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Mendez Romero, U., Velasco, M., Licea Jimenez, L. et al (2021). Long-term evolution of the chemical and structural stability of graphene oxide after storage as solid and as aqueous dispersion. Nano select, 2(11): 2168-2175.
<http://dx.doi.org/10.1002/nano.202000274>

N.B. When citing this work, cite the original published paper.

RESEARCH ARTICLE

Long-term evolution of the chemical and structural stability of graphene oxide after storage as solid and as aqueous dispersion

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Funding information

Mexican National Research Council CONACyT

Abstract

Nanomaterials are intended for industrial applications, for that purpose scalability needs to be addressed, therefore an important issue comes to the picture: storage. Graphene oxide (GO) is of great interest for practical applications in optoelectronics, chemical sensors, supercapacitor electrodes, among others. GO properties are related to its O/C ratio and its precise control allows fine tuning of properties such as conductivity, chemical reactivity and band gap. Nevertheless, GO has a critical storage restriction, due to its chemical self-reduction, that is, the oxygen loss not only alters its properties, but also promotes aggregation through time. In this work, the impact of storage conditions on GO properties was studied by comparing two systems: a solid sample and a liquid dispersion, which were analyzed during the course of 3 years. For this purpose, stability, O/C ratio and optical band-gap of the stored samples were analyzed through time by means of zeta potential, X-ray photoelectron spectroscopy (XPS) and UV-Vis. Results show the difference in stability between the samples due to oxygen loss in the GO structure, confirmed by XPS. Moreover, optical band-gap shows that the solid sample decreases its value around 64% compared to the liquid dispersion.

KEYWORDS

chemical properties, chemical self-reduction, graphene oxide, kinetics, metastable compounds, storage stability

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1 | INTRODUCTION

Nanotechnology is playing an important role in a wide range of applications and it will continue growing in the future, from everyday products to more complex purposes. Two of the most relevant research fields in nanotechnology are related to nanomaterials synthesis and production, where its immediate application in small-medium scale laboratories is a commonly used strategy. It means that frequently, the synthesized nanomaterials are used as produced and if more nanomaterials are required, a production of a second batch is prepared, minimizing any waste. However, on industrial scale, the latter is not feasible, as batches of nanomaterials are to be stored until further use, therefore, an important aspect during storage of these nanomaterials is the stability of their properties over the course of time.

Graphene oxide (GO) is an interesting nanomaterial, it is a highly oxidized graphene nanostructure, with a variety of oxygen functional groups such as hydroxyl, epoxy, carbonyl and carboxyl, produced from oxidation and exfoliation of graphite.^[1] GO has myriad applications, attributed to the fact that GO's properties can be tuned by modifying its oxygen content.^[2] As described in previous works,^[3] modifying GO oxidation degree and recovering sp^2 domains, allows the control of its optical,^[4] electrical^[5] and mechanical^[6] properties. Moreover, GO could be considered as a precursor for graphene-like structures through its chemical, thermal or photo reduction.^[7] Because all the promising GO properties, it could be highly desirable to be stored for indefinite time for later studies or use.

In this context, there are scarce reports that address the issue of GO chemical self-reduction over time that is, its metastability. Kim et al.^[8] studied the change of oxygen concentration in GO films over one hundred days under the presence of light and oxygen at ambient conditions. In short, the analysis reveals that solid GO should be kept under dark conditions. Also, Chua et al.^[9] stored GO powder for 30 weeks to study an approach to restrain its chemical modification in different conditions. It was found that darkness and inert atmosphere conditions were the preferred methods to maintain GO with a high O/C ratio. To preserve a high O/C ratio is important to achieve good dispersion of GO in water or other polar solvent, also to maintain the chemical groups for further functionalization.^[10] As previously mentioned, most of related works on the storage of GO, were done in samples stored in solid form. GO is produced through aqueous processes, such as Hummers method and commonly dried for further use. GO, is easier to handle as liquid dispersion, saving time, and energy to re-disperse the solid GO.

If a research group is working in the synthesis and control of GO's properties through oxygen content,^[2,10b,11]

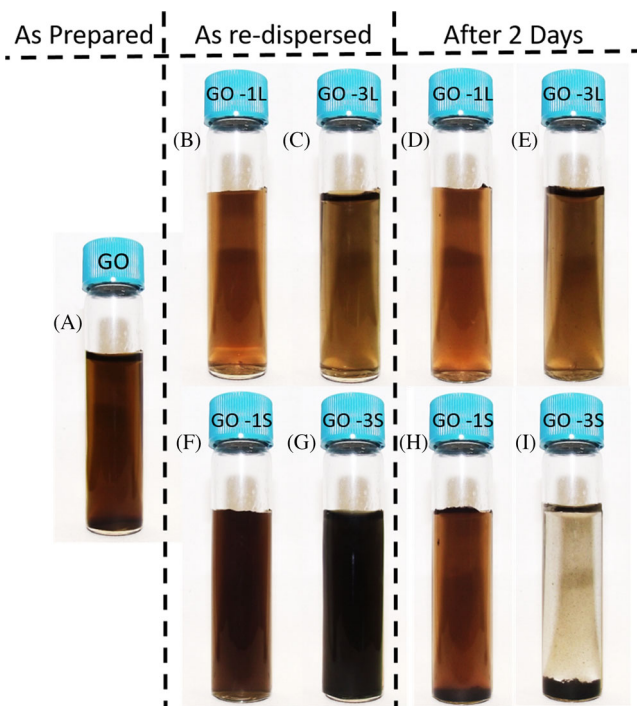


FIGURE 1 Digital picture of GO liquid stored water dispersions after sonication. A, GO as prepared. B, GO after stored 1 year in liquid and re-dispersed (GO-1L). C, GO after stored 3 years in liquid and re-dispersed (GO-3L). D, GO-1L 2 days after re-dispersed. E, GO-3L 2 days after re-dispersed. F, GO after stored 1 year in solid and re-dispersed (GO-1S). G, GO after stored 3 years in solid and re-dispersed (GO-3S). H, GO-1S 2 days after re-dispersed and (I) GO-3S 2 days after re-dispersed

always two questions arise: How long could be GO stored while maintaining its properties unmodified? And which is the best way (solid or liquid) to be stored? In the present work, an extensive assessment of how the GO oxidation degree changes when a sample is stored as a solid or as a liquid dispersion under darkness and room temperature is presented.

2 | RESULTS AND DISCUSSION

2.1 | Stability of GO samples

After storage, samples were observed, and visual results are presented in Figure 1. The initial pH of GO solution was 3. The as-prepared sample (no storage) in Figure 1A is presented as reference. At first glance, the liquid stored samples in Figures 1B-E presented the typical reddish color and the translucent dispersions remain stable, without visible aggregation and precipitation, even after 3 years. In the case of solid stored samples, Figure 1F and 1G, black dispersions were observed, suggesting that a

reduction process occurred. However, for Figures 1H,I) a notorious agglomeration and precipitation can be seen. Moreover, the solid stored sample for 3 years Figure 1G) (GO-3S) begins to precipitate just after 10 minutes from sonication. After 2 days, it is completely precipitated (Figure 1I), showing the classical behavior of a reduced GO in water dispersion.^[12] For Figures 1F,H) (GO-1S), an enhanced stability (compared to GO-3S) was observed, only a small fraction of solid was noticed at the bottom of the vial. The effect of precipitation can be explained as a consequence of chemical reduction, where sp^2 domains originate attractions through van der Waals forces, leading to the precipitation of GO after 1 and 3 years when stored as solid. Thus, better stability through time is shown when samples are stored in liquid form.

Zeta potential indirectly measure the charges around the particles or molecules, the technique provides information about the loss of oxygen functional groups which contribute to repulsion forces. As previously stated, GO is commonly described as a large molecule containing hydroxyl, carbonyl, carboxylic and epoxy groups. Highly oxidized GO means more quantity of such groups, which are responsible for the stabilization and repulsion of the GO layers. Reduced GO means less functional oxygen groups, less repulsion, and higher van der Waals attraction forces overcoming the repulsive forces; this is in accordance with Figure 1, where aggregation and precipitation are present for the solid stored samples, but not for the liquid stored ones. Zeta potential measurements were carried out just after samples were sonicated.

The starting material (GO) show a high stability of |54| mV, the GO-1L sample resulted on |39.8| mV and GO-3L finalized on |32.3| mV; while GO-1S sample resulted on |35.7| mV and finally GO-3S on |29.1| mV. From both series, it can be seen that the solid stored samples show a tendency to rapidly reduce its zeta potential in comparison to the liquid stored samples, becoming less stable in water, and leading to aggregation and precipitation.

2.2 | XPS analysis

In order to understand if the loss of oxygen functional groups was the cause of the aggregation during storage, X-ray photoelectron spectroscopy (XPS) analysis was performed. The binding energy for electrons associated to C-C (284.7 eV), C-O (286.9 eV) and C = O (288.5 eV) bonding were recorded, and herein used for the analysis. Oxidation degree for the different GO samples are presented in Figure 2, it can be seen that signals at 286.9 and 288.5 eV for the liquid stored sample, slowly decrease but remains constant after three years, contrary to the solid stored sample, which in the first year shows a decreased

TABLE 1 Functional group percentages for liquid stored and solid stored GOs

Liquid			
Sample	C-C (%)	C-OH (%)	C = O (%)
GO	37.26	48.99	13.74
GO-1L	39.05	46.36	14.57
GO-3L	43.19	46.28	10.52
Solid			
Sample	C-C (%)	C-OH (%)	C = O (%)
GO	37.26	48.99	13.74
GO-1S	48.01	44.15	7.83
GO-3S	54.38	39.59	6.01

area, suggesting a faster reduction in solid stored samples. Normalization was applied for all samples, remaining a constant value at 284.7 eV binding energy related to C-C bonding, in order to compare the intensity of the 286.9 eV signal related to C-O from alkoxy and epoxy functional groups. Table 1 shows the percentages of each functional group, for liquid samples minor changes are observed for the C-OH groups (2.71%), as well as an increase (6%) for the C-C groups. Solid stored samples show a decrease in both the C-OH (9%) and in C = O (7.7%) groups, and an increase (17%) in C-C groups; implying that liquid stored samples have lost less oxygen than solid stored samples.

The oxidation degree in the samples, was calculated from Equation 1, related to the oxygen fraction area of carbon as described elsewhere.^[13]

$$R_{O/C} = \frac{A_{C-O} + A_{C=O}}{A_{C-C} + A_{C=O} + A_{C-O}} \quad (1)$$

Where A_{C-O} stands for the area of the signal related to C-O bonding at 286.9 eV, $A_{C=O}$ the area of the signal related to C = O bonding at 288.5 eV, and A_{C-C} is the area of the signal at 284.7 eV and $R_{O/C}$ is the ratio of areas of oxygen functionalities by only carbon bonding, or the signals at 286.9 and 288.5 eV.

For GO, GO-1L, GO-3L, GO-1S, and GO-3S values of $R_{O/C}$ were obtained and displayed in Figure 3, where it results evident that the major decrease in O/C ratio, corresponds to the solid samples. The O/C retention, in the case of solid stored has a dramatic drop of its values being 64% and 49% for GO-1S and GO-3S, respectively, while for liquid stored, GO-1L slightly drops the O/C ratio retention from 93% to 78% for GO-3L.

In previous works dealing with mechanisms of the thermal reduction of GO^[13,14] and first-principles calculations by Eigler,^[15] have shown that GO tends to decompose into CO_2 and water, mostly proceeding from the carbonyl groups with preference at the edges of GO, at low temperatures around 50°C.

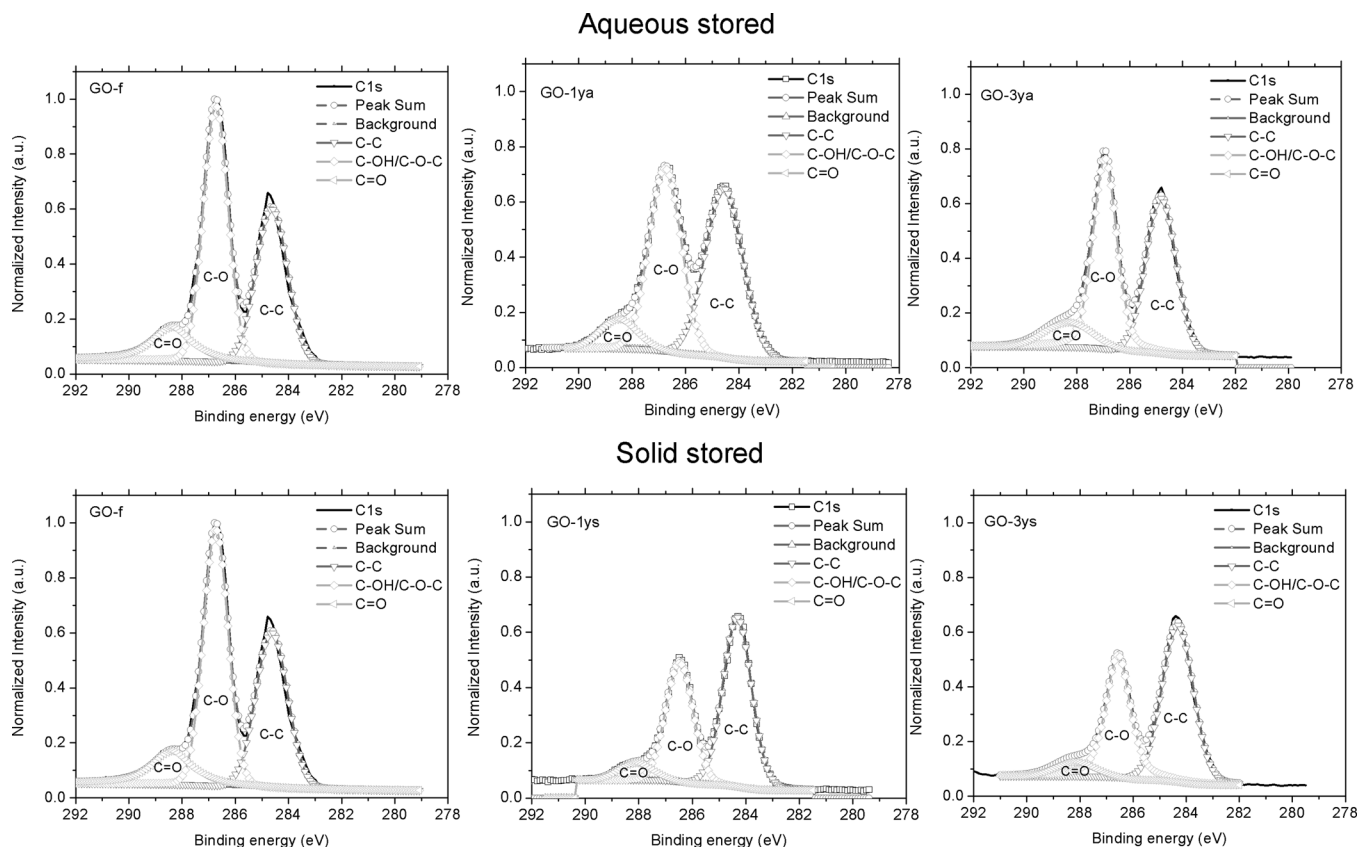


FIGURE 2 Evaluation of oxidation degree in GOs stored as dispersion and solid by high resolution XPS C1s

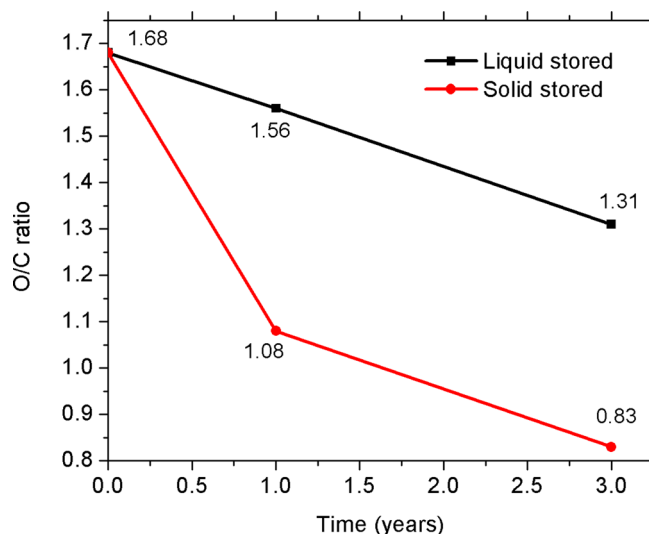


FIGURE 3 Plot of the O/C ratio for liquid stored GO and solid stored GO obtained from high resolution XPS C1s

Also, Ghaderi^[14] showed in his theoretical study that the presence of water can turn epoxy groups to hydroxyl groups on GO. Furthermore, Larciprete^[16] suggested that one of the decomposition mechanisms for epoxides in GO exposed to 27°C, would be that two epoxide groups

will combine to form molecular oxygen. This mechanism would apply in the solid stored GO but at a slower rate, the signal at 286.9 eV diminishes through time while losing the C-O groups.

So, according to Figure 3, when GO is stored in liquid solution, reduction goes slower compared to solid stored samples. In the first-year, solid samples reduce faster; this could be attributed to the reaction among epoxides with the release of oxygen as suggested by Larciprete. But in the liquid stored samples, Eigler mechanism would play a greater role through carbonyl reduction, and Ghaderi proposed mechanism would turn epoxide to hydroxyl groups without further change in the liquid stored sample.

The results indicate that, the samples stored in solid form for 3 years, contains less oxygen atoms and a 50% reduction in the O/C ratio. On the other hand, in samples stored in liquid solution, the O/C ratio decreases linearly with storage time, suggesting that only one type of functional group has decreased, carbonyl, through the mechanism proposed by Eigler, and again, Ghaderi mechanism would hinder the oxygen loss through the conversion of epoxide to hydroxyl groups in the presence of water. In solid form, carbonyl groups could decompose to CO₂, and epoxy groups could react through Larciprete mechanism.

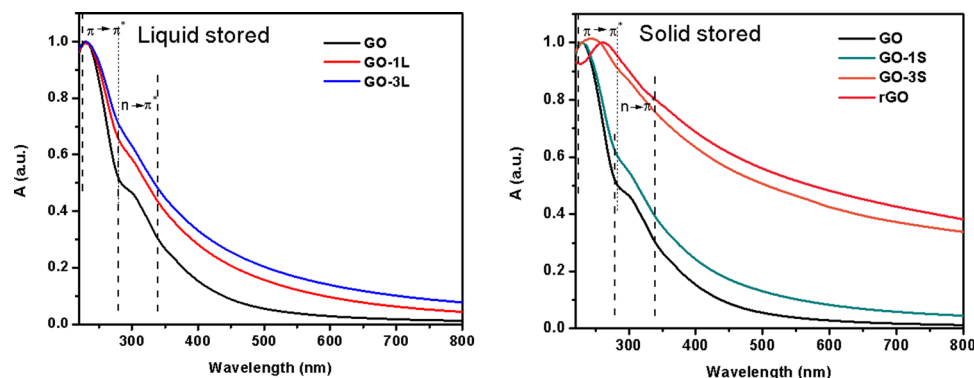


FIGURE 4 Absorption spectra for liquid stored GO and solid stored GO

In summary, liquid stored samples of GO, would be affected mainly by Ghaderi mechanism by hindering the reduction of epoxy groups. In solid stored samples, Larciprete and Eigler mechanisms, would explain the reduction observed in this work. The results shown by XPS are in accordance with theoretical calculations and high temperature reduction processes predicted by previous authors and confirmed in this experimental study.

2.3 | Optical properties between liquid stored and solid stored

In this work, the XPS study in Figure 2 show that storage of GO in liquid dispersion circumvent the loss of oxygen content much better than in GO stored as solid powder. Also, it is well known that the optical properties in GO depend on the oxidation level and can be monitored by UV-Vis absorption spectra. Figure 4 shows the UV-Vis absorption for liquid stored GO (left) and for solid stored GO (right). The as-prepared GO sample, shows an absorption spectrum with two characteristic bands, the strongest at around 230 nm, associated to $\pi \rightarrow \pi^*$ transitions of aromatic C C rings, and a shoulder at around 300 nm, which is attributed to $n \rightarrow \pi^*$ transition of the C = O carbonyl groups. Regardless of how the samples were stored, it is observed that in all samples, longer storages times result in an increase in the absorption intensity in whole spectral range, however the increase is larger in GO stored in solid form. It can also be seen that the shoulder at 300 nm becomes less visible for longer storage times, especially for samples stored in solid form. Thus, an increment in overall intensity, as well as a lower intensity of the shoulder at 300 nm, indicate an increase of C-C bonding, in agreement with the XPS results. For comparison, the absorption spectrum for a fully reduced GO sample (rGO)^[2,10b] was added to the figure on the right. Briefly, rGO was prepared using 1 mg ml⁻¹ GO dispersion and mixed with an equal volume of a 20 mg ml⁻¹ fructose/NH₄OH solution (pH 10)

for 6 days, as previously reported.^[2] As can be seen, it is quite similar to that of GO-3S sample, indicating similar degrees of reduction.^[16,17]

Figure 5 shows the indirect optical band gap (E_g) for all samples as calculated from the Tauc plot. The E_g values were 3 eV for the GO sample and 2.69 and 2.42 eV for the samples stored for 1 year in liquid dispersion and solid forms, respectively. In samples stored for 3 years, the E_g was 2.34 and 0.85 eV, for samples in liquid dispersion and in solid, respectively. The fully reduced GO (rGO), present an E_g of 0.5 eV. These changes in E_g also reflect the oxidation level, lower optical band gap corresponds to lower oxygen contents. These results suggest that the storage medium and/or storage time could be a way of fine-tuning the optical band of GO.

Also, based on the UV-Vis results, it is possible to confirm the similarities between solid stored sample to rGO or graphene, due to its strong photon coupling with the electrons as seen in the fine constant absorption behavior.^[18] Then, XPS results in addition to UV-Vis absorption and Tauc plots showing a band gap evolution for the solid samples and minor changes in the band gap for liquid stored, confirm that storing GO as aqueous dispersions has advantages in preserving optical and chemical properties of GO.

2.4 | The effect of oxygen content on morphology of GO

For the morphological study, the oldest samples (GO-3L and GO-3S) were analyzed. The STEM results are shown in Figure 6A,B. In both cases, the micrographs show large electron transmission, suggesting that the samples are composed of few layer stacks. In addition, flat surfaces are observed in GO-3L samples, while GO-3S presents a surface with wrinkles and bends mostly at the edges. It was previously investigated that the asymmetry of bond-lengths in graphene is amplified on the edges and near defects, thus increasing the ripples density in these

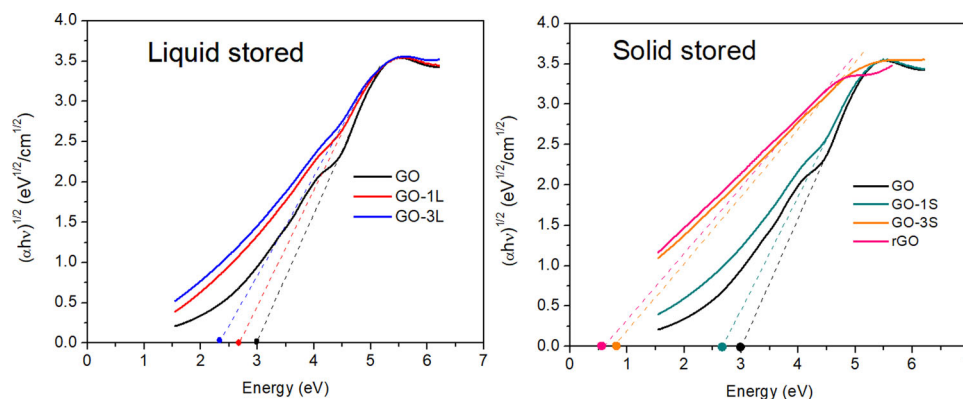


FIGURE 5 Tauc plots of liquid and solid stored GO

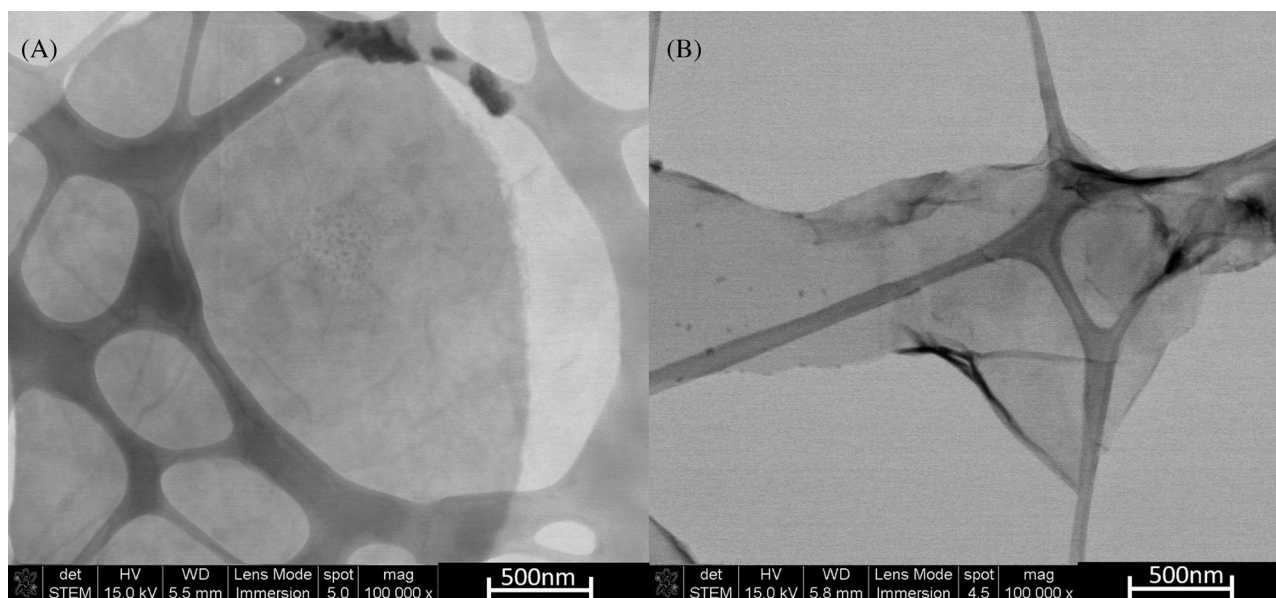


FIGURE 6 STEM micrographs of (A) GO-3L and (B) GO-3S

regions,^[17] it would mean that the GO-3S morphology is closer to graphene than GO.

Based on all the results, we can point out that GO must be stored in a proper way depending on the application. In the case of electronic, optical or other application where preservation of the chemical integrity and properties are desired, then the use of liquid dispersions is recommended. Usually dried GO is maintained and preserved via vacuum desiccators in laboratory scale, and it has been reported by Shen^[19] that even vacuum at room temperature has more detrimental effects on GO oxygen content, than having it at room temperature exposing to air. Moreover, for industrial applications and processing, the best way to store GO samples would be in the form of liquid dispersions, but at higher concentrations, requiring further studies for such conditions. On the other hand, storing GO as solid samples for longer periods of time can have a drawback in the

properties of the material and therefore of the performance in the final application.

3 | CONCLUSION

It was evident that different properties of the GO can change unintentionally depending on the storage procedure. It was found from zeta potential measurements that GO maintains a considered stable potential of around 35 mV after 3 years of storage as a liquid dispersion. The said stability is related to the oxygen content, being 1.31 O/C found by XPS. Also, the optical properties became drastically modified when GO is stored as solid, starting from a fresh GO with an indirect band gap of 3.0 eV and finishing with a 1.1 eV. In this regard, if GO will be used for optical applications, liquid storage is the best way

especially if used after one year, since the O/C ratio difference is only 7%. Thus, the water hinders the oxygen loss, which could be related to kinetic parameters and the delay of the reaction for the epoxy groups, explained by the proposed mechanism. With this in consideration, the most proper way to store GO for long periods of time, is by storing it as liquid dispersion, instead of solid or powder and setting the limit as one year.

4 | EXPERIMENTAL SECTION

4.1 | Materials

Graphite nanoplatelets from Superior graphite Co were used. KMnO_4 , H_2SO_4 , and KNO_3 , HCl were purchased from CTR scientific. All the chemicals were used as received.

4.2 | Graphene oxide synthesis

GO was prepared via a modified Hummers method as reported elsewhere.^[2] Briefly, 0.5 g of graphite nanoplatelets were oxidized in 30 mL of H_2SO_4 and 0.295 g of KNO_3 with 3 g of KMnO_4 to achieve formation of Mn_2O_7 complex. The reaction was carried out for 6 hours, stirring the solution at 450 rpm controlling the temperature below 15°C . The reaction was quenched with 100 mL of DI H_2O and 6 mL of H_2O_2 30%. Next, the obtained bright yellow dispersion (graphite oxide) was centrifuged at 3500 rpm for 10 minutes to remove the supernatant and 100 mL of HCl 10% were added to the precipitate and centrifuged under the same conditions. The washing process was repeated 3 times with DI H_2O . Afterwards, 80 mL of DI H_2O were added, and the dispersion was placed in the ultrasonic bath for 1 hour for exfoliation. Finally, the supernatant in water dispersion was recovered, stored and labeled as GO.

4.3 | Storage of GO as solid

Two aliquots of GO were adjusted to 6 mg mL^{-1} , then transferred into two beakers followed by dry filtering at 25°C for 48 hours with the aid of Whatman $0.2\mu\text{m}$ PTFE vacuum membranes. It is important to mention that in these conditions, thermal reduction is negligible.^[15,20] At the top of the membrane a reddish-orange GO solid could be peeled off. Samples were stored in sealed petri dishes for two different periods: one year (sample labeled as GO-1S) and three years (sample labeled as GO-3S). The storage conditions were at room temperature, darkness and ambient pressure.

4.4 | Storage of GO as liquid dispersion

In order to study the effect of liquid storage, GO aqueous dispersion was adjusted to 6 mg mL^{-1} and stored in two different vials in darkness, ambient temperature and ambient pressure as standard conditions. GO liquid samples were stored and analyzed after one year (labeled as GO-1L) and three years (labeled as GO-3L).

4.5 | Preparation of GO dispersions after storage

In order to characterize the effect of storage after one and three years, GO samples were re-dispersed by sonication in an ultrasonic bath VWR Model 97043–944, at 180W and 35 kHz for 5 minutes in water at 25°C with a concentration of 1 mg mL^{-1} . These new dispersions were stored two days for visual stability observations.

4.6 | Characterization

Stability analysis for all samples were carried out by zeta potential in a Malvern Zetasizer Nano S. High-resolution XPS measurements were done to determine the oxygen content of the samples using a Thermo Scientific Escalab 250Xi instrument. The base pressure during the analysis was $\sim 10^{-10}$ mbar and the photoelectrons were generated with the $\text{AlK}\alpha$ (1486.68 eV) X-ray source, using a monochromator, and a spot size of $650\mu\text{m}$. The X-ray voltage and power were 14 kV and 350 W, respectively. The acquisition conditions for the high-resolution spectra were 20 eV pass energy, 45° take-off angle and 0.1 eV/step. Selected regions spectra were recorded, covering the C1s and O1s photoelectron peaks. Results were fitted using a Gaussian-Lorentzian function and a Shirley background subtraction. The recorded photoelectron peaks were curve-fitted using the Advantage software V 5.41. Samples for XPS were prepared as follows: for aqueous dispersion five drops of dispersion were deposited onto copper tape and left to dry at room temperature in a vacuum desiccator; for solid samples, the solid was pulverized using mortar and pestle until acquiring fine powder.

Optical characterization was done in a Varian Cary 5000 UV-Vis-NIR spectrophotometer, in order to analyze the absorption spectra of GO dispersions and to determine the optical band gap (E_g) of each sample. E_g was calculated by Tauc plot analysis from UV-Vis absorption spectra assuming an indirect band gap, as described in a previous work.^[2] Here, wavelengths of 200 to 800 nm were used with a step of 0.1 nm. Morphological characterization was carried out by Scanning Electron Microscopy with a FEI

Nova NanoSem200 in Scanning Transmission Electron Microscopy (STEM) mode, samples for microscopy were prepared using sonication in an ultrasonic bath VWR Model 97043-944, 180W, and 35 kHz for 5 minutes of 0.1 mg mL⁻¹ GO dispersions, then a drop was deposited on a copper mesh grid.

ACKNOWLEDGMENTS

Authors are thankful for the technical support and facilities at CIMAV Monterrey and the Mexican National Research Council CONACyT for the scholarship. We also would like to thank Lilia Bautista for UV-VIS spectra and zeta potential, Geraldo Silva for XPS, and Nayeli Pineda for STEM micrographs.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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How to cite this article: U. A. Méndez-Romero, M. A. Velasco-Soto, L. Licea-Jiménez, J. González-Hernández, S. A. Pérez-García, Long-term evolution of the chemical and structural stability of graphene oxide after storage as solid and as aqueous dispersion. *Nano Select* **2021**, 2, 2168. <https://doi.org/10.1002/nano.202000274>