Laser power influence on Raman spectra of multilayer graphene, multilayer graphene oxide and reduced multilayer graphene oxide

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Abstract. In this work, the influence of laser power on Raman spectra on different carbon based materials was studied: multilayer graphene (MLG), multilayer graphene oxide (MLGO) and reduced multilayer graphene oxide (rMLGO). The presence of oxygen and hydrogen was verified by means of Fourier-transform Infrared Spectroscopy, indicating that our oxidation and reduction process was success in our multilayers graphene. Through the position and width of the band G, we discuss the effects of the incorporation of oxygen by the graphene matrix in terms of thermal expansion and doping effects. The ID/IG ratio was used to determine the presence of defects and showed a similar behavior for MLGO and rMLGO demonstrating a feature of partial reduction and reduction effects caused by the power supplied by laser.

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1. Introduction

Graphene has triggered new studies since its discovery by Novoselov and Geim [1], who used the process of mechanical exfoliation [2] to obtain the first two-dimensional stable material consisting of hexagonal networks of carbon with sp² hybridization. An example of these studies is the incidence of a laser beam on the surface of graphene, which makes this system to behave as an ideal sensor that exposes intrinsic properties of environmental perturbations, showing that the charge-carrier density of exfoliated graphene on a substrate of SiO²/Si can be transported reversibly between the hole and electronic doping with visible photons. This photo-induced doping occurs under moderate conditions and with a total control of the laser power (P_l) that fall on the samples. These findings suggest that optically closed graphene devices that operate on a scale of less than one second time and expected from Raman spectroscopy is not always as noninvasive as is generally assumed [3].

Graphene has many superior interesting properties, such as high electronic and thermal conductivity, high mechanical strength [4], electronic quantum transport, gap band space tunable, high mobility, high elasticity, electromechanical modulation [5], as well as properties for applications in nano-electronic devices [6], water decontaminant [7], etc. Another material worth studying is graphene oxide (GO); for their applications in biosensors [8], water decontamination [9], thin film transistors [10], transparent conductive films [11], just to mention a few examples. Being the
Hummer-Offeman method [12] the most used, due to the fact that it allows us to work with different amounts of powdered graphite or flake type, as well as to modify quantities and solvents that are used during the synthesis process. In this way, we can obtain significant amount of graphite oxide and it is consequently reduced.

Raman spectroscopy is a technique used for the study of a wide range of materials, one of which is graphite and its derivatives such as graphene and graphene oxide. This technique allows the determination of the layers [13, 15] and crystallite size [16] among other studies widely reported in the literature [14]. In particular, the increasing in local temperature at the point where the Raman laser hits the material under study causing a shift of the D and G bands due to thermal expansion and phonon dispersion. Therefore, the local temperature at the measuring point can be represented as a function of the laser intensity absorbed by graphene [17]. In this direction, we have studied the effects produced by applying several laser power on three systems: multilayer graphene (MLG), multilayer graphene oxide (MLGO) and reduced multilayer graphene oxide (rMLGO) thermally at a temperature of 80 °C. In this way, clear relationships between the laser power than incident on MLGO and rMLGO were observed fixing an only laser energy. These results are shown and discuss.

2. Experimental procedure

For the synthesis of MLGO, the process started from a solid mixture of graphite and sodium nitrate. Under constant stirring sulfuric acid was added and then potassium permanganate was slowly poured, forming a reddish coloration corresponding to MnO2 [18].

The reaction was maintained for about 2 hours and then 50 ml of water was added, increasing the reaction temperature, which was set between 95-98 °C. After 40 minutes, the sample displays a greenish color.

After cooling the sample to room temperature, hydrogen peroxide was added to stop the oxidation reaction [19] with constant stirring, forming on the basis of a beige precipitate, and then it was washed 2 times with water, hydrochloric acid and ethanol. Finally, this solution was filtered and allowed to dry at room temperature.

Once graphite oxide was obtained by chemical technique; multilayer graphene oxide (MLGO) was obtained through the process of mechanical exfoliation [2]. Worked out on a substrate of SiO2/Si, through the Zeiss optical microscope, the number of layers that the composite of graphene presents can be observed [20, 21]. An annealing process is then performed at low temperature, approximately 80 °C to improve its stability and obtain the reduced multilayer graphene oxide (rMLGO) [22], and then their properties were studied using the Raman spectroscopy manipulating the laser power. At each moment, the incidence of the laser on each sample was the same, and the intensity variation was from the lowest value to the highest without damaging the sample.

The equipment used was the Horiba T64000 Triplo Raman spectrometer on micro-Raman mode with a focal objective of 100x; studies were performed with an excitation green laser at 532 nm (photon energy of 2.33 eV) for a laser power controlled and checked by a potentiometer Laser check (ROHS), Coherent. Therefore, we can obtain the values of each of these intensities than incident on the sample. In this work, the values used were from 0.06mW until 3.00mW reaching the sample.

The morphological images of graphene derivatives were performed in a JEOL JCM-6000 Scanning Electron Microscope. Fourier-transform infrared spectroscopy (FTIR) performed in a Varian-Agilent 640 FTIR on ATR mode was used to determine the functional groups in multilayer graphene oxide.

3. Results and discussion

In figures 1 (a) and (b), SEM micrographs display different morphological structures, before and after the oxidation process performed by the method of Hummers [12]. The different morphology between samples is an indicative of the presence of oxides. Since multilayers graphene was not chemically
treatment appreciating a smooth surface; while for obtaining the multilayers of GO, it was worked with sulfuric acid to the intercalation of the graphite layers and other process as mentioned in the experimental procedure forming oxygenated functional groups showing an irregular surface as can be observed in figure 1 (b).

Figure 1. SEM image to pure graphite (a) and (b) after chemical process to obtain graphite oxide.

After exfoliation the graphene multilayer, MLGO and rMLGO were deposited on SiO$_2$ substrate to be studied by Raman spectroscopy as observed in the figure 2 (a), (b), (c), as a function of laser power. Thus, as we can see in the figure 2 (a) the G band appears well defined around 1585 cm$^{-1}$ and approximately not changes with the laser power (figures 4 (a) and 4 (b)). On the other hand, when oxygen is incorporated in graphite by Hummers–Offmen method and is obtained the MLGO by exfoliation, the D and D' bands appear in 1354 cm$^{-1}$ and 1620 cm$^{-1}$ respectively shown in the figure 2 (b). Figure 2 (c) shows the Raman spectra of rMLGO. In all cases, these bands increase even more with the increase of the laser power.

The amount of defects generated by the oxidation of graphite, as well as the degree to which the system of $sp^2$ hybridization is regenerated after the annealing process at 80 °C were studied by Raman spectrums as shown in the figure 2 (c). In the G band, shows an increase in the bandwidth due to the influence of $sp^3$ hybridization, defined path amorphous material. The appearance of the band D' occurs due to relaxation which allows high frequency phonons to be scattered [13-15]. On the other hand, when the peak D is observed in graphene and graphite systems is directly related to disorder or defects being used as a quality measure [14].

Even doping of electrons or holes can be detected from Raman measurement and it is reflected on the stiffness and the sharpness of the band G [13].

Figure 3 shows FTIR spectroscopy for MLGO, obtaining the characteristic bands of its structure, around 1645 cm$^{-1}$ corresponding to the vibration of the C = C, in addition to the bands associated with vibration stretch of flexing of the OH bond around 3400 cm$^{-1}$ [23], for a wavenumber of 1060 cm$^{-1}$ C-O bond, at 1220 cm$^{-1}$ vibration tension to C-OH and a band at 1720 cm$^{-1}$ which is attributed to C = O bonds of the carboxyl corroborate the formation of oxygenated functional groups.
Figure 2. Raman spectrum of the (a) multilayer graphene (MLG) (b) multilayer graphene oxide (MLGO) and (c) reduced multilayer graphene oxide (rMLGO) to the different laser power $P_l$.

Figure 4 shows the properties of the G band of the Raman spectrum as a function of laser power for the three studied systems MLG, MLGO and rMLGO. We decided to study the G-band because it is present in all systems and is one of the most important bands for the characterization of carbon materials. On the impact of the laser intensity, it is important to consider that for some materials, it is possible to damage or alter the sample with this parameter without modification the laser energy. The effect of relatively small changes in the laser intensity, the effect induces small changes of temperature in the samples. Most carbon nanomaterials are black and absorb significant amounts of visible light, most of this absorbed energy is converted into heat, and thus changing the sample temperature in the area where the laser beam is focusing.

Figure 3. FTIR-ATR spectrum for multilayer graphene oxide.
Figure 4. Properties of G band: (a) Width band (FHWMG) and (b) band position (Pos(G)) worked for different laser power at a wavelength of 532 nm; (c) Width band (FHWMG) as a function of the band position (Pos(G)). The dashed curves are only to better visualize the behavior in (a) and (b).

The different intensities of the laser should not necessarily cause changes in the energy of the scattered phonon due to the quantization effect of the network vibrations, but they work to improve the signal-to-noise ratio in obtaining the Raman spectrum.

In figure 4 (a) the position of the G band represents the average energy of phonon generated in the system by the scattered laser photon. For the MLG this energy does not vary considerably depending on the different laser power. However, for MLGO there is considerable dependence. In the latter case, a tendency to return to the same behavior of the MLG due to the elimination of the functional groups by the heat treatment process is observed for the rMLGO for low laser power. It is likely that physicochemical changes caused by oxygenation of graphene alter the modes of attachment of the crystalline lattice of the material, inserting defects and / or altering the length of the bonds and the crystalline lattice. This configuration of changes makes the system more susceptible to influence the intensity of the incident laser. By influencing the laser on MLG, MLGO and rMLGO to different powers, gives changes in temperature causing a change in the peak positions of the Raman spectra. As temperature increases, there is a linear shift of the G peak (Pos(G)) due to increased anharmonic phonon coupling increased thermal expansion in the lattice. The lattice expansion changes the energy center of dispersion of the phonons Pos(G) and is much more significant in the presence of defect elements (functional groups such as oxygen) in the crystalline lattice. In addition, the presence of these defects increases the dispersion of the phonons (figure 4 (b)) and is not fully reversed with the thermal reduction. Because this, there remains an oxygen doping in the rMLGO matrix, which causes nonlinear effects with the temperature in the regime of lower power of the laser (figure 4 (a)). In figure 4 (c) finally, we observed the difference in the response of each studied property of the system to the variation of laser power. It is observed that the MLG system maintains the characteristics of the vibrational mode only by increasing the phonons population (increase of the dispersion), the MLGO alter the vibrational characteristics and add dispersion, and the rMLGO system presents a tendency to return to the MLG vibrational modes but still maintaining higher dispersion due to non-complete elimination of the functional groups by the annealing process.
The ratio of the intensity (area) of the peaks D and G (I_D/I_G) in figure 5 is used to characterize the level of disorder in samples. It exists a regime of density of "low" defects where I_D/I_G will increase as a higher density of defects creates more elastic scattering, this happens until a regime of "high" density of defects, at which I_D/I_G will start to decrease as there is a growth of the density of defects, this results in a more amorphous structured carbon, and attenuating the Raman peaks [13, 24]. Besides to a peak D occurs, a charge carrier should be excited and be inelastically scattered by a phonon, and then a second elastic scattering by a defect or boundary region must occur to result in recombination. As both processes are of the same order, it was expected that the area relationships would remain constant for different P/\gamma. The observed differences indicate that each scattering mechanism produces a slightly different response with the increase in the number of photons arriving on the material, even presenting a similar ratio I_D/I_G for MLGO and rMLGO. This similarity may indicate that the reduction process is not able to eliminate the defects of the matrix entirely. In addition, the behavior of the graph (figure 5) shows that there is a process of apparent clutter reduction when more power is supplied to the sample.

Figure 5. The relation between D and G bands (I_D/I_G) ratio for different laser power P/\gamma. In all cases, to an only laser energy of \lambda = 532nm.

4. Conclusion
In this present work we did prepared multilayer graphene and by chemical reaction we have produced graphene oxide and reduced. Using FTIR spectroscopy we have verified that an oxidation process was obtained. Raman spectroscopy was also performed, but we have focused our study on the influence of the laser power on the spectra using moderate range of power. According to Raman results, the produced multilayer is free of defects, while the oxidized and reduced multilayers show clearly a Raman peak related to the presence of defects. The defects we attribute to the crystal structure modification produced during the oxidation process.

We show that the laser power does not affect the position of the G band peak to the MLG, as expected, but it affects the position in different ways for the MLGO and rMLGO. We believe that these effects are related to the effects of thermal dilation and oxygen doping of the matrix. In addition,
the oxidation process increases the dispersion of the phonons, and, conversely, the reduction process increases further. This increase in dispersion is possibly associated with the fact that the reduction does not totally eliminate the defects of the crystalline lattice that may persist even after the release of the associated functional groups, and the presence of more dispersed oxygen in a smaller quantity. These defects and the not completely eliminated oxygen alter the heating mechanisms of the matrix, demonstrating different vibrational properties with the power provided by the laser. In this way, we show how that the range in laser power used in this work affect these materials (MLG, MLGO and rMLGO), which can be used as reference in the future to investigate similarly produced samples.

5. References

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