

# Graphene for a green-environmentally methodology with organic surfactants

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**Abstract—** Two methods for the preparation and characterization of graphene using 5 commercial detergents and sodium cholate were tested. Sonication bath and a mix reactor are presented. For the experiment, a sonic bath with variable frequency and a beaker were used for testing. There were used different reactive varying its concentration 0.01 g/mL to 1 g/mL, duration of the experiment (30 minutes to 25 hours), initial concentration of graphite (0.1 g/mL to 8 g/mL), spin time (15 minutes to 1 hour), the centrifuge speed (500 rpm to 2000 rpm) and frequency for sonication (20 kHz to 45 kHz). Samples were taken and subsequently washed on a Buchner funnel with deionized water and methanol, and then be dried to store it as powder. Finally, they were analyzed by UV-VIS to determine the concentration in the samples, Raman spectroscopy looking for crystallization patterns of graphene, TEM and HRTEM in order to determine the number of layers of graphite stacking.

**Keywords—** Graphene, Shear exfoliation, Surfactants, environmental friendly

## I. INTRODUCTION

Novoselov and Geim has revolutionized the vision of nanomaterials with the discovering of graphene [1]. Graphene has shown outstanding heat transfer, energy and hardness properties [2], [3]. Nowadays there are investigating methods to help mass production without damaging the environment. Methods that involve peeling in aqueous medium are developed technologies that have potential for industrialization. Mainly there are two methods that involve physical phenomena: sonification, which is in sonic bath, and the shear exfoliation, which is done in a container with propeller to generate turbulence [4].

Extensive efforts in this approach have been made to improve the yield and the quality of graphene. Organic solvent based exfoliation, polymer based exfoliation and surfactant based exfoliation are three different approaches in liquid phase exfoliation method. Despite some defects brought by surfactant, the last one was proved to be an ideal

way of preparing graphene dispersion with high graphene concentration, and more importantly, with excellent stability [5]. Ionic surfactants were first introduced to assist the exfoliation process. For instance, Vadukumpully et al. used a cation surfactant cetyltrimethylammonium bromide [6], Hernandez et al. used sodium dodecyl benzene sulfonate, sodium cholate and other ten kinds of surfactants to exfoliate graphite flakes [7]. Nuvoli et al. designed a series of works to get extremely high graphene concentration. Graphene concentration as high as 5.33 mg/mL is obtained in a commercial ionic liquid 1-hexyl-3-methyl-imidazolium hexafluorophosphate, 2.21 mg/mL in Nmethylpyrrolidone solution, 9.45 mg/mL in polymerizing media, and 8.00 mg/mL in organosilanes [8]. Du et al. introduced some organic salt to assist exfoliation and enhanced the exfoliation efficiency [9]. For nonionic surfactant, Guardia et al. first explored the differences between ionic and nonionic surfactants in assisting exfoliation and verified the ascendancy of nonionic surfactant, and then extended the method to synthesize inorganic graphene analogues [10]. In addition, Niu et al. obtained graphene dispersion with enhanced graphene concentration with the assistant of inorganic salts. Wang et al. introduced ethanol into the surfactant/water solution to reduce exfoliation energy in surfactant/ water medium and enhanced graphene concentration up to 3 times [11]. Samoilov et al. adopted an effective fluorinated surfactant for graphene production, which is environmentally friendly [12].

All the previous works show the advantage and the potential of surfactant assisted liquid phase exfoliation method. The continuous research on in this field is thus necessary and meaningful [13]. To improve the approach of surfactants in exfoliation methods there are two significant problems to be considered. Firstly, what are the main factors that can influence the degree of exfoliation. Secondly, which parameters can represent the effectiveness

of a method. For the first question, based on the predecessors' works, some particular factors, for instance surfactant type, sonication time, centrifugation speed and initial graphite concentration were discussed as a function of graphene concentration. For surfactant type, Smith et al. proposed that, ionic and nonionic surfactants have different mechanisms for stabilizing graphene dispersions. For sonication time, half hour sonication may have a decent marginal benefit over longer or shorter sonication time [14]. For centrifugation speed, the increase of centrifugation will negatively affect graphene concentration and graphene sheet's quantity. However, to the best of our knowledge, the influence of surfactant concentration on graphene concentration have not been deeply explored. For the second question, Coleman et al. first used the dispersion absorption as a main index for exfoliation according to the Lambert-Beer Law, and used transmission electron microscope (TEM) and other characterization tools to examine the quality of the dispersion. Whether graphene dispersion with high graphene concentration has the same quality as the one with relatively low concentration is not solidly confirmed [15].

In this paper, five different of commercial detergents with different proportions of surfactants are used to give possible answers to these questions based on a file from Procuraduría Federal del Consumidor (PROFECO) of 2014 [16]. The optimum concentrations of reactive for exfoliation were found. In order to get a full understanding of the factors that influence graphene concentration, many controlled experiments are carried out. Characterization methods are performed to examine the quality (sheet size, number of the layers and structural defects) of the product. The results provide valuable data and references for graphene exfoliation in water/surfactant dispersion. The objective of the research was to synthesize graphene using biodegradable detergents by two methodologies: Shear exfoliation and sonochemistry. They were tested and with them determining the quality of the graphene obtained by Raman spectroscopy, Uv-Vis, TEM and High Resolution Transmission Electron Microscopy (HRTEM).

## II. METHODOLOGY

A mixture of graphite flakes from Sigma-Aldrich, deionized water and 5 commercial products with different surfactant concentration were used, additionally Sodium cholate was used as a contrast patron. All reactive were mixed in a polymer reactor of 2 L with two blades of 7 cm, enhanced the turbulence in the container made in lab. There was performed a range of mixing experiments varying a range of parameters: Initial concentration of graphite, blade speed, type of reactor and mixing time. The mixer was operated at 25,000 rpm for 45 minutes. The engine of the reactor is not designed for continuous operation at high speeds for long times due to excess heating. After the mixing, aliquots of the resultant dispersions were collected (5 mL) and centrifuged at 1500 rpm for 45 minutes.

The methodology used for the method of the samples in sonic bath together with exfoliation shear were as follows:

The amount of surfactant for each of the runs were weighed and mixed first with deionized water for a period of 5 minutes so that the concentration in the sample was homogeneous. The procedure for the reactor and for sonic bath were the same, with the variation that the reactor volume used was 500 mL. In the case of the reactor, the methodology involves testing a minute in the reactor on the other in an ice bucket, because the heat of the blades is transferred to the mixture of graphite with water and may actually cause evaporation mixture and this will cause change in concentration. Temperature plays a role in the surface tension, therefore, the smaller the variation in temperature, better control of the properties of the mixture, then the surface tension to be constant is controlled [7].

One of the advantages of sonic bath process is that it can continually work, it means that, once the process started it did not require supervision. The process inside both reactors suffered heating in the mixture at 48 °C, measurements were made on the samples and that was the maximum temperature reported for the process. Instead, the process reactor has to be intermittent as it undergoes heating in the motor can reach the boiling point of water, causing problems in the mixture, so was one minute turned on for one minute in ice bath. In both processes it has been observed that the average temperature throughout the process remained around 35 °C.

Exfoliation in the sonic bath was carried out as specified in the methodology. In general, to identify each of the samples was assigned a number to the level of each factor, the first number indicates the surfactant used, numbered 1 to 7. The second number indicates the concentration that was used, based on the table 2, and goes from number 1 to 3, where 1 is the lowest concentration of surfactant and 3 the greatest. The last number indicates the level in the sample, for sonic bath was operated level 1 indicates 75% power the equipment and two 100% power. To the reactor level 1 is referred to the speed computer 2 and level 2 to speed 3.

## III. RESULTS

5 different commercial detergents (CD) with distinct composition were evaluated besides Fairy liquid and Sodium Cholate. First, a relationship between concentration of commercial detergent and surface tension had to be found. It was reported that a surface tension of 46.7 mN/m [17] was necessary to exfoliate graphene from graphite in solvents. N-methyl-Pirrolidine (NMP) is the solvent with the best properties to exfoliate graphene because of its inherent surface tension at room temperature. The concentration of the CD has to achieve the values of NMP to provide a well exfoliated graphene.

Table 1 depicts the different concentrations that were tried to achieve comparing the surface tension. It was reported that the best for graphite exfoliation is 46.7 mN/m. The method used for this purpose was the Du Nouy ring. It consists in the use of a wheel to measure the force to bring out a ring from the surface of the liquid contained.

With the data obtained, the concentration was estimated and then the process to evaluated were sonic bath and shear exfoliation. In table 2 the values of the highest concentration obtained for each CD are presented (0.15 mg/mL), based in the relation between concentration and surface tension, the highest value of concentration was used because the value of surface tension was close to that reported for sodium cholate.

There are also presented the power used for the production of graphene and the final concentration of graphene obtained.

Table 1. Surface tension of each type of detergent related to its concentration

Detergent	Concentration [mg/mL]	Surface tension [mN/m]
1	0.05	48.45
1	0.1	41.99
1	0.15	47.4
2	0.05	47.75
2	0.1	48.01
2	0.15	47.49
3	0.05	47.06
3	0.1	46.7
3	0.15	48.45
4	0.05	53.25
4	0.1	43.21
4	0.15	48.45
5	0.05	48.36
5	0.1	50.45
5	0.15	54.99
6	0.05	48.45
6	0.1	45.65
6	0.15	43.65
7	0.05	44.95
7	0.1	46.44
7	0.15	46.7

The absorbance was analyzed with the Uv-Vis equipment, in order to determine the concentration, the measurements were performed from 190 nm to 800 nm. In table 3 are the data obtained by sonic bath of the highest concentrations for each of the detergents, the detergents 2, 3 and 5 are those with higher concentrations of graphene, while the others had a deficient performance, It is important to emphasize that is sought is a higher concentration of graphene based on the wavelength of 660 nm.

Table 2. High concentration of graphene for sonic bath of each type of detergent.

Detergent	Level of concentration of detergent	Level of power	Concentration of graphene [mg/mL]
1	3	2	0.053
2	3	2	0.086
3	3	1	0.081
4	3	2	0.052
5	3	1	0.086
6	3	1	0.069
7	3	2	0.070

The reagents with the highest concentration, those with the best results were 2 and 5 with a value of 0.086 mg/mL surpassing that found for sodium cholate, represented by reactive 3. In the case of the results obtained by shear exfoliation (Table 3), a similar behavior was presented regarding the 3 products with better yields, however, sodium cholate had a higher performance in terms of obtaining graphene compared to detergents proposed 2 and 5. From the two methods used, the one were higher concentration values were obtained was sonic bath, however it has been reported that the technique is not as scalable as the shear exfoliation, hence the interest to study and compare both.

In the case of Raman spectroscopy for sonic bath there is a match with the results. Two more samples of reagents 2 and 5 were also analyzed since the other levels of the treatments also had graphene concentrations similar to the highest. Figure 1 shows the spectra of each of the samples analyzed, D ( $1350\text{ cm}^{-1}$ ), G ( $1583\text{ cm}^{-1}$ ) and 2D ( $2680\text{ cm}^{-1}$ ) bands are signposted with dash lines. For sample 231 and 232, no significant difference was seen in terms of intensities of D and G band, the presence of other bands or a spectral shift, but in the case of samples 331 and 332 this change was similar. The sample 332 does not present the band D' related to the lack of impurities, however a greater value is presented as regards the relation of the bands D with G, resulting in larger sheet sizes.

Finally, for the detergent 5, the sample 531 presents a spectrum similar to the detergent 2, which depicts of the presence of impurities but which it is still possible to use.

In the case of shear exfoliation in the Raman spectra (Figure 2), in general, the lack of G' band is observed, indicating a lack of impurities. A determining factor to take into account is the ratio of the D and G bands, which presents the largest values of the analyzed samples are those belonging to the detergent 5, indicating a better graphene quality obtained. Supported by the intensity of the spectra. This D / G ratio is comparable to that observed by the sonic bath method but with better results since the band G 'belonging to the impurities is not shown.

Although Raman spectroscopy is a useful for determining hybridization of sp<sup>2</sup> and sp<sup>3</sup> in carbon atoms. The presence of D ( $1350\text{ cm}^{-1}$ ), G ( $1583\text{ cm}^{-1}$ ), the D' ( $1620\text{ cm}^{-1}$ ) and 2D ( $2680\text{ cm}^{-1}$ ) are "footprint" of graphene. Each band gives different information. D band is caused by a disorder in the structure of graphene. The presence of disturbances in the system sp<sup>2</sup> hybridized carbon is showed in the band with high intensity. Therefore, Raman spectroscopy is a technique used to

Detergent	Level of concentration of detergent	Level of power	Concentration of graphene [mg/mL]
1	2	1	0.011
2	3	1	0.035
3	2	2	0.040
4	2	1	0.012
5	3	2	0.026
6	3	1	0.019
7	2	1	0.012

determine the hybridization of a material. In a perfect

Table 3. High concentration of graphene for shear exfoliation of each type of detergent.

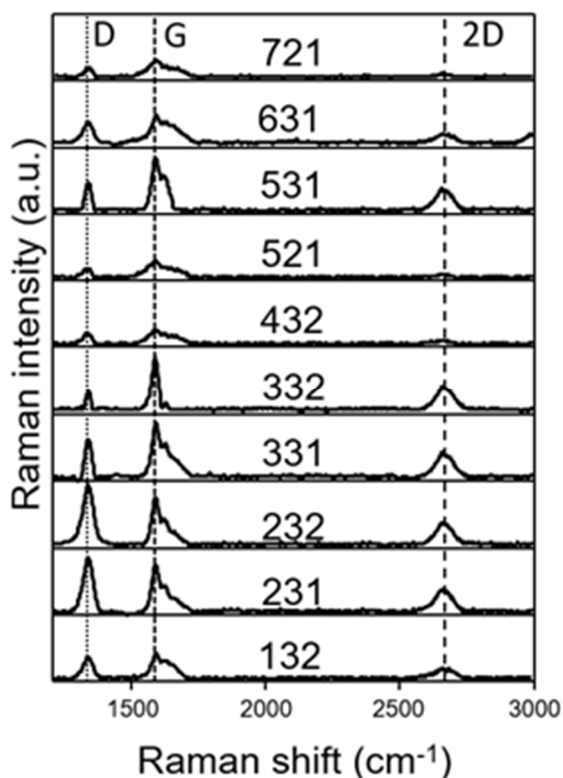


Figure 1. Raman spectroscopy of graphene obtained by different treatments of sonic bath exfoliation

structure of graphene D band is almost imperceptible. The G band is due to a mode E<sub>2g</sub> in gamma dots. The G band arises by stretching the carbon graphite, which makes common systems sp<sup>2</sup> hybridized. The G band is sensitive to stress [18]. If there is any impurity or surface charges in graphene, the G band can be divided into two peaks, the G and D'. The main reason for this behavior in materials is due to phonon interaction, causing a division in bands [19].

All materials with sp<sup>2</sup> hybridized carbon, exhibit strong intensity in the range of 2500-2800 cm<sup>-1</sup>. In combination with band G becomes a foot print of graphitic materials sp<sup>2</sup> hybridized. G' or 2D' band is given by the process of phonon interaction of second order, this behavior has a strong frequency dependence of the laser used[20].

In addition, the 2D band can be used to estimate the number of graphene layers present in a sample. The shape of the 2D band single layer graphene is different from a multilayer sample.

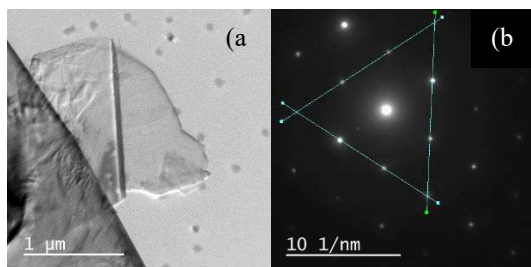


Figure 3. 231 sample of shear exfoliation. (a), TEM of the sample. (b),

diffraction pattern.

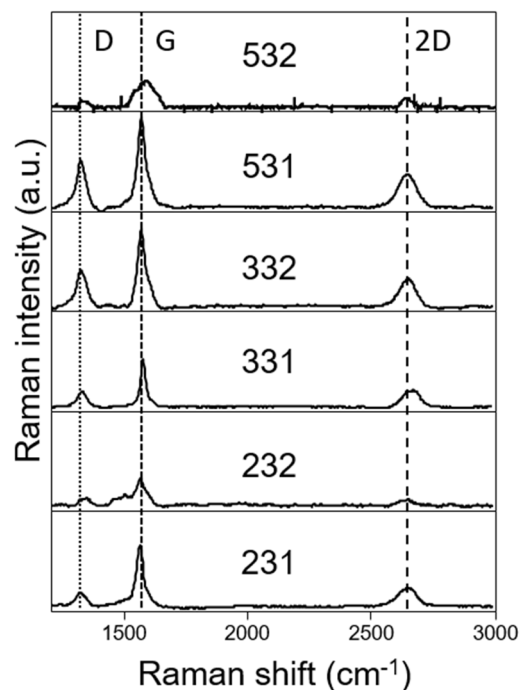


Figure 2. Raman spectroscopy of graphene obtained by different treatments of shear exfoliation.

In order to corroborate, the observed by Raman spectroscopy, HRTEM was used to compare. In Figure 3, the sample 231 shows four images of the graphene sheet at different magnification (left side), the area of the sheets is superior of the 1 μm<sup>2</sup>, and when analyzed the diffraction pattern for the same sample (right side), each line represents, as Hernandez et al suggested, that the brightness of the inner dots must be bigger than the outsiders. This are represented with the graphics below the diffraction pattern. If the inner picks are greater, then the graphene sheet most have one or two layers, like in this case.

On the other hand, the analyses for the sample with the higher quality for shear exfoliation according to the Raman spectra was 531. In the left side there are 4 images with different magnification. In image a) and b) there are graphene sheets with are equal to sonic bath, but in a) there is a roll of a sheet what could it be inferred as a carbon nanotube. Images c) and d) depict section of sheet with planes that were analyzed with a diffraction pattern. On the right side of figure 4, there are 3 graphics below the diffraction pattern that represent each of the lines crossing. In this case, the inner picks are shorter than the outsiders meaning that the graphene sheets are stacking with more of 5 layers.

In the sample 531 there is a stacking effect. The stacking effect is the superposition of sheets of graphene because of it is in suspension. There are two types of possible order of the stacking: the ABAB and the ABCAB.

The order of the layers modifies material properties as thermal or electric conductivity. The ABAB stack consists in the superposition of sheets of graphene in parallel. While, ABCAB arrangement consists in stacking sheets covering the vacancies of space, forming the graphite cluster[5].

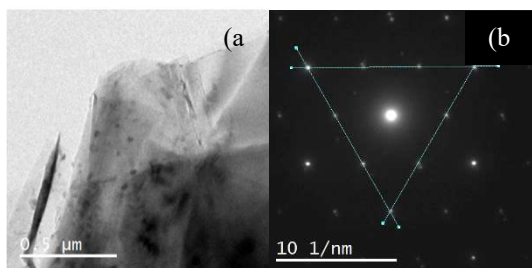


Figure 4. 531 sample of shear exfoliation. (a), TEM of the sample. (b), diffraction pattern.

The second form is weaker than the first and the properties are more like an insulator. According to Hernandez, after 10 layers the stack of carbon sheets is in an ABCABC form. This is the reason that after 10 layers of carbon the properties of graphene change into graphite.

#### IV. CONCLUSION

It has been demonstrated that graphite can be exfoliated to give few layers graphene using a simple methodology of rotating blade mixer reactor. Moreover, sophisticated surfactants as sodium cholate are not necessary to stabilize the exfoliated graphene, commercial detergent works extremely well. It has been found that, the concentration of exfoliated graphene increases linearly with time, resulting in a time independent production rate. In addition, concentrations of 1 mg/mL were achieved, it was higher with rotor–stator mixers than what can be achieved with sonication.

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