ROLE OF TRAPPED WATER IN THE MICROWAVE ASSISTED REDUCTION AND EXFOLIATION OF GRAPHENE OXIDE

EFECTO DEL AGUA ATRAPADA EN LA REDUCCIÓN Y EXFOLIACIÓN DE ÓXIDO DE GRAFENO ASISTIDAS POR MICROONDAS

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Abstract

Chemical methods to produce graphene involve strong oxidation of graphite and its subsequent exfoliation and reduction to obtain reduced graphene oxide (rGO). Recently, a novel method to produce rGO has been proposed, which consists on the exposure of GO to microwave irradiation. However, the mechanisms of reduction and exfoliation of GO by using this technique are not clear yet. In this work, the reduction and exfoliation of GO by using microwaves was analyzed with a focus on the water content that allows a successful process. For this, three samples of commercial GO were exposed to different atmospheric conditions and further irradiated in a commercial microwave oven. The samples were characterized before and after irradiation by using different microscopic and spectroscopic techniques. It was found that the water trapped in the samples is the key parameter for a successful reduction and exfoliation of GO by using microwaves. The reduction and exfoliation of GO were macroscopically visible as a significant volume change and color, as well as an increase in conductivity and further corroborated by spectroscopic techniques. For the conditions utilized in this work, the amount of water in GO samples required for a successful process was estimated as ~5 wt% of the sample.

Keywords: graphene oxide, reduction, exfoliation, microwave irradiation.

Resumen

Los métodos químicos para producir grafeno involucran una oxidación fuerte del grafito y su subsecuente exfoliación y reducción para obtener óxido de grafeno reducido (OGr). Recientemente se ha propuesto un nuevo método para producir OGr, el cual consiste en la exposición de OG a radiación de microondas. Sin embargo, los mecanismos de reducción y exfoliación de OG cuando se usa esta técnica aún no son claros. En este trabajo, la reducción y exfoliación de OG usando microondas fue analizada centrándose en el contenido de agua que permite un proceso exitoso. Para ello, tres muestras de OG comercial fueron expuestas a diferentes condiciones atmosféricas y además irradiadas en un horno de microondas comercial. Las muestras fueron caracterizadas antes y después de la irradiación usando diferentes técnicas microscópicas y espectroscópicas. Se encontró que el agua atrapada en las muestras es el parámetro clave para la reducción y exfoliación exitosa del OG usando microondas. La reducción y exfoliación del OG fueron visibles macroscópicamente como un cambio significativo de volumen y color, así como un incremento en la conductividad, y adicionalmente corroboradas por técnicas espectroscópicas. Para las condiciones usadas en este trabajo, la cantidad de agua intercalada entre las láminas de OG requerida para un proceso exitoso fue estimada en alrededor del 5 %p/p de la muestra.

Palabras clave: óxido de grafeno, reducción, exfoliación, irradiación de microondas.

1 Introduction

Graphene has become a promising nanomaterial that can be used in a range of applications, from electronic devices and high sensitivity biosensors due to its high electrical conductivity and transparency in thin films [Ray (2015); Brownson *et al*. (2014); Mathur *et al*. (2016); Mukhopadhyay *et al*. (2012); Sadasivuni *et al*. (2015), Kourentzi and Willson (2014)] up to as reinforcement in polymer nanocomposites due to its capability to withstand high stresses [Gong *et al*.

(2012); Potts *et al*. (2011); Kuilla *et al*. (2010); Zhen *et al*. (2010); El Achaby *et al*. (2013); Wang *et al*. (2011)].

Graphene can be obtained by several methods as chemical vapor deposition, epitaxial grown and chemical or electrochemical methods among others. Of particular interest has become the production of graphene by wet chemistry methods since they have the potential for massive production [Quintana *et al*. (2014)]. Overall, chemical methods to produce graphene involve strong oxidation of graphite and its subsequent exfoliation and reduction to obtain reduced graphene oxide (rGO). In most cases, however, successful applications rely on efficient reduction and exfoliation of GO, since the presence of oxygen functional groups in GO makes it hydrophilic with poor electronic properties. Hence, an efficient reduction process can make reduced GO a good electric conductor and change its character from hydrophilic to hydrophobic, which can make it, additionally, compatible and useful for reinforcement in non-polar polymers.

Different methods have been proposed to reduce GO whether via chemical routes or by annealing at high temperatures [Stankovich *et al*. (2007); Acik *et al*. (2011); Pei *et al*. (2012); Singh *et al*. (2016)]. Nevertheless, removal of oxygen functional groups during reduction is never complete and often results in the formation of defects in the graphene structure [Seung (2011); Acik *et al*. (2011); Pei *et al*. (2012); Singh *et al*. (2016)]. Very recently, Voiry *et al*. (2016) reported preparation of high-quality reduced graphene oxide (rGO) via microwave reduction of solution-exfoliated GO. The use of microwave irradiation in materials processing is a new area that has grown considerably in the last years and has been applied to different materials, including ceramics, composites, biomaterials and food among others [Ramos-Ramírez *et al*. (2015), Zarazua-Aguilar *et al*. (2017), Pérez-Grijalva *et al*. (2018)].

Voiry *et al*. (2016) started with a slight reduction of GO by thermal annealing followed by 1 to 2 s pulses in a 1000 W conventional microwave oven. The authors suggested that absorption of microwaves produced quick heating of the GO and desorption of oxygen functional groups. Different research groups had previously reported the use of microwaves for reduction and exfoliation of GO [Zhu *et al*. (2010); Pei *et al*. (2014); Yin *et al*. (2015); Han *et al*. (2015)]. In particular, Zhu *et al*. (2010) used a low-power microwave oven to obtain exfoliated and reduced graphene with few defects from GO powders by using less than one minute of microwave irradiation. The process of exfoliation was described by these authors as a large volume expansion accompanied by "violent fuming". Also, from thermal gravimetric analysis (TGA) measurements, Zhu *et al*. suggested substantial removal of water and oxygen containing groups in their rGO. Finally, these authors also reported the success of their procedure for reduction of GO in suspensions.

From the above mentioned references, it is clear that microwave irradiation is a promising and inexpensive method for reduction and exfoliation of graphene oxide in large scale applications. However, there is still an open question regarding the mechanism that makes this method of reduction and exfoliation of GO feasible, particularly when working with dry GO, which is a common commercial raw material whose shape includes, both powders and flakes. In order to answer this question, in this work we have carried out a study of the process of reduction and exfoliation of dry GO via microwave irradiation. We have characterized the GO as well as the rGO by using different techniques and we have found that the water content in the GO plays a key role in the process or reduction and exfoliation of GO, namely, a certain amount of absorbed water is necessary for this to occur efficiently, which has been estimated as ∼5 wt% of the starting GO. Details of the research are given below.

2 Materials and methods

Graphene oxide flakes (Graphene Supermarket) were utilized in this work. The morphology of the as received dry flakes consists of micrometric particles as shown in Fig. 1a. Figure 1b shows a scanning electron microscopy (SEM) image of dispersed GO, which exhibits laminates of several layers with some folds and lateral sizes of several micrometers.

The GO flakes were placed in a HERAtherm oven (ThermoScientific) at 60 °C for two hours in order to have a uniformly dried starting material. Then, three samples of this GO with different conditioning processes were prepared as explained next. The first two samples (GO1 and GO2) were conditioned at 0% and 100% relative humidity at room temperature for 40 hours in desiccators with silica gel and bi-distilled water, respectively. The weights of these samples before and after conditioning, respectively, were 0.9991 and 0.9866 g for GO1, and 0.9988 and 1.5612 g for GO2, which evidence a significant
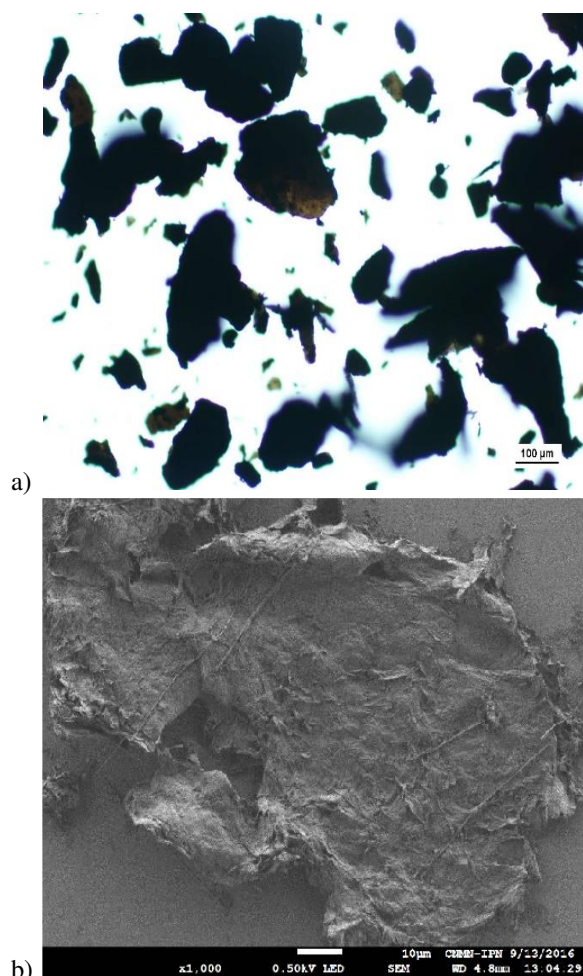
a)

b)

Fig. 1. a) Morphology of the as received GO as seen by optical microscopy. b) Laminates of GO as seen by SEM.

absorbance of water in sample GO2. Sample three (GO3) was dispersed in bi-distilled water (at a weight ratio of one part of GO per six parts of water) using an ultrasonic bath for one hour. Then, the sample was dried at 100 °C in the oven for two hours. Note that this procedure does not allow the evaluation of the water absorbed by GO3, but further information on the absorbed water may be gained from a thermal analysis of the samples. At this point, however, it should be clear that these conditioning processes allowed for obtaining different degrees of absorbed humidity in the samples. Thus, once conditioned, the three samples were subjected to TGA in a Simultaneous Thermal Analyzer (STA i 1000) with a heating rate of 10 °C/min in a temperature range from 40 to 800 °C with a N_2 atmosphere. Finally, 100 mg of each sample

were placed separately in Pyrex beakers covered by Petri plates and irradiated for two minutes at maximum power in a commercial microwave oven of 1000 W.

Following microwaves irradiation, the three samples were analyzed by Fourier transform infrared spectroscopy (FTIR, Frontier PerkinElmer), and only GO1 and GO3 by Raman spectroscopy (Horiba Jobin Yvon). The morphology and sizes of the reduced GO3 (rGO) were analyzed by using scanning electron microscopy (SEM, JSM 7800-JEOL). Finally, the degree of exfoliation was assessed by measurements of the specific surface area using the Brunauer-Emmett-Teller (BET) method (Quantachrome Instruments).

3 Results and discussion

3.1 TGA analysis

Figure 2 shows the results of the TGA analysis, presented as weight percent *versus* temperature, for the three samples of conditioned GO as well as for the microwave rGO. In the temperature range from 40 up to around 120 °C the three GO samples behaved in a similar way, namely, the rate of loss weight was the same in the three materials. The weight loss in this temperature range has been attributed to water evaporation [Zhu *et al.* (2010)]. Above this temperature range (between 120 and ~200 °C), the mass loss increases faster in a regime that has been ascribed to the loss of oxygen groups [Zhu *et al.* (2010)]. This temperature range, however, becomes wider for GO3 (see the insert in Fig. 2), suggesting that not all the water was removed in the previous temperature range. It can be seen from the insert in Fig. 2 that when the sharp weight loss occurs (in the neighborhood of 200 °C), the weight difference between samples GO1 and GO3 is 5.2%. Since the three samples contain the same amount of oxygen functional groups (it is the same raw material), this difference may be attributed to a larger amount of water trapped in GO3. Finally, beyond 200 °C and up to 500 °C the mass remains almost constant with the greater loss, presumably of water, occurring for GO2 and GO3, respectively. Lastly, the quick mass loss between 500 and 800 °C has been attributed by some authors to the pyrolysis of the carbon backbone [El Achaby *et al.* (2012); Wojtoniszak *et al.* (2012)]. Thus, from this analysis we can conclude that the largest amount of water after conditioning was trapped in GO3.
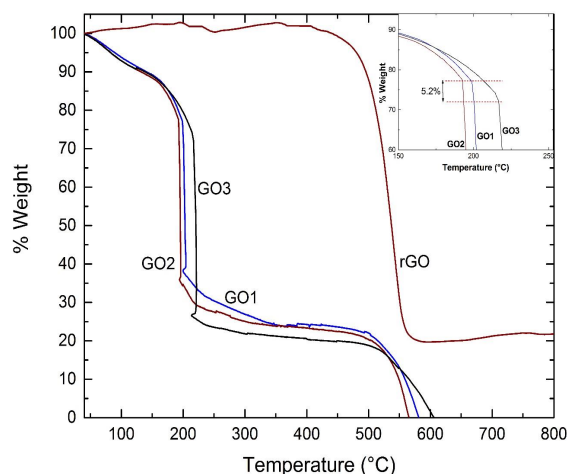
Fig. 2. Thermogravimetric analysis of GO samples and rGO.

Fig. 3. Snapshot of the oven during the reduction process of GO3. Note the ionization of the atmosphere as GO3 becomes conductive due to reduction.

The power of water retaining in the GO structure is related to the oxygen groups bounded at the basal plane, which have a strong polar character and allow water molecules to accommodate between the layers of GO, linked to oxygen groups via hydrogen bonding. This strong interaction between water and oxygen groups have been considered as an important contribution to maintain the stacked structure of GO [Dreyer *et al*. (2010); Mohan *et al*. (2015)]. Apparently, the different processes of conditioning of the samples in this work result in different degrees of absorbed water. While the difference in the retained water between GO1 and GO2 is evident from the conditioning process, it is not so for sample GO3. It seems that the dispersing process via sonication and further agglutination results in more trapped water, which as discussed below, helps in heating and exfoliating GO by microwave irradiation. An evaluation of the thermograms in Fig. 2 after the pronounced weight loss (at 300 °C), gives a weight difference of 5.07 % between GO1 and GO3, which as stated above may be attributed to excess water in GO3.

On the other hand, a sample of rGO was also subjected to TGA for the purpose of comparison and the corresponding results are included in Fig. 2. In this case, the mass remained almost constant in the temperature range from 40 to 400, suggesting that most of water molecules and oxygen groups were already removed during the reduction process. It should be noted, however, that some authors have reported some residual water molecules in rGO after a drying process [Mohan *et al*. (2015)].
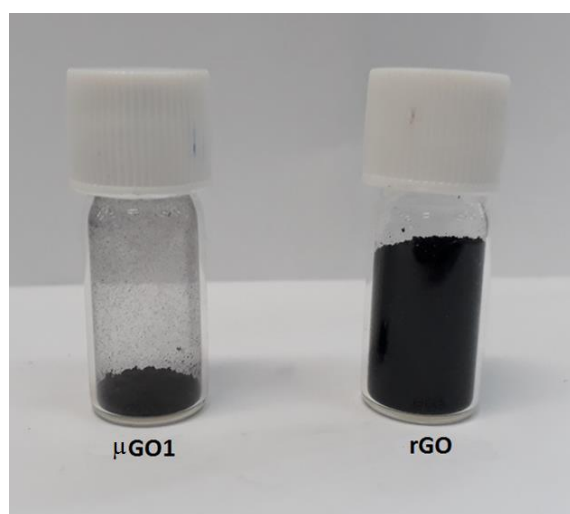

Fig. 4. Volume occupied by the same amount in weight of samples μGO1 (left) and rGO (right).

3.2 Process of microwave irradiation

Observation of the irradiation process as well as the morphology of the samples after this was completed led to significantly different findings in each case. First, while irradiation of GO1 and GO2 did not show any remarkable behavior, GO3 produced periodic ionization of the atmosphere inside the beaker, which arose from electrostatic charging of the atmosphere as the GO3 was reduced and became conductive; Figure 3 shows a snapshot of the oven during the process. It is noteworthy that for samples GO1 and GO2 the irradiation time was increased up to three minutes, but no changes in their behavior were observed. Also, even though it is not shown here, the particle size of the GO1 flakes was reduced by milling with mortar and hand and the same result was observed, namely, the sample was not reduced nor exfoliated.
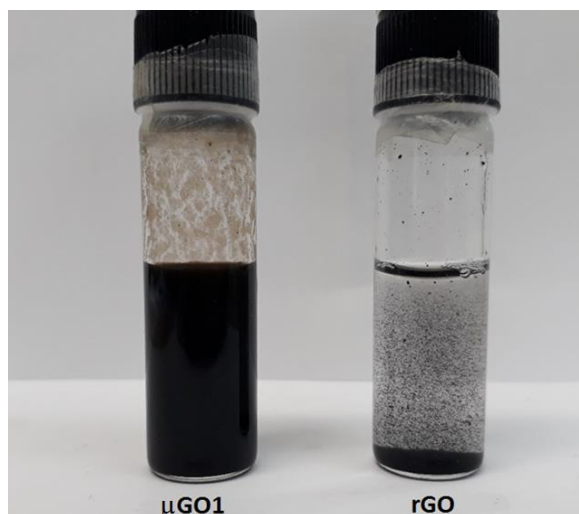
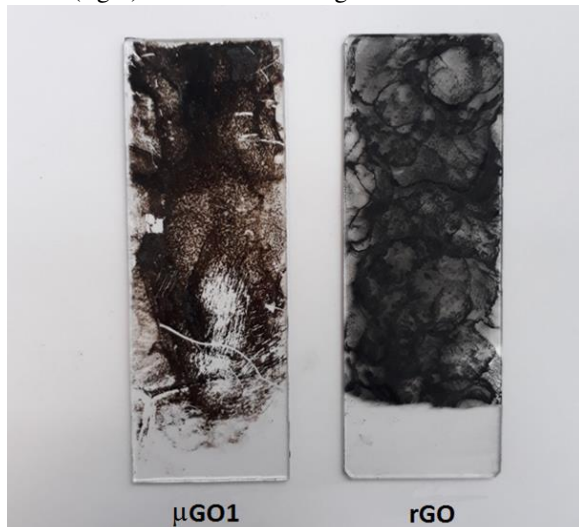Fig. 5. Alcohol dispersions of μGO1 (left) and rGO (right). Note the change in color in rGO.

Fig. 6. Dispersions of μGO1 (left) and rGO (right) painted into glass slides. Note the change in color of rGO.

On the other hand, there was a significant volume change in sample GO3 after irradiation (see Fig. 4) as compared to irradiated samples GO1 and GO2 (named from this point on as μGO1 and μGO2), which indicates a significant degree of exfoliation in rGO (see the BET analysis below). Also, μGO1 and rGO samples were suspended in ethanol and sonicated, as well as painted onto glass slides; the corresponding results are shown in Figs. 5 and 6, respectively. It can be observed from the photograph in Fig. 5, which was taken one day after sonication, that while μGO1 remained suspended due to its hydrophilic character, rGO exhibited aggregation and
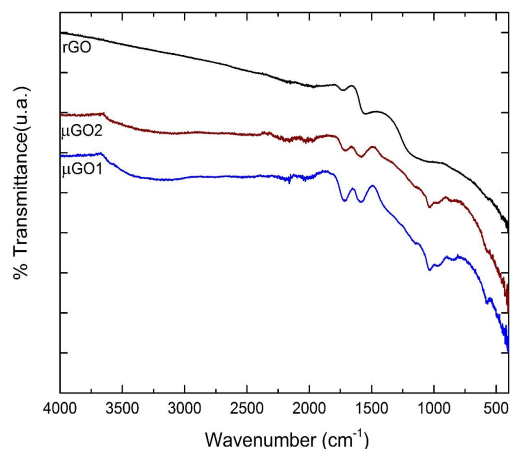

Fig. 7. FTIR analyses for three GO samples after irradiation with microwaves.

sedimentation [Stankovich *et al.* (2007); El Achaby *et al.* (2012)], a result consistent with a change to a hydrophobic character. Regarding to Fig. 6, a change in color occurred for the rGO sample as compared to the μGO1; i. e., while μGO1 appeared brown-like, rGO changed to black color, which is in agreement with the reported colors for GO and rGO, respectively [Stankovich *et al.* (2007); Zhu *et al.* (2010); Pei *et al.* (2012)].

3.3 FTIR and Raman spectroscopic analysis

The results from the FTIR analysis for the three irradiated samples are shown in Fig. 7. For μGO1 and μGO2, the wide band around 3300 cm^{-1} corresponds to the stretching deformation of the O-H bonds in water, carboxyl and alcohol groups. The peak at 1700 cm^{-1} pertains to the stretching of C=O bonds in carboxyl groups and the peak around 1613 cm^{-1} is due to the stretching of C=C bonds. There is a band around 1155 cm^{-1}, which is assigned to C-O bonds of the carboxyl acid and alcohol groups, meanwhile the band in 1040 cm^{-1} corresponds to the epoxide groups.

It may be observed from Fig. 7 that most of the peaks corresponding to oxygenated functional groups in μGO1 and μGO2 are absent in the rGO spectrum, which furnishes additional evidence of GO3 reduction. It should be noted, however, that some C=O peaks still remain; as reported by other authors [Acik *et al.* (2011); Pei *et al.* (2012)], a total reduction is never achieved and in most cases, a few oxygenated groups and defects remain, decreasing in this way the quality of the rGO.
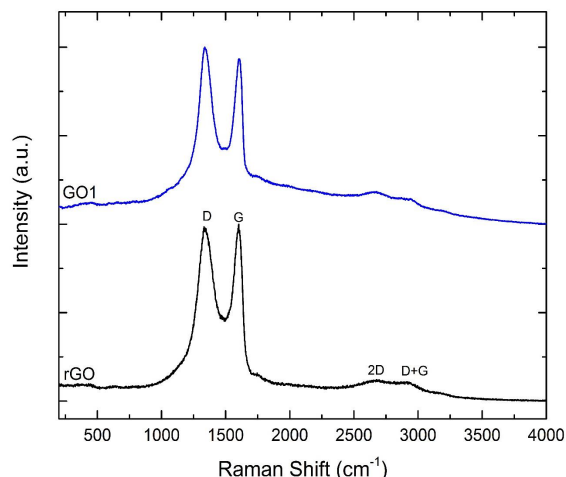
Fig. 8. Raman spectra for GO1 and rGO samples. Note the decrease in the I_D/I_G ratio in rGO, which gives indication of reduction of GO.

Separately, the corresponding Raman spectra for GO1 and rGO samples are shown in Fig. 8. It may be seen that there is an increase in the resonance of the G band in rGO with respect to the same band in GO1, as well as a relative increase in the intensity of the G band with respect to the D band in rGO, which provides further evidence of its reduction. The G band results from the stretching due to in plane vibration of sp^2 bounded carbon atoms [Pimenta *et al*. (2007); Cui *et al*. (2011); Perumbilavil *et al*. (2015)]. The fact that the G band increases in intensity in rGO as compared with that observed in GO1 is due to the increase in the number of sp^2 domains because of reduction. It can also be observed that the G band in rGO is shifted towards lower wavenumbers, which indicates a decrease of the oxygen groups, or equivalently, and increase of sp^2 carbon atoms [Perumbilavil *et al*. (2015)].

Regarding the D band, it is due to out of plane vibrations and is related to the presence of structural defects, vacancies and distortions, as well as to the size and number of sp^2 domains [Ferrari *et al*. (2006); Cui *et al*. (2011); Perumbilavil *et al*. (2015)]. Note in this case that the D band in rGO, even though it is reduced in intensity, does not disappear, as is the case for pristine graphene, which suggests that the irradiated rGO structure may show some disorder or the presence of defects. A measure of the defects in graphene structure may be obtained from ratio of intensities between the D (I_D) and G (I_G) bands, I_D/I_G. In this work, for the GO1 sample $I_D/I_G = 1.06$, meanwhile it was decreased for rGO to $I_D/I_G=0.988$,

which indicates the removal of a significant part of oxygen containing functional groups [Perumbilavil *et al*. (2015)].

3.4 Measurements of BET specific surface area

In the BET method the specific surface area of a sample is quantified by measuring the amount of gas (nitrogen) physisorbed at a surface. In this work, multi-point measurements were carried out for the GO1 and rGO samples, resulting in the specific surface area values of 4.216 m^2/g and 338.5 m^2/g, respectively. There was an increase in surface area of two orders of magnitude in rGO, which indicates a significant degree of exfoliation (see Fig. 4 as well as Fig. 9 below). This result is in agreement with the value reported by Zhu *et al*. (2010) of $\sim$ 463 m^2/g for microwave reduced and exfoliated graphene oxide, as well as with that of $\sim$ 320 m^2/g in graphene oxide reduced with hydrazine [Singh *et al*. (2011)]. It should be noted, however, that these surface area values are well below the theoretical value in pristine graphene of 2600 m^2/g [Singh *et al*. (2011)]; this may be due to agglomeration of graphene sheets and the fact that a complete exfoliation cannot be achieved by these means.

3.5 Influence of water on reduction and exfoliation of GO

It has been reported that the interlayer trapped gases and water play a key role in the exfoliation process during the thermal expansion of GO [Schniepp *et al*. (2006)]. Decomposition of oxygen functional groups is an exothermal process meanwhile water vaporization is an endothermal one. Then, it has been suggested that the presence of interlayered water is detrimental for the successful thermal exfoliation of GO. Nevertheless, the results in this work point to a different effect of trapped water for microwave assisted reduction and exfoliation of GO.

As it occurs in foods, microwave ovens heat water molecules in GO by making the polar molecules to oscillate at a specific frequency. The motion of the water molecules relative to each other creates frictional heating, which is used to vaporize water suddenly. This process explains the observation by Zhu *et al*. (2010) regarding a large volume expansion accompanied by "violent fuming". Thus, it is the presence of intercalated water in GO which allows quick heating and results in evaporation and
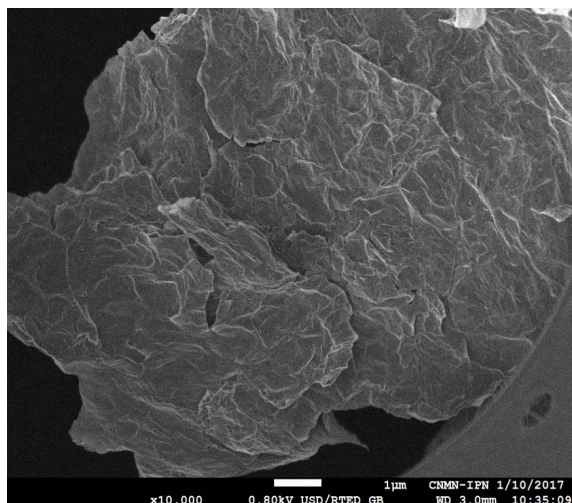
Fig. 9. Sheets of reduced and exfoliated GO3 (rGO) as seen by SEM.

volatilization of water and oxygen containing groups, accompanied by delamination (exfoliation) of the GO structure. From the TGA analysis, we have calculated that a 5 weight percent of water is enough to produce successful reduction and exfoliation.

Finally, even though it may be clear from this work the influence of water on successful reduction and exfoliation of GO using microwave irradiation, there are still some variables whose effect remains to be explored in order to have a deeper insight of the phenomenon, for instance, the limit of water content or the microwaves power. These are the subjects of ongoing work at our lab.

Conclusions

The reduction and exfoliation of GO by using microwave irradiation was analyzed in this work with a focus on the water content that allows a successful process. Three samples of commercial GO were exposed to different atmospheric conditions and further irradiated in a commercial microwave oven. The samples were characterized before and after irradiation by using different microscopic and spectroscopic techniques. From the results of this analysis it was possible to recognize that the water trapped in the samples is the key parameter that determine a successful reduction and exfoliation of GO by using microwaves. Only sample GO3, which was sonicated and dried prior to irradiation, resulted in successful reduction and exfoliation. The reduction

and exfoliation of GO were macroscopically visible as a significant volume change and color, as well as an increase in conductivity. Also, FTIR and Raman spectroscopy, as well as BET specific surface area measurements corroborated these findings. Finally, for the standard conditions utilized in this work, namely, power of the oven and irradiation time, the amount of intercalated water between GO layers required for a successful process was estimated as ~5 wt% of the sample.

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