

# 3D GRAPHENE OXIDE AEROGELS BY SUPERCRITICAL CO<sub>2</sub>

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## ABSTRACT

In this work, three-dimensional graphene oxide (GO) aerogels are prepared by supercritical CO<sub>2</sub> (scCO<sub>2</sub>) technology. The adoption of scCO<sub>2</sub> in this study prevents the usage of toxic substances or more complex procedures as previously seen in the literature. We use solid state techniques to characterize the monolith samples, obtaining high values in the surface area, CO<sub>2</sub> adsorption and pore volume. We also demonstrate the control on the graphene aerogels nature, with a tuneable degree of oxidation meaning a wide range of potential applications, such as water and air purification, battery and supercapacitor improvements or even biological applications.

## INTRODUCTION

Graphene oxide (GO) combines the textural advantages of graphene with convenient hydrophilicity and fascinating surface chemistry. The presence of functional groups enables the exfoliation of GO sheets in polar liquids, leading to stable colloidal dispersions. One current challenge is to achieve the drying of GO dispersions, while keeping exfoliation and oxygenated functionalities in order to translate the key properties of individual GO building blocks into macroscopic architectures. Common drying techniques, such as air and vacuum drying, induce re-stacking of the flakes, giving powders with low surface area values. The alternative is to create rigid three-dimensional (3D) structures in the form of xerogels and aerogels. The preparation of these architectures requires the formation of a transitional gel, being the most used procedure the reductive self-assembly of water dispersed GO sheets under hydrothermal conditions. Direct gelling is also possible upon acidification and sonication, but only in systems involving high concentrations of GO and sheets with large lateral dimensions [1]. Different drying paths for the gel have been designed to avoid the collapse of the pore structure, such as freeze-drying/lyophilization, and drying in the critical point. Lyophilization is used to dry hydrogels in which frozen water is removed by sublimation under vacuum. Critical point drying techniques are used to dry alcogels by forming a supercritical fluid before solvent (short C-chain alcohol) elimination through isothermal depressurization. Drying in the critical point is the best technique to minimize the shrinkage of the alcogel. However, these procedures require high critical temperatures (>250 °C), being alcohols dangerously flammable at these conditions.

Although several techniques have been proved to successfully produce high surface area GO aerogels [2], a method integrating the advantages of efficiency, environmental friendly, safety and low-cost together is still being pursued. For GO aerogels, supercritical fluid technology has mainly been applied at the critical point of ethanol [3]. Few reports describe the supercritical carbon dioxide (scCO<sub>2</sub>) drying of pre-formed hydrothermal GO alcogels. Aside from the inherent energetic disadvantages of hydrothermal and ethanol critical point drying methods, both techniques remove the vast majority of oxygen-containing functional groups in GO sheets giving products with a high degree of reduction (rGO). The method developed in this work is devoted to the formulation of GO aerogels directly from GO dispersions using exclusively low temperature scCO<sub>2</sub> technology, avoiding the use of any cross-linking agent. The low-temperature supercritical drying process has been previously applied to the drying of pre-formed inorganic -silica- and organic -carbon- alcogels [4]. Sol-gel gelling induced by compressed CO<sub>2</sub> is only described for highly reactive inorganic monomers, such as silsesquioxanes [5], and some biopolymers [6]. Examples of gelation by self-assembly of anisotropic sheets induced by scCO<sub>2</sub> addition have not been found in the literature.

## MATERIALS

GO sheets were purchased from Graphenea Inc., supplied as a dispersion in water of 4 mgmL<sup>-1</sup>. Compressed CO<sub>2</sub> (99.95 wt %) was supplied by Carbueros Metálicos S.A., and analytical grade ethanol (EtOH) was obtained from Panreac.

## EQUIPMENT AND METHODS

Before supercritical treatment, water in the commercial GO dispersion was first exchanged by ethanol, with a concentration of *ca.* 3 mgmL<sup>-1</sup>. Aerogel monoliths were prepared in small assay tubes of 2 mL loaded with 1 mL of ethanol dispersion. The supercritical standard preparation of GO monoliths was carried out in a non-stirred and sealed reactor, kept at 60 °C and 200 bar of CO<sub>2</sub>, during 2 days and using GO sheets of *ca.* 30 μm lateral dimensions.

## RESULTS

### Gelling and drying mechanism

Processed aerogel were synthesized starting from commercial colloidal suspensions of GO in water.

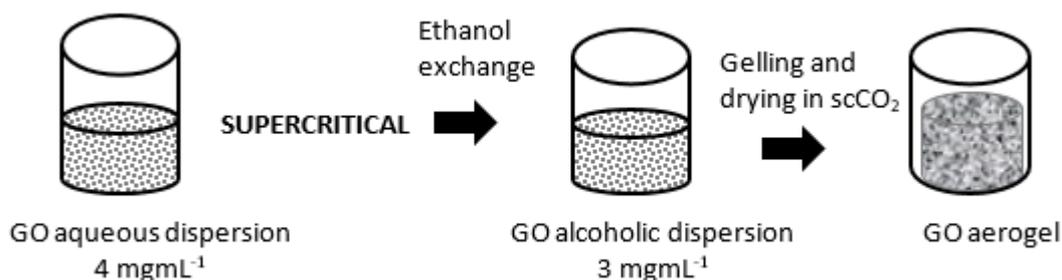


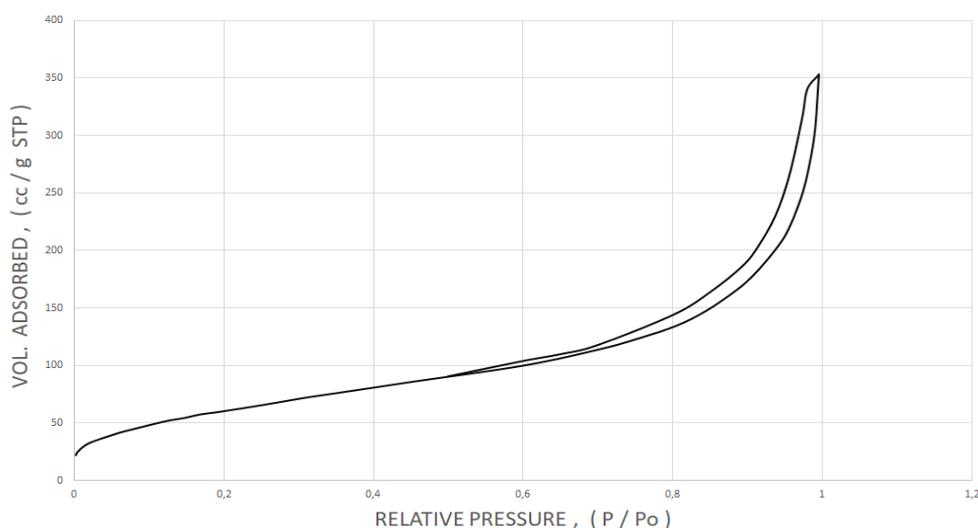
Figure 1. Schematic representation of the main synthetic steps employed in the supercritical (scCO<sub>2</sub>) tested technique.

Figure 1 schematically shows the main steps involved in the procedure. In the supercritical procedure, due to the miscibility gap in the CO<sub>2</sub>/water system, a previous step consisting in water exchange to an organic solvent miscible with scCO<sub>2</sub> was required. EtOH was chosen for this purpose. At room temperature, treatment with EtOH, also seems to produce a noticeable reduction of GO sheets.

XPS of the obtained monolith at 60 °C indicates that the use of the low temperature scCO<sub>2</sub> technology for foaming and drying did not caused any significant reduction in the structure of GO. The measured ratio O/C was of 0.48, similar to that obtained for GO in the alcoholic colloidal dispersion (0.47). Quantified substantial conversion of GO to rGO in scCO<sub>2</sub> has been observed a temperatures between 200-300 °C [7].

### Textural and adsorption properties

The supercritically prepared monoliths have a weight of *ca.* 3.3-3.5 mg, which is slightly higher than the initially added GO weight to the vial (*ca.* 3 mg). However, this value is reduced to *ca.* 2.5-2.8 mg after sample evacuation under vacuum at 120 °C. This weight loss is assigned to residual ethanol solvent and adsorbed CO<sub>2</sub> during synthesis. Using the evacuated samples, the density of the monoliths ( $\rho_m$ ) was calculated as the weight of the cylinder after evacuation divided by the geometrical cylinder volume. For the supercritically dried samples, this value is *ca.*  $7-9 \cdot 10^{-3} \text{ gcm}^{-3}$ . Density values measured for the scCO<sub>2</sub> aerogels are close to those of air.



Evacuated monoliths were used to acquire surface area values (Fig. 2). Foamed GO samples exhibited type IV isotherms according to the IUPAC classification, characteristic of mesoporous materials. Isotherms have an H3-type hysteresis loop related to slit-shaped pores or aggregates of plate-like particles, the latter of which is representative of the studied GO system. In this work the BET equation was used only to estimate the surface area ( $S_a$ ) values in the relative pressure range  $P/P_0$  of 0.01-0.10. These values were of 207 and  $226 \text{ m}^2\text{g}^{-1}$  for samples obtained at 60 and 90 °C, respectively. The pore volume ( $V_p$ )

Figure 2. N<sub>2</sub> adsorption and desorption isotherm, with IUPAC type IV-H3 structure

was roughly estimated by subtracting from the cylinder geometrical volume the volume occupied by the graphene sheets (graphene weight/graphene density reported as  $1.06 \text{ g cm}^{-3}$ ) [8]. This calculation leads to empty volume specific values of  $0.64 \text{ cm}^3 \text{ g}^{-1}$  for the supercritically dried samples.

### Microstructure

Details of the microstructure of the graphene-based aerogels were revealed by SEM. Samples obtained following the supercritical standard procedure showed a sponge-like porous structure of multiple exfoliated GO sheets (Fig. 3).

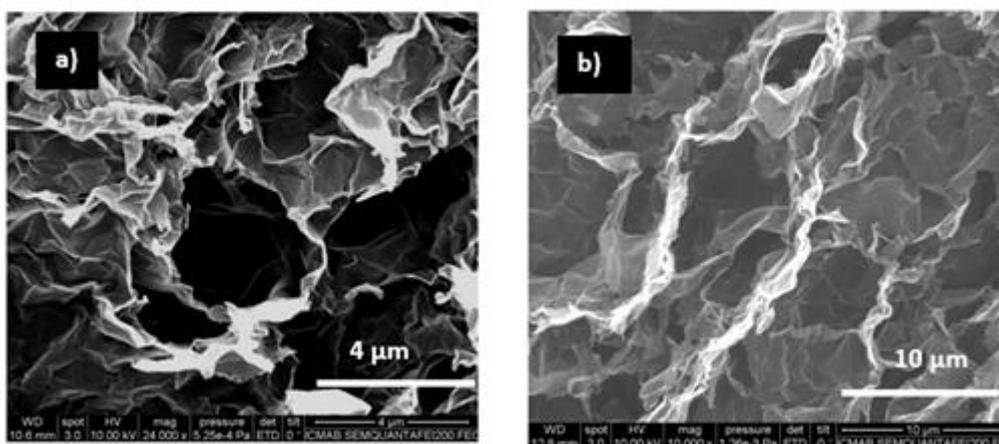


Figure 3. SEM images of monoliths obtained at 60

The aerogels were compressible and elastic to some extent. A simple test was performed in the solids obtained at 60 °C (Fig. 4).

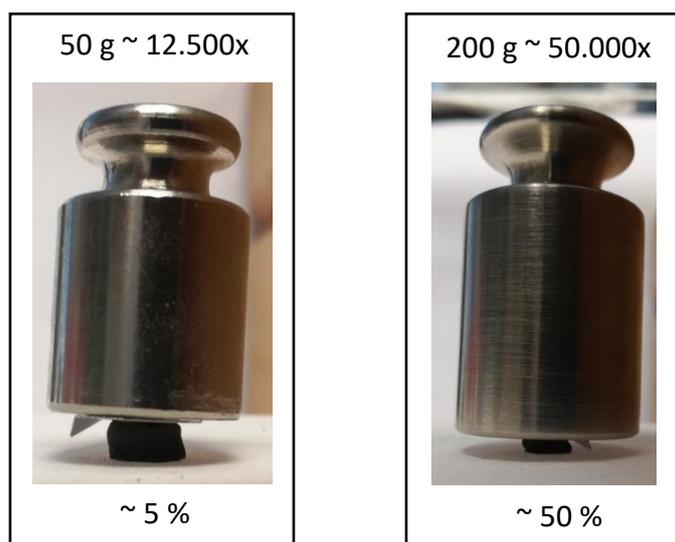


Figure 4. Optical images of the static pressure experiments. 50g (left) and 200g (right)

The size of the monolith was reduced in *ca.* 5 % when applying static pressure with a weight of 50 g (12500 times the weight of the monolith), but it mostly recovered the initial shape after releasing this pressure. Thus, the inherent flexibility of graphene sheets was

translated to the 3D macrostructure. However, the monolith was heavily shrunk (*ca.* 50 %) after applying a weight of 200 g (50000 times the weight of the monolith), and the size was not recovered by eliminating the weight. This behavior was likely due to partial break of the interior network of the monolith under compression.

In some cases, after the gelation and drying process, the aerogels suffered a severe shrinkage, obtaining aerogels with a 20 v% of the initial volume (Fig. 5a).

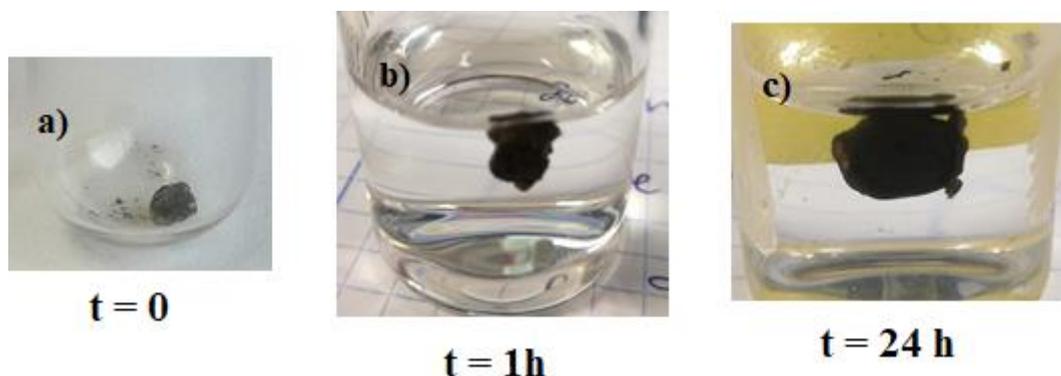


Figure 5. Optical images of the swelling process. a) reduced size aerogel  $t = 0$ , b)  $t = 1$  h, c)  $t = 24$ h.

After addition of ethanol in the vials containing the reduced aerogels a process of swelling was observed (Fig 5b, c). The monolith volume increased up to 80 v% of the added monolith volume. Meaning that the aerogel was not only stable in water or ethanol, but also capable of absorbing it. Ethanol swelled monoliths were dried in  $scCO_2$ , returning the aerogels to their reduced volume (Fig. 6).

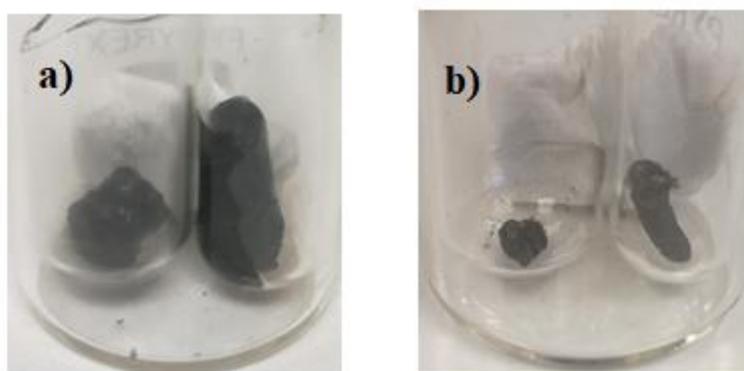


Figure 6. Optical images of the reversible drying process. a) swelled aerogels b) reduced size monoliths after the drying process.

## CONCLUSION

The aerogel monoliths obtained by  $scCO_2$  gelation and drying have a very low density and high specific surface area, which rivals with that of most light-weight graphene aerogels reported in the literature. These aerogels are formed under mild conditions which fosters the stability of the functional groups during the procedure. The use of low temperature  $scCO_2$  technology as the main step implies a lower environmental impact compared to other methods such as hydrothermal or drying at the supercritical point of

ethanol. This method allows the fabrication of a versatile material that could be introduced in several application fields, such as water and air purification, battery and supercapacitor improvements or even biological applications.

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