# Hybrid chemical-thermal process using NaBH<sub>4</sub> to obtain reduced multi-layered graphene oxide

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Abstract– Using glassy carbon (GC) as matrix material made it possible to obtain graphite oxides using the Hummers-Offeman method. After this procedure, it was possible to synthesize the graphite oxide (GrO) and the reduced multi-layer graphene oxide (rMGO). On this form, we propose the reduction, via hybrid method, which consists on the thermal and chemical reduction in presence of NaBH<sub>4</sub>, in order to obtain GrO and rMGO. In this way, using FTIR and Raman spectroscopy we determinate the functional groups existent, the nanocrystal size, the distance between defects, the defects density and the optical gap in those systems. With this, we observe that the hybrid reduction is an efficient method for reducing the defects on the graphite oxide and consequently the decrease of optical gap. Finally, a morphological study by AFM was made on the rMGO, observing that these have nanometric dimensions.

Keywords-- Reduced Multi-layer graphene oxide (rMGO), Chemical-thermal Reduction, Micro-Raman Spectroscopy and Atomic and Force Microscopy (AFM).

## I. INTRODUCTION

Graphene is a pseudo two-dimensional material formed by the union of carbon atoms with sp<sup>2</sup> hybridization, with a structure similar to a "bee hive" which has superior properties when compared to its allotropes, the polymorphous compounds (CNTs, fullerenes, diamond, graphite, and others) as mechanicals, electronics, optical and the electronic transport, as a big superficial area, high thermal conductivity and high transparency [1]. Thanks to several properties, it has been showing us an important number of potential applications in the development of super capacitors, fuel cells, biosensors, electrodes, catalytic supports, and conductor films for its application in transistors development [2]. After it's discovering in 2004 by Novoselov and others, the investigations in this material have been intensifying in the search of new synthesis routes. The most cited techniques are micro-mechanical exfoliation, chemical exfoliation and chemical vapor deposition (CVD), thanks to its predisposition in the graphene obtaining process on industrial scale [3]. For obtaining graphite oxide (GrO) through chemical exfoliation, we can mention the centralization in the oxy-functionalization of the scales of graphene which are set in graphite through a strong oxidative process. In that process it is possible to change the graphite's scale polarity in an aqueous medium thanks to a polar colloidal dispersion, with this it an interplane rupture between graphene sheets may occur, which conforms into graphite in a controlled way, obtaining a stable colloidal suspension [4].

As it was said before, the chemical exfoliation is centered in the alteration of structural and electronic properties of original scales of graphene; generated mostly by ruptures inside and outside in the planes, by the use of the ultrasound device or other dispersion technique, which can be chemical or physical, to cause the oxy-functionalization on the graphene sheets [7]. Many techniques have been proposed, which allow the partial restitution for electronic properties, through GrO reduction by chemical agents as NaH<sub>4</sub>B, N<sub>2</sub>H<sub>4</sub>, and ascorbic acid, and the use of surfactants or organic polymers, as glucose and gelatin; the ones which have the function to repair structural properties [8]. Instead of the common sense, modification on graphene grade can give to it new properties and expand the studies on it and its applications. Because of that the ruptures of the mono-layer of graphene are used for obtain sheets of graphene which are needs for develop biosensors [9]. In the other side, Kaner et al reports obtaining micro-scales of GrO and rMGO for development of super capacitors [10]. Kamat et al, described the advantages of the functionalization rate in rMGO, which one were obtained through reduction using UV radiation, in the development of photo-catalysts which uses rMGO/TiO<sub>2</sub> as raw material [11].

There is broad knowledge about the relations between the syntheses in chemical and physical routes of GrO and rMGO; undoubtedly is less common to find literature about its physical-chemical properties and is even harder to find studies about the possible chemical routes for its obtainment. It is important to highlight that the N2H4 reduction mechanism is the most reported currently, despite the existence of a big variety of reduction agents and techniques, as NaH4B and thermal reduction. In this way we present a spectroscopic study of GrO's functionalization rate and one structural analysis of rMGO's micro-scales.

## II. EXPERIMENTAL

Through Hummers-Offeman modified process, 1.0 g of glassy carbon scales (GC), used to elaborate electrodes, with 99.5 % of purity (Tecnofil S.A., Peru); it has obtained 0.68 g of GO [12-15]. For which, the GC powder sample was mixed with NaNO<sub>3</sub> (pp. = 99 %, Sigma Aldrich), after reacting with  $H_2SO_4$  concentrated (pp. 98 %, MERCK) under low and constant agitation. After this, the sample was homogenized and it was added slowly KMnO4 (pp. 97 %, MERCK) and H2O Milli-Q (18.2 MΩ.cm) with the temperature fixed between 95-98 °C. The obtained liquid was dark brown and

reacted with H2O2 (30% wt, MERCK) in constant agitation, we obtained one final light brown liquid, which was centrifuged a 5000 RPM by 45 minutes and it was washed in double sessions with bi-distillated water, HCL 30 % and with ethanol, after it was dried at room temperature. The solid material is called acidic graphite oxide (aGO). After this, aGO solid was dispersed in NaOH (pH between 10 and 12), by ultrasound during 60 minutes. Lately, the liquid was centrifuged a 10000 RPM during 5 minutes in the way the material which was exfoliated by the ultrasound is eliminated, finally obtaining a colloidal suspension of stable GO. In this stage the hybrid reduction process was set in two stages: The first is a chemical reduction in which 30 mL of GO colloidal suspension (0.3 mg mL<sup>-1</sup>) reacts with 20 mL of a NaHB<sub>4</sub> (pp. = 99 %, Sigma Aldrich) solution in a concentration of 150 mmol  $L^{-1}$ , in constant agitation and the temperature between 98 - 100 °C by 24 hours. After this the rMGO solid material, pre-reduced was filtered and dried at room temperature [16-18]. The second stage, in which solid rMGO pre-reduced is sustained above Si / SiO<sub>2</sub> 300 nm substrates, through the Scotch Tape technique and thermally treated in a muffle at 500 °C [1,19-20].

With the initial characterization we analyzed the aGO, GO and rMGO colloidal suspensions through UV-visible spectroscopy, for that we used one Perkin Elmer spectrometer, model lambda 25 in a 200 to 500 nm rage. On the other side we realized one analysis of the functional groups which was presented in the solid samples and in the carbon vitreous (GC), reduced graphite oxide (GO) and reduced multilayer graphene oxide (rMGO) through an FTIR-ATR spectrometer, using a range from 500 to 4000 cm<sup>-1</sup> in wave number. With this, we did a structural analysis of solid samples of carbon vitreous (GC), graphite oxide (GO) and reduced multilayer graphene oxide (rMGO) through the study of D and G band; through an dispersive Raman spectrometer T64000, Horiba Jobin-Yvon with the 532 nm wave number. Finally the Raman analysis was complemented with a profilometric study using an atomic force microscope 5500 Agilent Technologies in tapping mode, which has allowed us to estimate the layer number which compound the rMGO scales, obtained after the chemicalphysical reduction process.

## **III. RESULTS AND DISCUSSIONS**

First we realized an analysis in UV-visible spectra in aGO, GO and rMGO samples in the colloidal suspensions. We observed first a bathochromic shift in the maximum absorption band since 230 to 243.5nm, after the stabilization process of aGO and GO in basic medium, which can be explained as an alteration on the absorption of color-sensible groups present in aGO by the presence of extra presence of OH- groups in solution. Even with this there is a second maximum absorption band in 300nm, which has been reported by Luo et al. and can be related with electronic transitions between the **n** and  $\pi^*$  states presents in C=O groups in aGO structure.

By the other side, this second absorption peak represents a hypochromic shift which that can be related with the lowering size in proportion of auxchrome or oxygenate functional groups, presents in aGO and in GO structures through the chemical reduction , as carboxyl (-COOH) and carbonyl (C=O). This has been reported by Robert Vajtai, explaining the elimination of this band is characterized by the recuperation of a  $\pi$  conjugated system, but it is even more related with the reduction of –COOH group presents in the border of GO sheets [21-22]. Against what is reported by Pei et al., for the ones the reduction realized by NaHB<sub>4</sub> is highly effective on C=O groups and less effective in carboxyl groups (-COOH) and epoxy (C-O-C), because this is yet a debate theme [23] (Fig. 1).



Fig. 1 UV-visible spectrum of acid graphite oxide (AGrO), graphite oxide (GrO) and reduced multi-layered graphene oxide (rMGO) colloidal suspensions.

Considering that the GO and rMGO structural characteristics are different in the percentage of carbon present and in graphite, as in the route of synthesis used for oxidation and reduction. It is obligatory to have a description of the functionalization rate of graphite in its conversion to GO and estimate the restitution rate of the p conjugated system, through the reduction of GO to rMGO.

For obtaining a better description of IR spectra in GO and in rMGO, this was took in two regions: (a) Finger print – region, since 600 to 1400 cm<sup>-1</sup> and (b) Region of simple and double bonds since 1400 to 2000 cm<sup>-1</sup> and from 2500 to 3800 cm<sup>-1</sup>. In GrO there is a change in hybridization state from sp<sup>2</sup> to sp<sup>3</sup> in carbon atoms which forms the  $\pi$  conjugated system in graphene sheets, this happens with the formation of C=O, COOH, C-O-C, (-O-) and C-OH that can be find in the edges of GO sheets. Because of this changes on hybridization states would change the percentage of  $\pi$  bonds and it would decrease the number of electronic states in Fermi level, in which causes in a restriction on conductivity of GO [24].



Fig. 2 (a) FTIR-ATR spectrum of the "fingerprint" region of the solid samples of vitreous glassy-carbon (GC), graphene oxide (GrO) and reduced multilayered graphene oxide (rMGO). (b) Differential FTIR spectrum for the transition GC → GO within the "fingerprint" region. FTIR spectrum (inset).

Specifically, in the (a) region of FTIR spectra there are four bands associated with the vibrational modes which are one of the characteristics of GC, GO and rMGO structures. The band located between 700 a 800 cm<sup>-1</sup> corresponds to one vibrational mode of asymmetric tension of the epoxy groups (-O-) existents in the edges of GO structure, against this in GC this vibrational mode corresponds the vibrational modes of the tension in the C-C bonds located in the edges existents in graphene sheets. By the other side, the band located from 900 to 1100 cm<sup>-1</sup> is associated with tension modes presents in the following groups: C=O y C-O-C, -COOH y C-OH, they are present in GO and in minor proportion in graphite. Anyway, the two last bands from 1100 to 1250 cm<sup>-1</sup> and 1300 to 1400 cm<sup>-1</sup> are equally related with vibrational modes existents in ether (C-O-C), carbonyl (C=O) and epoxy (O-) [25]. In order to gain knowledge about the direction of functionalization process in GC structure during its transformation to GO were accomplished one differential analysis of transmittance. In which has shown that the functionalization of GC happens mainly in the edges of the sheets in concordance with Lerf's model, with the formation of epoxy groups and that can be appreciated as an increase in the intensity of the band existent between 700 and 800 cm<sup>-1</sup>. In the same way the differential IR spectra has shown the increase in percentage of transmittance in the oxidation process of GC, in the region located between 1050 to 1250 cm<sup>-1</sup>, which has shown as an overlap of many bands and according to Aick and col. this band is originated by contribution of many functional groups oxygenated as -COOH, C=O, C-OH y C-O-C (Fig. 2a, 2b).



Fig. 3 (a) FTIR-ATR spectrum of the double-bonds (1400 to 2000cm-1) and simple-bonds (2500 to 3800 cm<sup>-1</sup>) regions of the GC, GO and rMGO. (b) FTIR differential spectrum for the transition GC → GO in both regions verifies the presence of epoxy (-O-), carboxyl (-COOH) and hydroxyl (-OH) groups. FTIR spectrum of GC and GO (inset).

Similarly an analysis on (b) region in the IR spectra for GC, GO and rMGO shows us characteristic vibrational modes of some known functional groups as C=C in 1550 to 1650 cm<sup> $^{1}$ </sup>, the groups –COOH and C=O existents from 1650 to 1800

cm<sup>-1</sup>, as well as from 2800 to 3000 cm<sup>-1</sup> and the groups COH and HO-H from 3200 to 3750 cm<sup>-1</sup>. Besides the existence of ketones and carboxyl between 1700 to1900 cm<sup>-1</sup>, as the existence of a stretch the "stretching" existent in C=C groups in the planes on the carbon net represented by an absorption band from 1550 to 1650cm<sup>-1</sup>. On the other hand it has one absorption band from 3200 to 3750 cm<sup>-1</sup> corresponding to hydroxyl groups OH, existents in –COOH or in water molecules that can be interleaved between the mono layers of GO, which indicates a certain degree of hygroscopic in GO. On the other hand, the differential analysis on the region b, it shows to us that the variations on transmittance is caused majority by the functionalization of GC by epoxy groups (-O-), ether (C-O-C), carboxyl (COOH), ketone carbonyl (C=O) and hydroxyl (C-OH or H<sub>2</sub>O) (Fig. 3a, 3b).

Through Raman spectroscopy it is possible to quantify the formation of defects in the GC  $\rightarrow$  GrO transition, which were caused by the oxidation process and by the regeneration of the  $sp^2$  system in the GO  $\rightarrow$  rMGO transition after the chemicalthermal reduction process. Given that the existence of a D vibrational mode in the graphite structure is forbidden and it only occurs when there are defects, it is possible to infer the disorder rate existent in the graphene sheets after the oxidation process. Fig. 4 it has shown a considerable increment on the D vibrational mode, and it is caused by the formation of defects in the functionalization process of the carbon atoms and considering the results obtained in FTIR-ATR analysis of this process occurs on the carbon atoms existent in the borders forming epoxy, carboxyl and ether or on the intern network generating hydroxyl. On the other hand, we observe that the replacement in the intensity of the D band after the reduction process of GO to rMGO, with which we can verify the recovery of  $\pi$  conjugated system. The first approximation of the rate of defects formation can be given through the relation I(D) / I(G), where the G band is intricately related with the defects density of carbon atoms which has  $sp^2$  hybridization. On the other hand, the D band is related with the presence of defects in a carbon network in the angle of union, in the longitude of union or in the kind of hybridization that exists on this ones. On this way we report that the first transition presents the relative increase of defects of 87 %, even after that we observed that the chemical-thermal reduction process reduces 42 % in the number of defects existents, it can be explained by the partial restitution of the  $\pi$  conjugated system.

Given that the G band is related with the presence of C (sp<sup>2</sup>) atoms it is possible to do an analysis of the displacement in its position POS (G). We observed the decrease of POS (G) in the first transition (GC  $\rightarrow$  GO) from 1591 to 1587cm<sup>-1</sup> and in the second transition (GO  $\rightarrow$  rMGO), from 1587 to 1581cm<sup>-1</sup>, this one has been reported as a transition from nanocrystalline graphite to amorphous carbon with a change in the maximum hybridization kind for 20 % of sp<sup>2</sup> to sp<sup>3</sup>. This reinforces the idea of the existence of defects caused by a change on

hybridization, to expand our Raman analysis we realized the measurement of optical gap  $(E_g)$  which is inversely related with the density of atoms with sp<sup>2</sup> hybridization. Because of that we can say a decrease on the gap's value would indicate a decrease on the C (sp<sup>2</sup>) density (Fig. 4).



Fig. 4 Raman spectrum of GC, GO and rMGO powders at 532 nm of wavelength.

In the model proposed by Robertson and O'Reilly in a graphite cluster, the  $\pi$  system has one lower band energetic level, which can be approximated as [26-27]:

$$E_g = 2\gamma(a/L_a)$$
(1)

Being,  $E_g$  the optical gap,  $\gamma$  an energetic contribution constant from  $pp\pi$  bond, "a" a parameter of reduction and  $L_a$ the nanocrystal size [28]. Thus,  $L_a$  value that one is direct related with the I(D) / I(G) value, according to the Tuinstra and Koening (TK) model as [29]:

$$I(D)/I(G) = C(\lambda)/L_a$$
(2)

Where  $C(\lambda)$  is an empiric constant related with Raman intensities Raman I(D) / I(G) and the value of  $L_a$  is obtained from Scherrer relation, through the X-Ray diffraction technique (XRD), and it has the value of C (515.5) = 4.4*nm*. One of the major disadvantages in this relation is the fact that it can only be applied in systems in which the small crystals have a big contribution Raman dispersion. As well as, these

crystals have a high orientation. Because of this, we only referenced this relation because it is one of the first reported and related with our study. On the other hand, Pimenta et al in a study similar to TK presents the following relation used in a nanocrystalline graphite system [30]:

$$L_a(nm) = (560/E_l^4)[I(D)/I(G)]^{-1}$$
(3)

Being,  $L_a$  nanocrystal size and  $E_l$  is the laser excitation energy, used in Raman analysis in electron volt (eV). This relation can be applied in function of the laser wavenumber,  $\lambda_l$ in the following equation:

# $L_a(nm) = 2.4x10^{-10} \cdot \lambda_l^4 [I(D)/I(G)]^{-1}$

(4)

Considering that in our study we used laser radiation with wave number equal to 532 nm (2.33 eV). We determined the difference on crystalline size  $L_a$  for transitions GC  $\rightarrow$  GO and GO  $\rightarrow$  rMGO. Anyway, we can quantify the distance between defects ( $L_D$ ) and the density of defects ( $n_D$ ) existents on both transitions, through the following relations:

$$L_D^2(nm^2) = 1.8x 10^{-9} . \lambda_l^4 [I(D)/I(G)]^{-1}$$
(5)  

$$n_D (defects. cm^{-2}) = 10^{14}/(\pi. L_D^2)$$
(6)



Fig. 5 AFM analysis of (a1-a3) supported GrO flakes and (b1-b3) rMGO flakes onto Si/SiO<sub>2</sub> wafer.

That's how in function of the expressed relations (1) and (4), and considering the value of the network parameter "a" and the energetic contribution of interaction  $(pp\pi)$ , equal to 0.246 nm y 2.90 eV respectively. It is possible to determinate the variation on value of optical gap, for each transition. Looking up there is no increase in the value of gap from 0,01eV to 0,07eV for the transition from GC  $\rightarrow$  GO which means an increase in the generation of defects by the exchange of hybridization from de  $sp^2$  to  $sp^3$ , anyway the second transition GO  $\rightarrow$  rMGO features a discussion in the value of optical gap from 0.07 to 0.04 eV which can be related with an increment of the density of sp<sup>2</sup> system. It is interesting to observe that this trend is confirmed by the calculation of the distance between defects ( $L_D$ ) and the density of defects  $n_D$ , because an increment in the gap comes with the formation of defects which can be related with an increment on the density of defects from 2.39  $10^{10}$  to 21.71  $10^{10}$  defects cm<sup>-2</sup> for the first transition and in the chemical-thermal reduction process causes a partial restoration in the sp<sup>2</sup> system in which is observed as a decrease in the density of defects from 21.71  $10^{10}$  to 12.30  $10^{10}$  defects cm<sup>-2</sup> in the second transition.

In contrast, a high density of defects would indicate the proximity between these and a decrease in the value of  $L_D$ , this tendency is presented on table N° 1, in which the distance between defects ( $L_D$ ) decrease from 36,5nm to 12,1nm for the first transition and in the second transition it increases from 12.1 to 34.5 nm (Table I).



		GC	GO	rMGO
D band	POS (D)	1362.8	1357.3	1356.3
	I (D)	5.84	13.01	0.97
G band	POS (G)	1591.0	1587.6	1581.6
	I (G)	53.97	13.23	1.75
Parameters	I(D) / I(G)	0.11	0.98	0.56
	La (nm)	177.62	19.55	72.13
	LD (nm)	36.50	12.11	34.51
	$n_{\rm D}  10^{10}$	2.39	21.71	12.30
	(defects cm <sup>-2</sup> )			
	E <sub>g</sub> (eV)	0.01	0.07	0.04

Finally, we present an analysis of the crystal's size, because this should decrease in each of the transitions studied. In contrast a decrease has been reported from 177.6 to 19.6 nm in the transition GC  $\rightarrow$  GO and an increment in the size of the crystal for the second transition from 19.6 to 72.1 nm. GO  $\rightarrow$ rMGO. The first case can be explained by a decrease on the value of  $L_{a}$ , as a consequence of the sub process of chemical interaction of  $SO_4^{2-}$  groups and ruptures that were caused by the ultrasound device present in the oxidation stage on the first transition. After this, the anomaly on the second transition can be explained as a des-functionalization process of the oxygenated groups after the chemical-thermal reduction process, which would reduce the superficial charge that allows us to keep apart the rMGO sheets, given to it the capacity to stack again. This last process is confirmed with an increment on the dimensions of the supported sheets of GO and rMGO observed through atomic force microscopy (AFM). It was observed sheets of GO with dimensions ranging from 1.3 to 1.8 µm (Fig. 5 b1, b2). Comparing to rMGO sheets whose dimensions ranges from 0.6 to 0.9µm (Fig. 5 a1, a2). On the other hand, we observed a big topological improvement on rMGO sheets obtained after the hybrid chemical-thermal reduction process, as a decrease in its thickness from 30 to 15 nm indicating that it was formed approximately 10 to 15 sheets of graphene, according to profilometry analysis (Fig. 5 a3, b3).

### **III. CONCLUSIONS**

As part of the synthesis process, it is important to highlight that the oxidation process is oriented by the functionalization of carbon atoms located on the edges, oxidizing them to carboxyl, ether and carbonyl groups. On the other hand, the chemical reduction by NaBH<sub>4</sub> has shown, in a similar way to oxidation, to be a selective process because it restores the sp<sup>2</sup> hybridization in carbon atoms which are functionalized in GOES. Certainly, this reducer agent has showed to have the capacity to restore the p conjugated system, since the initial system had a fraction of defects equal to 0.98 (GO) and after the chemical-thermal reduction process the fraction of defects was equal to 0.56 (rMGO), after this we can conclude that the reduction of the superficial defects was equal to 0.42 according to the analysis made with Raman spectroscopy. Anyway we report that for the transition GC  $\rightarrow$ GrO, a decrease in the POS(G) related with the diminution in the number of  $C(sp^2)$ , which is quantified with an increase in

the defects density  $(n_D)$  and a decrease in the distance that separate them  $(L_D)$ . On the other hand, the transition GrO  $\rightarrow$ rMGO presents an increase in the distance between defects as a decrease in the partial density of defects from 21.71 to 12.30  $10^{10}$  defects cm<sup>-2</sup>, with a partial restitution of C=C system, it is observed a decrease of optical gap from 0.07 to 0.04 eV.

This last confirms that the value of optical gap is inversely proportional to defects density of C  $(sp^2)$ . Additionally happens a diminution in size of the crystals (La) that exists initially on GC, from 177.6 to 19.6nm which is caused by the ruptures on the nets of carbon, as consequence of intercalation process and the ultra sound has provided the transition stage. Anyway after the chemical-thermal reduction process we observed an increase on size of the crystal (L<sub>a</sub>), what indicates a partial enlargement of the scales of rMGO. On this analysis the functionalization grade is confirmed through atomic force microscopy, AFM. Principally is highlight the dimensions of the sheets of rMGO equals to 0.6 to 0.9 µm, what indicates a sectioning on the initial sheets of graphite, not only in the inter-plane direction but in plane ruptures too; this increases the proportion of superficial defects and it raises difficulties the restore of p system on the final product. Anyway the profilometry analysis of the thickness of this sheets of CMG, showing us that after the process of chemical-thermal reduction they have a thickness of 10-15 nm, this would indicate the existence of 10 to 15 monolayers of graphene in its structure.

## IV. ACKNOWLEDGMENT

The authors acknowledge to the Cnpq – Concytec, Innovate-Peru (FINCyT-138-IA-2013) for their financial support and the CEM-UFABC for the equipment used in this work.

## V. REFERENCES

[1]. Novoselov, K.S et al. Electric field effect in atomically thin carbon films. Science 2004, 306, 666–669.

- [2]. William s. Hummers, Jr., and Richard E. Offeman. Preparation of Graphitic Oxide. J. Am. Chem.Soc., 1958, 80 (6), pp 1339–1339.
- [3]. Sasha Stankovich, Dmitriy A. Dikin, Geoffrey H. B. Dommett, Kevin M. Kohlhaas, Eric J. Zimney, Eric A. Stach, Richard D. Piner, SonBinh T. Nguyen and Rodney S. Ruoff. Graphenebased composite materials. Nature. 2006, 442, 282-286.
- [4]. Sasha Stankovich, Dmitriy A. Dikin, Richard D. Piner, Kevin A. Kohlhaas, Alfred Kleinhammes, Yuanyuan Jia, Yue Wu, SonBinh T. Nguyen and Rodney S. Ruoff. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon. 2007, 45 (7), 1558–1565.

[5]. Sungjin Park and Rodney s. Ruoff. Chemical Methods for the Production of Graphenes. Nature Nanotechnology. 2009, 4, 217 - 224.

[6]. F.M. Koehler, A. Jacobsen et al. Selective chemical modification of graphene surfaces: Distinction between single- and bilayer graphene, Small 2010, 6, 1125–1130.

[7]. L. Pietronero, S. Strässler, H.R. Zeller and M. J. Rice. Charge distribution in c direction in lamellar graphite acceptor intercalation compounds, Phys. Rev. Lett. 1978, 41,763.

[8]. Z. H. Ni, Y. P. Feng, H. M. Wang, J. Kasim, and Z. X. Shen. Graphene Thickness Determination Using Reflection and Contrast Spectroscopy. NANO LETTERS 2007, 7, 9 2758-2763.

[9]. Daniel R. Dreyer, Sungjin Park, Christopher W. Bielawski and Rodney S. Ruoff. The chemistry of graphene oxide. Chem. Soc. Rev. 2010, 39, 228-240.

[10]. Daniela C. Marcano, Dmitry V. Kosynkin, Jacob M. Berlin, Alexander Sinitskii, Zhengzong Sun, Alexander Slesarev, Lawrence B. Alemany, Wei Luand James M. Tour. Improved Synthesis of Graphene Oxide. ACS Nano. 2010, 4 (8), 4806–4814.

[11]. Kian Ping Loh, Qiaoliang Bao, Priscilla Kailian Ang and Jiaxiang Yang. The chemistry of grapheme. J. Mater. Chem. 2010, 20, 2277-2289.

[12]. E. Mauro Giraldo P. & Wilfredo Blas G. Minería actual del carbón en el norte del Perú. Revista del Instituto de Investigaciones FIGMMG-UNMSM. 2007, 10, 20, 76-81.

[13]. E. Mauro Giraldo P. El carbón: alternativa a la crisis energética en el Perú. Revista del Instituto de Investigaciones FIGMMG-UNMSM. 2008, 11, 22, 17-24.

[14]. Daniela C. Marcano, Dmitry V. Kosynkin, Jacob M. Berlin , Alexander Sinitskii , Zhengzong Sun ,Alexander Slesarev , Lawrence B. Alemany , Wei Luand James M. Tour. Improved Synthesis of Graphene Oxide, ACS Nano. 2010, 4 (8), pp 4806–4814.

[15]. Dan Li, Marc B. Müller, Scott Gilje, Richard B. Kaner & Gordon G. Wallace. Processable aqueous dispersions of graphene nanosheets. Nature Nanotechnology. 2008, 3, 101 - 105.

[16]. Chun Kiang Chua, Zdenek Sofer and Martin Pumera. Graphite Oxides: Effects of Permanganate and Chlorate Oxidants on the Oxygen Composition. Chem. Eur. J. 2012, 18, 13453 – 13459.

[17]. Ming Fang, Kaigang Wang, Hongbin Lu, Yuliang Yang and Steven Nutt. Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites. J. Mater. Chem. 2009 19, 7098–7105.

[18]. P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim. Making graphene visible. Applied Physics Letters. 2007, 91, 063124.

[19]. (19) Leandro Malard Moreira. Raman spectroscopy of graphene: probing phonons, electrons and electron-phonon interactions. Tese de doutorado. Universidade Federal de Minas Gerais, Minas Gerais-Brasil 2009, 58-67.

[20]. Robert Vajtai. Springer Handbook of Nanomaterials. Ed. Springer-Verlag Berlin Heidelberg. CAPS, 2013.

[21]. Zhengtang Luo, Ye Lu, Luke A. Somers, and A. T. Charlie Johnson. High Yield Preparation of Macroscopic Graphene Oxide Membranes. J. AM. CHEM. SOC. 2009, 131, 898–899.

[22]. Songfeng Pei, Hui-Ming Cheng. The reduction of graphene oxide. Carbon. 2012, 50. 3210–3228.

[23]. M. Acik, G. Lee, C. Mattevi, M. Chhowalla, K. Cho and Y. J. Chabal. Unusual infrared absorption mechanism in thermally reduced graphene oxide. Nat. Mat. 2010, 9, 840-845.

[24]. Daniel Pisapia, Carlos Barrios, Manuel Martínez, Katya Reategui, Williams Meléndez, Santiago Marrero y Marcos Escobar. Oxidation of natural graphite in the laboratory and comparison with the synthetic graphite oxide, by means of thermal and spectroscopic techniques. Rev. Téc. Ing. Univ. Zulia. 2009, 32, 3, 249 - 255.

[25]. A. C. Ferrari and J. Robertson. Interpretation of Raman spectra of disordered and amorphous carbon. Physical Review B. 2000, 61, 20, 14095-14107.

[26]. J. Robertson and E.P. O'Reilly. Electronic and atomic Structure of amorphous carbon. Physical Review B. 1987, 35, 6, 2946-2957.

[27]. J. Robertson (1986): Amorphous carbon, Advances in Physics. 2006, 35, 4, 317-374.

[28]. F. Tuinstra and J. L. Koenig. Raman Spectrum of Graphite. The Journal of Chemical Physics. 1970, 53, 1126-1130.

[29]. L. G. Cançado, M. A. Pimenta et al. General equation for the determination of the crystallite size La of nanographite by Raman spectroscopy. APPLIED PHYSICS LETTERS. 2006, 88, 163106.

[30]. L. G. Cançado, A. C. Ferrari et al. Quantifying Defects in Graphene via Raman Spectroscopy