

Multilayer graphene growth assisted by sulfur using the arc discharge method at ambient conditions

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Abstract— Graphene, a two dimensional 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 (MG) 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, plasma applications, spectroscopy, nanotechnology.

I. INTRODUCTION

GRAPHENE 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 synthesize graphene or many stacked MG

are mechanical exfoliation of graphite crystals [4], Chemical Vapor Deposition (CVD) using a hydrocarbon vapor and metals as support catalysts [5] and, finally, exfoliation of graphite crystals in a liquid media [2]. In the present work 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_6 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 5400-5800K) 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]. Additionally, the species observed with OES analysis indicates the existence of reactive sulfur species which may induce the formation of graphitic domains.

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II. EXPERIMENTAL SETUP AND THEORETICAL CONSIDERATIONS

The device used to synthesize the MG structures is a cylindrical reactor with two vertically positioned electrodes. 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 at.%S 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% O₂ balanced in N₂) at 30V and 70A. The resultant black powder was studied by Scanning Electron Microscopy (SEM) and Raman spectroscopy.

Vibrational properties of the carbonaceous materials were characterized by Raman spectroscopy using a 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 CCD camera was used to record the spectra, usually averaged for 100 accumulations of 20 sec in order to improve the signal to noise ratio.

Concerning the microscope analysis a JEOL JEOL JSM-6010 is used; it consists in a tungsten cathode scanning electron microscope equipped with secondary and backscattered electron detectors, as well as cathode luminescence and EDX 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 a iHR550 Imaging Spectrometer was used; it has a focal length of 550 mm, covers an spectral range of 150 to 1500 nm with a resolution of 0.025 nm.

The experimental setup is schematized on Fig. 1.

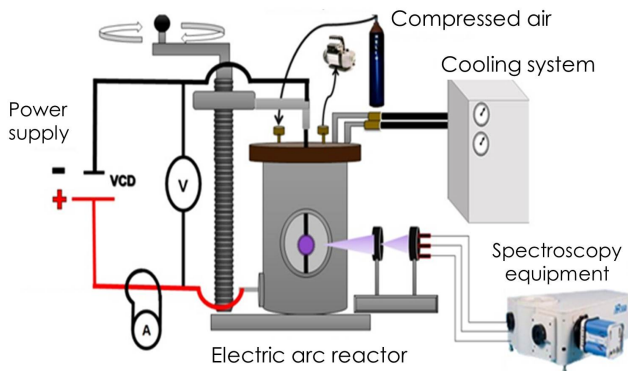


Fig. 1. Schema of the experimental setup used to synthesize graphenes (by Jesus Silva).

A. Electronic temperature

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

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

$$\varepsilon = \frac{hc}{4\pi\lambda} \frac{N(T)}{Q(T)} A_{hl} g_h e^{(-E_h/kT)} \dots \dots \dots (1)$$

Where:

- ε : Line emissivity
- h : Planck constant
- λ : 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 constant (8.6173324×10^{-5} eV K⁻¹).

From equation (1), the following expression is obtained:

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

Considering two lines at wavelengths λ_1 and λ_2 with excitation energies of, respectively, E_{h1} and E_{h2} equation (2) could be represented by equation (3) and graphically exemplified by Figure 2.

$$T = \frac{E_{h2} - E_{h1}}{k \ln \left[\frac{\varepsilon_2 \lambda_2 A_{hl1} g_{h1}}{\varepsilon_1 \lambda_1 A_{hl2} g_{h2}} \right]} \dots \dots \dots (3)$$

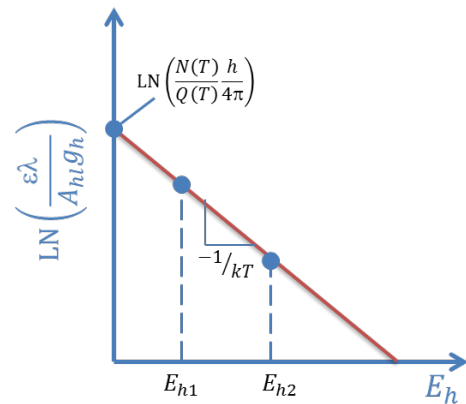


Fig 2. Boltzmann's Diagram

The spectroscopic data used to determine electronic temperatures were obtained from [14] and are reported in Table 1.

TABLE I
SPECTROSCOPIC DATA FOR SULFUR I AND CARBON I LINES.

Species	λ (nm)	A_{hl}	E_h (eV)	g_h
S I	768.61	2.0×10^6	9.480335	5
S I	772.50	1.38	2.7499638	1
C I	505.21	2.6×10^6	10.1381	5
C I	538.03	1.86×10^6	9.9885	3

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 equation (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:

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

Specifically, to simulate the C₂ (0-0) system of the Swan band, a Gaussian apparatus function was considered and can be written as:

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

Where

λ_0 : Wavelength at the center of the Gaussian shape

$\Delta\lambda = 0.1nm$

III. RESULTS AND DISCUSSION

From OES analysis, two sulfur lines were observed at 768.61nm and 772.50nm for both concentrations of sulfur. The different spectra above mentioned are showed on Figure 3.

For concentrations of 5at.% and 10at.%S the relation between S I lines situated at 768.61nm and 772.50nm are very close. Intensities obtained at 10 at. % S are higher of that

obtained when 5at.% 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 in equation (3).

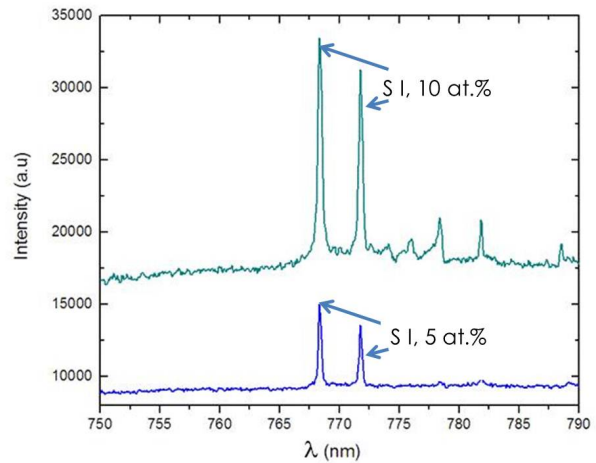


Fig. 3. Spectra obtained from OES analysis at different concentrations of sulfur (5 at.%, 10at.%)

By using equation (3) and data reported on Table 1, electronic temperatures of 5400K and 5390K were respectively obtained for 5at.% S and 10at.% S. Considering an experimental measurement error range of around 5%, these temperatures are close. This similarity means that the influence of sulfur at the concentrations of 5at.%S and 10at.%S, is not perceptible in OES analysis.

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

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

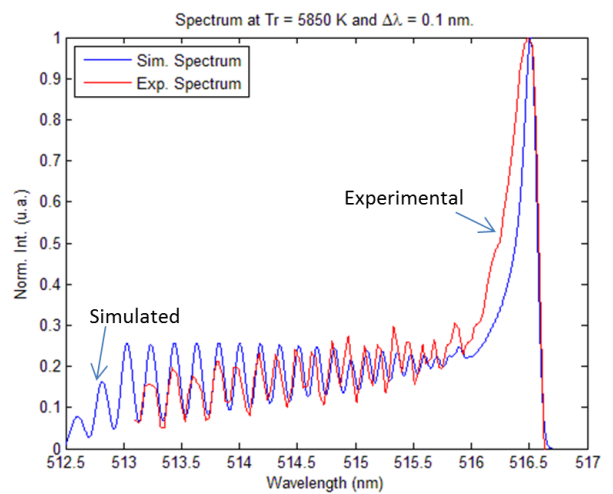


Fig. 4. Rotational spectra obtained from OES analysis.

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 a local thermodynamic equilibrium.

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].

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

Raman spectroscopy is a useful technique to characterize the different carbon allotropes. In particular, graphene and MG are characterized by G and 2D Raman bands, respectively situated at around 1580cm^{-1} and 2700cm^{-1} , 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 cm^{-1} , and the ratio of the D/G band intensities gives a measure of the disorder in the sample.

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 2D band consistent with a MG material [13].

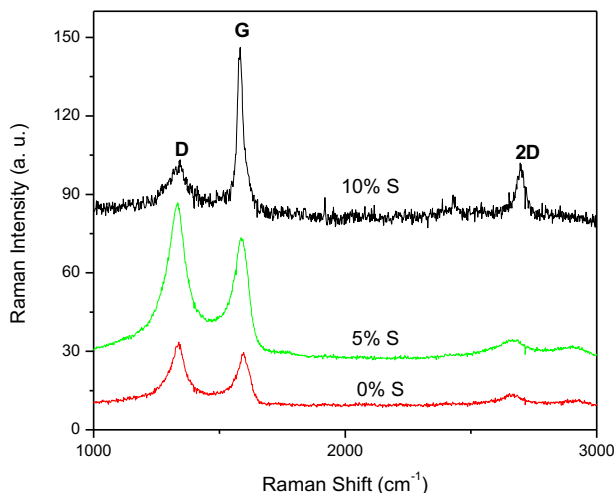


Fig. 5. Raman spectra at different values of sulfur

Research reported in [18] 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 Figure 5, this relation is superior than 1 when 10%at. S is used, demonstrating then the importance to add sulfur to the synthesis process.

SEM images of the carbonaceous material are presented in Fig. 6 to 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 one hour, MG begins to transform into microspheres. Similar results have been obtained in [19]. This spherical material could be used as a nano-spacer 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 [20], in this particular case, with the electric arc method.

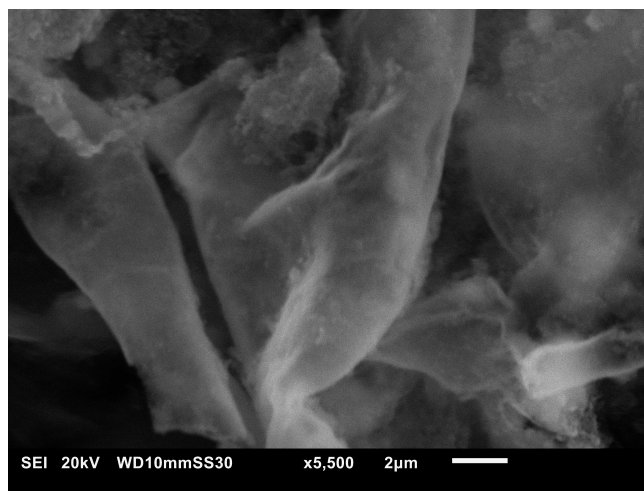


Fig. 6. MG obtained at 0at%S

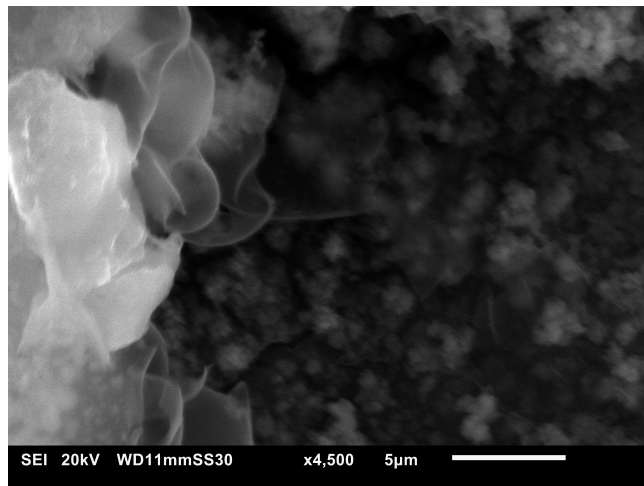


Fig. 7. MG obtained at 5at%S

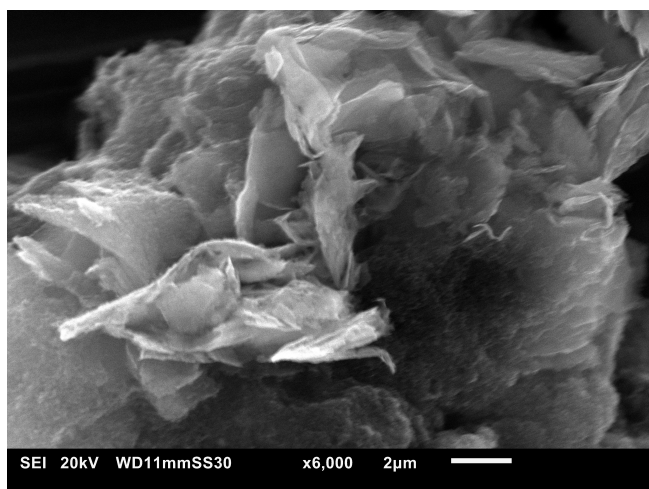


Fig. 8. MG obtained at 10 at%S

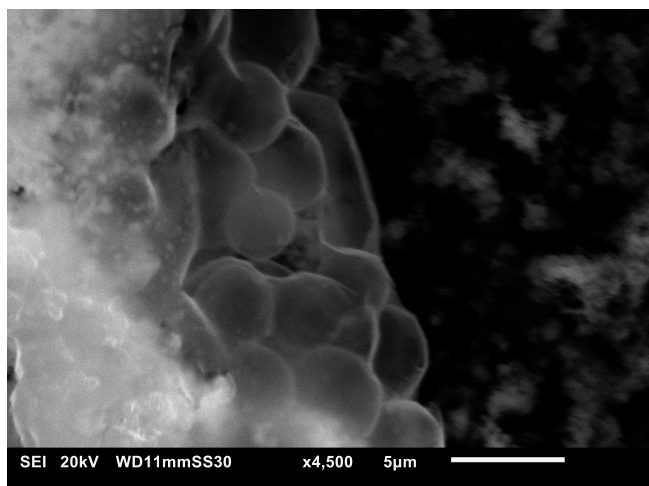


Fig. 9. Microspheres obtained after an ultrasonic bath of MG

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

A local thermodynamic equilibrium 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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