# Multilayer Graphene Growth Assisted by Sulfur Using the Arc Discharge Method at Ambient Conditions

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Abstract—Graphene, a 2-D hexagonal array of carbon atoms, has interesting physical properties, which make this material interesting in applications such as energy storage devices and supercapacitors. The approach here proposed is the use of sulfur as a promoter of  $sp^2$  bonds to form graphite domains and with the particularity of using air at atmospheric pressure to create an electric arc discharge. From diagnostic realized with Raman spectroscopy, it has been observed that the carbonaceous material obtained without the addition of sulfur has a defective graphitic structure, but when sulfur is added, the formation of multilayer graphene is enhanced. Scanning electronic microscopy corroborates the synthesis of graphene-like material. Optical emission spectroscopy studies were realized to the plasma; electronic and rotational temperatures obtained allow envisaging a local thermodynamic equilibrium; some spectra obtained show the existence of reactive sulfur species which possibly are nucleation centers of graphitic domains.

*Index Terms*—Arc discharges, nanotechnology, plasma applications, spectroscopy.

## I. INTRODUCTION

**G** RAPHENE has interesting physical properties [1] making this material useful in potential applications [2]. For example, due to its high electrical conductivity and by its high surface to volume ratio, graphene and related materials can be useful in energy storage devices, such as electrodes in ion-lithium batteries and in supercapacitors [3]. The most common methods to synthetize graphene or many stacked multilayer graphene (MG) are mechanical exfoliation

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of graphite crystals [4], chemical vapor deposition (CVD) using a hydrocarbon vapor and metals as support catalysts [5] and, finally, the exfoliation of graphite crystals in a liquid media [2]. In this paper, we explore the alternative method based on the arc discharge [6], a technique usually employed for the synthesis of carbon nanotubes, adding elemental sulfur to the carbon anode.

The effect of sulfur on the properties of graphene has been studied from the theoretical point of view, for example, predicting the existence of an energy gap [7], but also experimentally by the incorporation of sulfur into the graphene structure [8].

Different approaches have been used to incorporate sulfur; such as by a CVD method [9], by annealing at high temperatures in the presence of sulfur [10], [11], or by treatment of graphene in a SF<sub>6</sub> plasma process containing reactive sulfur species [12].

The approach here proposed is the use of sulfur as a promoter of  $sp^2$  bonds to form graphite domains at high temperatures [8] using the arc discharge technique; but, contrary to conventional one, here, the pressure is maintained at atmospheric conditions and no noble gases are needed, a mixture of nitrogen and oxygen was used.

During the synthesis of MG, some physical plasma properties were studied by using optical emission spectroscopy (OES). Electronic and rotational temperatures were thus obtained; specifically, electronic temperatures were obtained using S I lines and rotational temperatures were obtained from a superposition method using the Swan band.

Electronic and rotational temperatures were very close (around 5400–5800 K) confirming the theory of local thermodynamic equilibrium (LTE).

Results obtained from analysis of Raman Spectroscopy and scanning electron microscopy (SEM), indicate that the carbonaceous material obtained without sulfur addition has a very defective graphitic structure, but when sulfur is added these analyses are consistent with MG structure [13].

In addition, the species observed with OES analysis indicates the existence of reactive sulfur species, which may induce the formation of graphitic domains.

# II. EXPERIMENTAL SETUP AND THEORETICAL CONSIDERATIONS

The device used to synthesize the MG structures is a cylindrical reactor with two vertically positioned electrodes.

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Fig. 1. Schema of the experimental setup used to synthesize graphenes (by J. Silva).

Two frontal windows allow the OES analysis when the plasma is formed between the electrodes.

Those electrodes consist of graphite rods; the anode is filled with a mixture of carbon and sulfur powders at different concentrations (5 and 10 at% S). The carbonaceous product mainly composed of MG is deposited in the cathode and on the reactor walls. The product is manually collected from these sites.

The dc discharge was obtained using compressed air at ambient pressure  $(21\% O_2 \text{ balanced in } N_2)$  at 30 V and 70 A. The resultant black powder was studied by SEM and Raman spectroscopy.

Vibrational properties of the carbonaceous materials were characterized by Raman spectroscopy using an HR LabRam 800 system equipped with an Olympus BX40 confocal microscope. Raman spectra were acquired using a 100X objective lens with a 532-nm laser excitation at a power of 2 mW to prevent sample heating and structural changes. A cooled charge-coupled device camera was used to record the spectra, usually averaged for 100 accumulations of 20 s in order to improve the signal to noise ratio.

Concerning the microscope analysis a JEOL JSM-6010 is used; it consists of a tungsten cathode scanning electron microscope equipped with secondary and backscattered electron detectors, as well as cathode luminescence and energydispersive X-ray spectroscopy detectors. It has a resolution of 3 nm at 30 kV and 15 nm at 1 kV.

The optical arrangement allows obtaining a 1:1 image. To collect the spectra an iHR550 Imaging Spectrometer was used; it has a focal length of 550 mm and covers a spectral range from 150 to 1500 nm with a resolution of 0.025 nm.

The experimental setup is schematized in Fig. 1.

## A. Electronic Temperature

In order to determine the electronic temperature in the plasma, OES was applied using sulfur lines (S I) situated in the infrared spectrum; and carbon lines (C I).



Fig. 2. Boltzmann's diagram.

TABLE I Spectroscopic Data for Sulfur I and Carbon I Lines

Species	λ(nm)	$A_{hl}$	$E_h(eV)$	$g_h$
SI	768.61	$2.0 \times 10^{6}$	9.480335	5
SI	772.50	1.38	2.7499638	1
CI	505.21	2.6 x10 <sup>6</sup>	10.1381	5
CI	538.03	1.86 x10 <sup>6</sup>	9.9885	3

To obtain the electronic temperature (T), the Boltzmann equation (1) was applied

$$\varepsilon = \frac{hc}{4\pi\lambda} \frac{N(T)}{Q(T)} A_{hl} g_h e^{\left(-E_{h/k}T\right)} \tag{1}$$

where

 $\varepsilon$ : line emissivity;

*h* : Planck constant;

 $\lambda$  : wavelength (nm);

T : electronic temperature of plasma (K);

N(T): density of plasma species in function of temperature; Q(T): internal partition function of the species at temperature T;

 $A_{hl}$ : spontaneous emission probability;

 $g_h$ : statistical weight (upper level);

 $E_h$ : excitation energy (upper level) in eV;

*k* : Boltzmann's constant (8.6173324  $\times$  10<sup>-5</sup> eV  $\cdot$  K<sup>-1</sup>). From (1), the following expression is obtained:

$$\ln\left(\frac{\varepsilon\lambda}{A_{hl}g_{h}}\right) = -\frac{E_{h}}{kT} + \ln\left(\frac{N\left(T\right)}{Q\left(T\right)}\frac{h}{4\pi}\right).$$
 (2)

Considering two lines at wavelengths  $\lambda_1$  and  $\lambda_2$  with excitation energies of, respectively,  $E_{h1}$  and  $E_{h2}$  (2) could be represented as (3) and graphically exemplified by Fig. 2

$$T = \frac{E_{h2} - E_{h1}}{k \ln \left| \frac{\varepsilon_2 \lambda_2 A_{h11} g_{h1}}{\varepsilon_1 \lambda_1 A_{h12} g_{h2}} \right|}.$$
(3)

The spectroscopic data used to determine electronic temperatures were obtained from [14] and are reported in Table I.



Fig. 3. Spectra obtained from OES analysis at different concentrations of sulfur (5 and 10at%).

### B. Rotational Temperature

The calculus of rotational temperature consists in overlapping a reconstituted spectrum obtained at different temperatures, considering the apparatus function as described in (4), with the experimental spectrum, until they coincide.

Thus, by overlapping the simulated spectrum with the experimental one, the rotational temperatures could be obtained. However, it should be noted that this method can be only applied in the case of negligible self-absorption of the band head. More details are described in [15].

The response of the system to a signal  $\varepsilon \lambda$ () is equal to the convolution product of  $\varepsilon \lambda$ () by the apparatus function  $A_p(\lambda)$  and can then be written

$$\varepsilon(\lambda) = \int_{-\infty}^{+\infty} \varepsilon(T) A_p(\lambda - T) dT.$$
(4)

Specifically, to simulate the  $C_2$  (0-0) system of the Swan band, a Gaussian apparatus function was considered and can be written as

$$A_p(\lambda) = \frac{2}{\Delta\lambda\sqrt{\pi}} \exp\left[-\left(\frac{\lambda-\lambda_0}{\Delta\lambda/2}\right)^2\right]$$
(5)

where

 $\lambda_0$ : wavelength at the center of the Gaussian shape;  $\Delta \lambda = 0.1$ nm.

#### **III. RESULTS AND DISCUSSION**

From OES analysis, two S I were observed at 768.61 and 772.50 nm for both concentrations of sulfur. Different spectra above mentioned are shown in Fig. 3.

For concentrations of 5 and 10 at% S the relation between S I lines situated at 768.61 and 772.50 nm are very close. Intensities obtained at 10 at% S are higher of that obtained when 5 at% is used. This is because exposition time is twice in the first case; however, it is the relation between both lines that have a real impact on (3).

By using (3) and data reported in Table I, electronic temperatures of 5400 and 5390 K were, respectively, obtained for 5 and 10 at% S. Considering an experimental measurement



Fig. 4. Rotational spectra obtained from OES analysis.

 TABLE II

 Temperatures and Erosion Rates at Different Concentrations

Anode	Only C	5at.%S	10at.%S
Electronic Temperature	6120 K	5400K	5390K
Rotational temperature	5850 K	Not possible to calculate (overlapped lines)	Not possible to calculate (overlapped lines)
Erosion rate	2.09 mg/s	5.30 mg/s	11.01 mg/s

error range of around 5%, these temperatures are close. This similarity means that the influence of sulfur at the concentrations of 5 and 10 at% S is not perceptible in OES analysis.

Relating to C I lines at 505.217 and 538.034 nm, the electronic temperature results around 6120 K.

Concerning the rotational temperature of plasma in the absence of sulfur, the better correspondence of simulated and experimental spectra results to be at 5850 K, as can be seen from Fig. 4.

Temperatures and erosion rates are summarized in Table II. In particular, when no sulfur is added (the anode is only composed by graphite), the electronic and rotational temperatures are relatively close, this could confirm an LTE.

Temperatures obtained with carbon electrodes (without sulfur addition) are superior to these obtained when sulfur is present in plasma. Therefore, when sulfur is added, the erosion rates augment and temperatures in plasma diminish because of thermal losses originated by a richer spectrum (emissivity losses) [17].

Raman spectroscopy is a useful technique to characterize different carbon allotropes. In particular, graphene and MG are characterized by G and 2-D Raman bands, respectively, situated at around 1580 and 2700 cm<sup>-1</sup>, where the number of graphene layers in MG is mainly determined by the form of the later band [13].

When structural disorder and/or impurities exist in the material then a D-band appears at around 1350  $\text{cm}^{-1}$ , and the ratio of the D-/G-band intensities gives a measure of the disorder in the sample.



Υ.

Fig. 5. Raman spectra at different values of sulfur.



Fig. 6. MG obtained at 0at% S.

Results obtained are reported in Fig. 4. These results indicate that the carbonaceous material obtained without the addition of sulfur has a very defective graphitic structure, but when sulfur is added, there are some zones in the samples where the ratio of the G/D intensities is superior to 1, obtaining at 10% S a well-defined 2-D band consistent with an MG material [13].

Research reported in [6] with similar experimental conditions but with no sulfur addition, shows a Raman spectra for a raw material with a G/D relation very close to 1. In Fig. 5, this relation is superior than one when 10at% S is used, demonstrating then the importance to add sulfur to the synthesis process.

SEM images of the carbonaceous material are presented in Figs. 6–9; it is possible to observe a lamellar structure which indicates a graphene-like structure as indicated by Raman spectroscopy.

As a peculiar result, when the carbonaceous product is submitted to an ultrasonic bath for more than 1 h, MG begins to transform into microspheres. Similar results have been obtained in [18]. This spherical material could be used



Fig. 7. MG obtained at 5at% S.



Fig. 8. MG obtained at 10 at% S.



Fig. 9. Microspheres obtained after an ultrasonic bath of MG.

as a nanospacer to separate graphene nanosheets preventing their aggregations and enhancing capacitance of a graphene supercapacitor. Therefore from results obtained, the addition of sulfur enhances the synthesis of carbon nanostructures whatever the method of synthesis was, as reported by [19], in this particular case, with the electric arc method.

## IV. CONCLUSION

The electric arc technique could be a potential method to synthesize graphene-like structures (MG), above all their synthesis has been accomplished at atmospheric pressure using dried air and without hydrogen nor noble gases.

An LTE was depicted from OES analysis and, specifically, with this technique, it has been seen that the influence of sulfur in the plasma discharge allows the presence of reactive sulfur species which may induce the formation of graphitic domains; as has been confirmed by Raman spectroscopy and SEM, but more careful studies are deserved in this respect.

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