through the use of this method, but not in a reproducible way. In this configuration, reducing the relative amount of oxygen injected to the flame changes its temperature and as consequence the temperature of the substrate is also modified. The coupling between these two parameters limited our ability to control the synthesis reaction. The first upgrade to the burner was to introduce a way to control the temperature of the substrate independently. For this purpose the radio frequency heating of the substrate was added, in order to minimize the disruption of the flame. The best results, in terms of graphene formation, were obtained with minimal oxygen content in the flame and on the reversed side of the foil originally exposed to the flame or gas flow. It did not take long before the idea of using the flame was completely
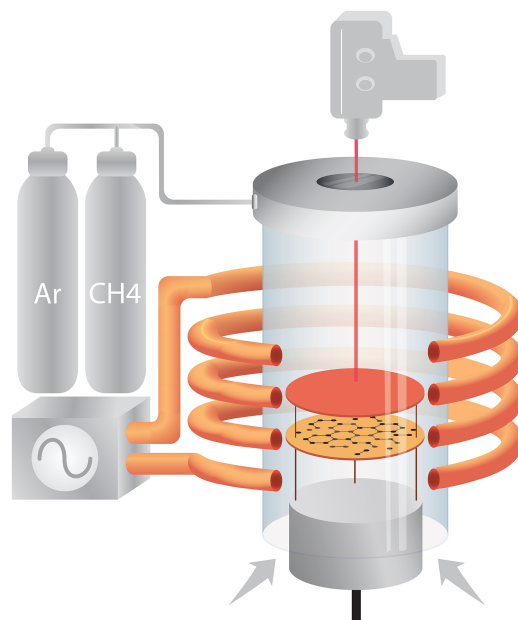

FIG. 1. Schematic representation of the experimental setup.

abandoned and the system was modified to the configuration presented in this paper. Only methane and argon were finally used without a flame and all the heating was provided inductively to the copper foils.

RESULTS

Raman spectroscopy[24,25] (Renishaw inVia) was used in the identification and characterization of the synthesis products. Comparing the relative intensities and widths of the different spectral features (D band $\sim$ 1350 cm^{-1}, D * $\sim$ 1622 cm^{-1}, G $\sim$ 1580 cm^{-1} and 2D $\sim$ 2700 cm^{-1}), both the number of graphene layers and the density of defects of the graphitic samples[26–28] can be estimated. Different wavelengths of the primary beam (514 nm, 532nm) were used directly on the C covered Cu surface[29] and also on samples transferred onto SiO$_2$/Si via standard procedures.[7] Figure 2 shows a schematic representation of the bi-foil configuration, together with a set of Raman spectra collected from the corresponding surfaces after synthesis. Both outside faces display some evidence of graphitic materials (G peak above Cu-fluorescence background) together with a very intense low energy band, which has been associated to surface oxidation.[30] On the other hand, the inner faces of the Cu foils show the characteristic Raman spectra of a Cu surface covered mostly with single layer graphene (SLG) and in some spots with double layer graphene (DLG), with a density dependent on synthesis parameters.

Three experimental parameters have been identified as having the stronger influence in the quality of the material: temperature of the sheets during synthesis (T), synthesis time (t) and separation distance between sheets (h). A coarse search for the optimal conditions is shown by the data displayed in Figure 3. Each experimental point for the intensity ratios 2D/G and D/G and the FWHM, corresponds to the average obtained from spectra collected in nine different locations of the substrate, the parameters were varied around a set of standard conditions (T = 970 °C, t = 15 min and h = 1mm). In summary, this data set indicates that the optimum condition occurs at high temperature, small foil separation and duration of about 12 minutes. Figure 4 shows characteristic Raman spectra of a sample synthesized by the OA-AP-CVD method and later transferred onto SiO$_2$. The synthesis parameters for this particular sample were optimized at 970 °C and 1 mm separation between the Cu sheets. The Raman spectra obtained show that the D/G ratio is $\sim$0.1, and the 2D/G ratio is slightly larger than 4,
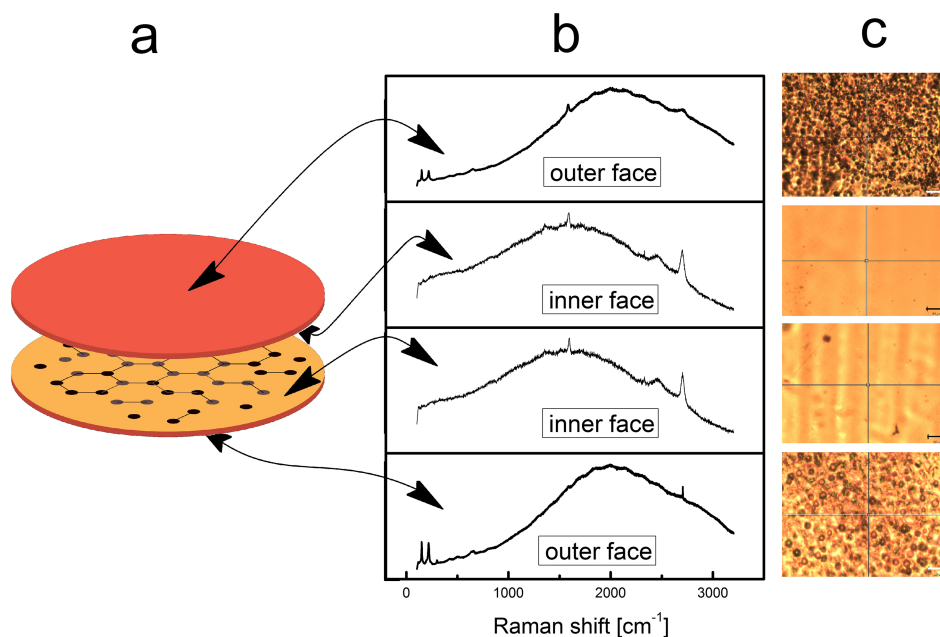

FIG. 2. a) Schematic diagram of the two copper foils in the reactor. b) Characteristic Raman spectra (532nm) of the corresponding sides of foils after synthesis. In c) optical microscopy images of the different surfaces are displayed. The scale bars in the micrographs are 10 µm long.
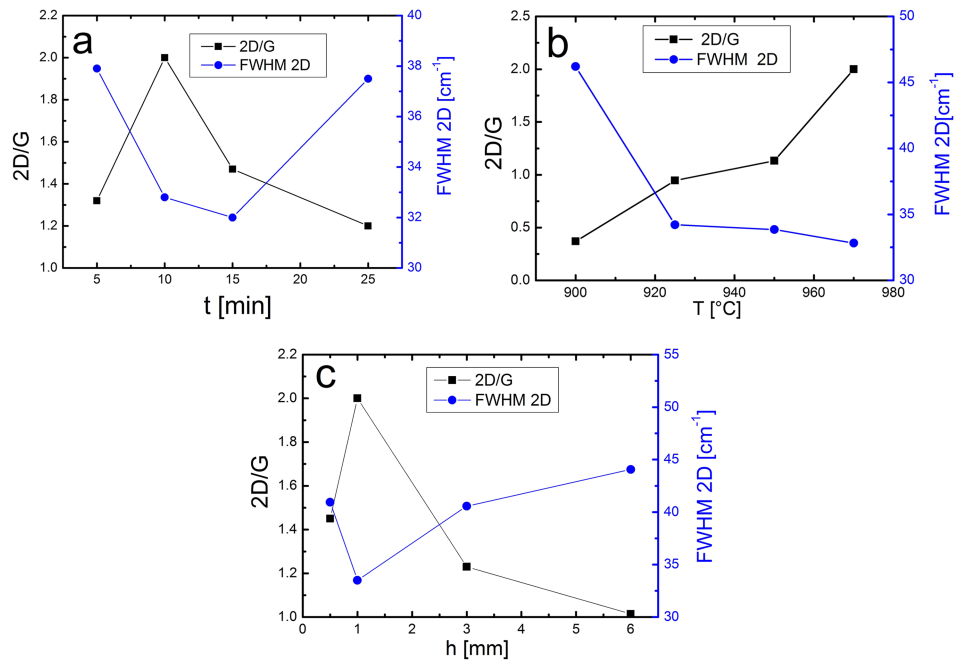
FIG. 3. a) Ratio of the 2D and G resonances (2D/G) and FWHM 2D v/s exposure time (t), b) 2D/G and FWHM 2D v/s temperature (T) and c) 2D/G and FWHM 2D v/s distance between the foils (h).
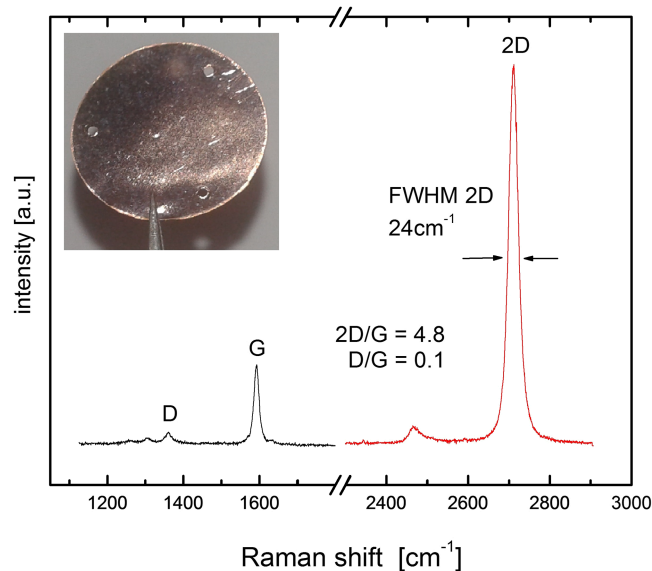

FIG. 4. Characteristic Raman spectrum (514nm@1mw) of graphene synthesized in the center of the Cu foil under optimal conditions and subsequently transferred to SiO2 ((D/G) ∼ 0.1, (2D/G) ∼ 4,8). Inset: Graphene covered Cu foil after synthesis (T = 970 °C, t = 15 min). The large ratio between the 2D and G intensities together with the reduced FWHM of the 2D peak are a clear indication of the formation of SLG.[24,25]

with the 2D resonance having a (FWHM) around 24 cm^{-1}. Hence, these results are consistent with the formation of SLG.[24,25] In order to assess the characteristic fluctuations within one particular sample we transferred a pie shaped cut of the graphene/Cu sample to a SiO$_2$/Si substrate. Figure 5 shows an image of the Cu substrate and the evolution of the Raman spectra collected along the radial direction (spots separated ∼ 1mm). There are some fluctuations in the relative intensities of the relevant peaks, nonetheless the spectra are consistent with the presence of SLG in the inner surface of the Cu foils.
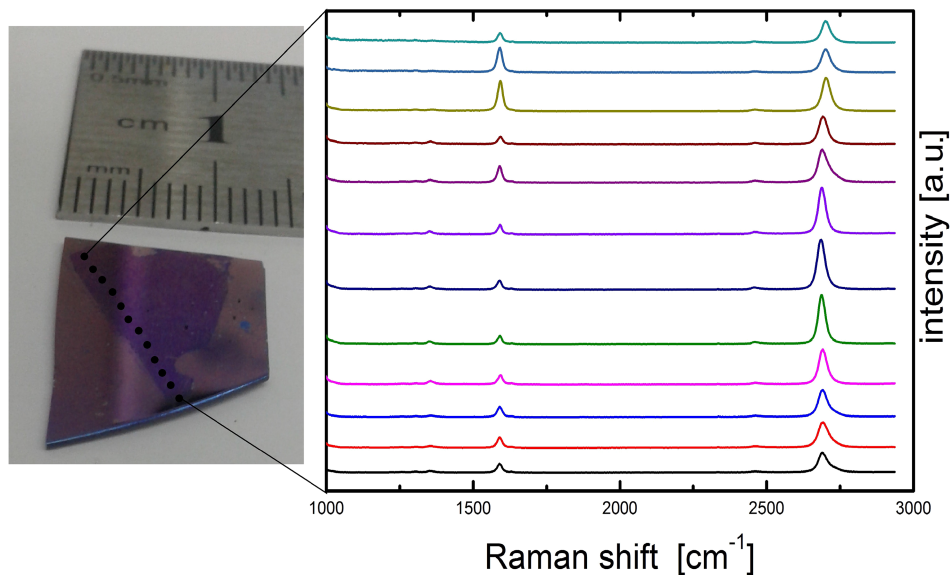
FIG. 5. Raman spectra (514nm@1mw) collected from transferred graphene along a radial path on the internal surface. Characteristic radial displacement: 1 mm.

The measured electrical sheet resistance was (supplementary material) 1,4 kΩ/□, a value which is comparable to those obtained from AP-CVD graphene.[6,31]

DISCUSSION

Even though the synthesis environment is just a pair of closely spaced Cu foils, open to air, the experimental conditions are such that SLG growth takes place, despite the apparent unfavorable environment. This is indeed a rather singular result, considering that in most graphene synthesis procedures currently used; hydrogen is specifically added to aid the synthesis process.

In our system, the residual oxygen present in the interfacial region does not interfere with graphene growth. This is evident in the Raman spectra from the inner surfaces, which show no substantial increase of the D and D* bands.[32,33] It is therefore plausible that the decomposition species are then able to completely suppress the detrimental effects of oxygen in the interfacial volume during synthesis. However, the outer faces of the Cu sheets, as shown in Figure 2, display Raman spectra consistent with the formation of amorphous carbon and also features that can be attributed to the oxidation of copper (150 cm^{-1}, 218 cm^{-1} and 299 cm^{-1}, 635 cm^{-1}).[30] Apparently, oxide can form on the outer surface of the Cu plates simply due to the drag flux induced here by the carrier gas, which removes the reducing species.

The calculated activation energy for methane[34] dissociation on copper oxide has been estimated to be close to 70 KJmol^{-1}, even lower than for clean Cu. Thus, methane fragments produced during the initial instants of the synthesis are capable of reducing the Cu surface. Eventually, after the removal of the oxide layer, the decomposition of methane into hydrogen and other intermediate species takes place over metallic copper. For our system, the optimum graphene growth time is around 15 min (see Figure 3a), which is very short considering this AP-CVD process occurs in the absence of a H$_2$ flux.

The reduced drag within the inter-laminar volume by itself is not enough to explain the growth of graphene under these harsh synthesis conditions, i.e, inside a chamber opened to air, over an oxidized surface and without the addition of hydrogen gas. It turns out that under the given experimental conditions, the thermo-diffusion effect[35–37] has to be included to get a proper description of the device operation. This mechanism concentrates hydrogen obtained from the decomposition of methane, and at the same time contributes to the depletion of atmospheric O$_2$ in the small volume delimited by the two Cu sheets. This diffusion process, also known as the Soret effect, is accountable for the separation of light and heavy molecules in a gas mixture subjected to a large temperature

gradient. Lighter species are directed towards the hottest zone, whereas the heaviest molecules are pushed to the colder regions. This phenomenon has been widely used in devices to obtain isotope separation.[38,39]

The relevance of the Soret effect in CVD has been addressed in several studies, particularly in those regarding the growth of carbon materials. A. Lysaght et al.[40] used molecular theory to predict the effect of thermal diffusion in the evolution of hydrogen and hydrocarbon feed streams during the growth of single wall carbon nanotubes. Yu and Camarero[41] modeled the synthesis of carbon fibers via laser-induced CVD, including the Soret effect. Their results indicate H_2 is enriched near the hot spots of the reactor. Similarly, Wu *et al.* measured a substantial H_2 enrichment around the reaction zone of a hot-filament reactor used in the preparation of diamond films by CVD.[37] In their explanation of this finding, the authors have identified the Soret effect as the cause for this gradient in the gas concentration.

There are many reports regarding the important role of hydrogen in graphene synthesis. See for example Refs. 10, 11 and 12. Even though our synthesis procedure does not include the addition of hydrogen, we believe it is indeed a relevant element during synthesis. Hydrogen is present in our device, primarily as a byproduct of the synthesis process.

The difference of our particular CVD setup with other standard systems is the large thermal gradient between the synthesis volume and the immediate surroundings, which influences dramatically the H_2 concentration between the copper foils.

We can estimate the effect of the thermo-diffusion over hydrogen and other fragments generated through the pyrolysis of CH_4 using a simple model of the experimental configuration. A laminar mass flow of the $CH_4/Ar/H_2$ mixture is assumed and since the CH_4 flux is ten times smaller than that of Ar, the gas within the reaction volume can be modelled as a binary Ar/H_2 mixture. Under this assumption, the diffusive flux of hydrogen at the boundary of the volume confined between the two Cu sheets is given by:[38]

$$J_{Hydrogen} = -\rho D \nabla C - \rho D \alpha C_o (1 - C_o) \nabla(\ln T). \tag{1}$$

Where ρ is the fluid density, D is the diffusion coefficient, α is the Soret coefficient, which is negative for the lighter specie,[38,42] C is the H_2 concentration and Co is the hydrogen content of the mixture. The first term on the right side of eq.(1) describes the standard Fickian diffusion and the second one is due to thermo-diffusion. The absolute value of the ratio between the Fickian diffusion and the thermo-diffusion is then roughly:

$$\left| \frac{\nabla C}{C_0(1 - C_0)\alpha \nabla(\ln T)} \right| \sim \frac{\Delta C/l}{C_0 |\alpha| \Delta(\ln T)/l}. \tag{2}$$

Where l is a characteristic length over which the gradients occur. For diluted species, Co << 1, thus $C_0(1 - C_0) \approx C_0$. In addition, since H_2 is generated mostly inside the volume defined by the Cu foils, then it can be assumed that outside this volume the hydrogen content is close to zero, $C_0^{out} \sim 0$. Therefore, $\Delta C = C_0 - C_0^{out} \approx C_0$. Substituting these approximations in eq. (2), we obtain for the ratio in eq. 1:

$$1/|\alpha|\Delta \ln T \sim 0.6; \tag{3}$$

where we have adopted $|\alpha| = 0.45$ for a mixture of Ar/H_2[43] and assumed that the temperature inside the volume defined by Cu foils is 1253 K, while in its surroundings it is 300 K, i.e. $\Delta \ln T = 1.4$. This estimate indicates that for this particular situation, both diffusion mechanisms, Fickian and Soret, have to be simultaneously included in the description of the system. Hence, mass separation of the different components in the gas mixture has to be taken into consideration while describing the operation of this setup. The low mass fragments are enriched in the high temperature zones and the higher molecular masses are segregated to the cooler regions. Hydrogen generated by the thermal decomposition of methane is then retained within the interfacial reaction zone, as long as the temperature gradient is maintained. The quality and physical characteristics of our synthesis products are a clear demonstration of this effect.

In terms of the quality of the synthesized material there is no real advantage of using this modified procedure over other CVD based approaches. Nonetheless, there are a few aspects that makes this method somewhat singular and worth considering depending on the application. 1.- Synthesis takes

place not just at normal atmospheric pressure, but the CVD vessel is open to air in normal conditions, thus reducing enormously the graphene growth processing time. 2.- Energy consumption during synthesis is extremely reduced, only the substrate is warmed up. 3.- A key aspect of this design is that the hydrogen required to promote the proper growth is obtained exclusively from the carbon source. Hydrogen is generated as a fragment of methane and is retained close to the Cu foil, due to the large temperature gradient allowed by the current design and the thermo-diffusion effect in the gas mixture.

CONCLUSIONS

A modified method for graphene growth is presented. It is based on an adaptation of the so-called vacuum free AP-CVD procedures. It makes use of copper foils as catalytic substrate, methane as the carbon source and takes advantage of the thermo-diffusion process in gas mixtures to obtain graphene. In this method graphene is synthesized in a one step process, inside a chamber opened to air and without the addition of gaseous hydrogen. The substrate is formed by two parallel sheets of Cu, slightly displaced from each other, and directly heated up to temperatures close to 1000 °C, via electromagnetic induction. The explanation of this result considers that the space between sheets retains the low mass molecular fragments obtained from CH_4. Thus hydrogen, obtained from the pyrolysis, reduces the surface oxide on Cu and promotes carbon adsorption. The strong thermal gradient, established between the catalytic substrates and the surrounding environment, promotes the enrichment of the hydrogen content of the gas mixture between the Cu foils. Consequently, single layer graphene growth is achieved on the inner surfaces of the parallel Cu sheets. Raman spectroscopy has been used to confirm the growth of single and bi-layer graphene.

SUPPLEMENTARY MATERIAL

See supplementary material for the information presented here describes the both the operation of the CVD system and results obtained for the sheet resistance measurement of the synthesized graphene.

ACKNOWLEDGMENTS

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