

# On the sustainable synthesis of graphene-like materials from wastes for electrochemical sensing

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The worldwide economic growth and increase of population is leading an ongoing transformation of traditional economies and industrial sectors driven by an urgent need to address climate changes. This new model moves towards sustainability based on different aspects such as circular economy and energy efficiency, favoring for example the use of so-called biofuels from renewable raw materials.

In this scenario, carbon nanomaterials, such as graphenes, plays an important role in different sectors, because of their outstanding properties, including electrical conductivity, mechanical stability, tunable morphology, and functionality. The development of graphene technologies is, however, limiting their production at large scale, mainly due to high costs. Graphene-based materials are usually obtained from graphites or even other fossils such as pre-graphitic materials [Sierra et al. 2015]. In recent years, and driven also by sustainable and renewable concerns, new green raw alternatives have been explored as different types of biomass and biomass wastes, which can be considered as carbon neutral. These materials usually present relatively high carbon content while offering low cost and high availability, enabling their drastic cost reduction.

One of the most important challenges in the production of graphene materials from biomass is to ensure their quality. The utilization of biomass resources, with many structural differences among them, usually leads to important graphene inconsistencies (in terms of morphological and physicochemical properties) which should be evaluated in detail, particularly when the materials are to be used in specific applications. Aspects as the selection of the biomass and the preparation methodology are key factors to be taken into account to obtain a graphene material with specific characteristics.

Bearing that in mind, the first objective of this work is to evaluate the utilization of biomass as raw material for the preparation of graphene materials and to study their further application in electrochemical sensors. [Chang et al. 2020]. Moreover, the biomass used herein is a residue (biochar) of the utilization of a *Sargassum* sp macroalgae used as raw material for bio-oil, bio-char and gas generation. Additionally, aiming to avoid oxidative treatments in the graphene preparation we used a more sustainable procedure based on planetary milling.

## Materials and methods

The raw material used in this work is a residual biochar obtained in the upgrading of *Sargassum* samples for the production of bio-oil. The original *Sargassum* sp macroalgae was collected from the coastal zone of Quintana Roo in México. A standard graphite was used for comparative purposes. The biological samples were initially purified (KOH, HCl) at room temperature.

The graphene-like materials were synthesized by mixing 2 g of raw material and 4 g of stearic acid (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>) in a planetary mill (Retsch, Fig. 1a). and subjecting the mixture to milling during 30 min - 1,5h at 1800 rpm forming a black thick film at the bottom of the vessel. The film was collected, and washed five times with fixed volumes (100 mL) of hot ethanol.

The samples were characterized by different techniques. The thermogravimetric study of the biochar was carried out on a TA Instruments thermobalance (TGA Q5000IR). X-ray diffraction measurements (XRD) were performed in a Bruker D8Advance ECO instrument selecting a radiation frequency of the  $\alpha_1$  line from Cu (1.5418 Å). The power supply was of 40 kV and 25 mA. Transmission electron microscopy (TEM) investigations, including conventional (CTEM), high-resolution (HRTEM), and elemental chemical analysis (EDX) methods, were performed on graphene specimens using an FEI TITAN 80–300 kV instrument (FEI Technology de México S.A., Monterrey, Mexico). It operated at an accelerating voltage of 300 kV. SPECS equipment (SPECS Group, SPECS Surface Nano Analysis GmbH, Berlin, Germany) operating under a pressure of 10<sup>-7</sup> Pa with a Mg K $\alpha$  X-ray source was used for the X-ray photoelectron spectroscopy (XPS) studies.

## Results and discussion

The preparation of graphene materials from biological residues was achieved by a modified milling procedure. For comparative purposes, a commercial graphite was also used.

The chemical composition of the biological sample was determined by elemental analysis, containing C (62.1%), O (25.2%), Na (2.3%), Cl (6.0%), S (0.8%) and K (0.9%). Due to that, the initial procedure optimized for graphene production with these samples comprises an initial purification step (KOH, treatment at room temperature) to eliminate the light carbonaceous compounds.

The remaining solid was then subjected to a planetary milling in the presence of stearic acid as intercalant. Several milling times were studied in the range of 30 min - 1,5h. The crystallinity of the parent and milled samples was evaluated by XRD (Figure 1 (b)). It was observed that the graphite signal intensity decreased after milling, which indicates a reduction in size and order. On the other hand, no signals were observed around  $2\theta = 11^\circ$  (typical of graphene oxide samples), revealing that the milling treatment was mild enough to avoid the oxidation of the samples.

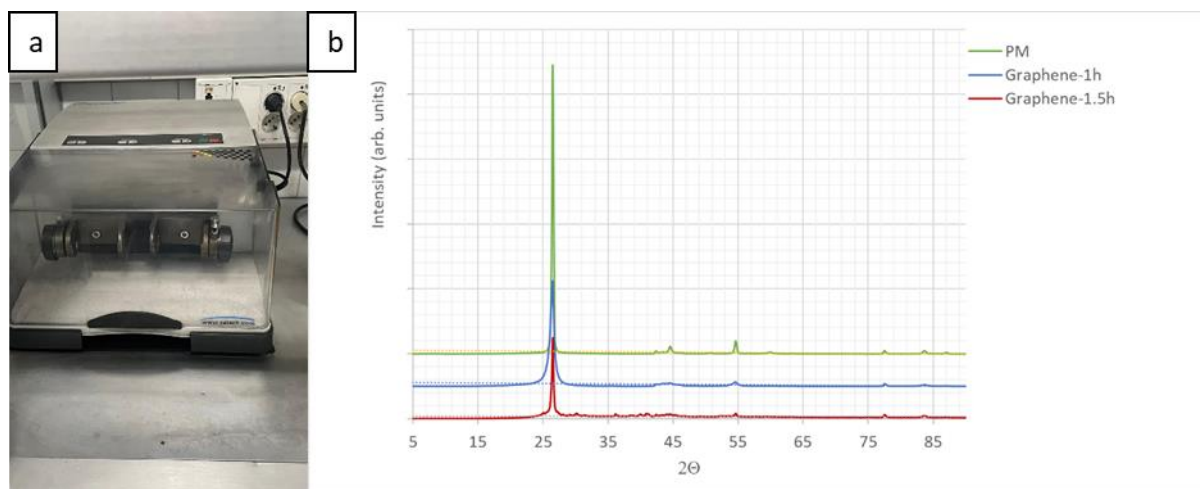


Figure 1: a) Image of the milling device used to obtain the graphene-like materials. b) XRD spectra of the parent materials (PM, green line) and the graphene materials obtained after 1h of milling with stearic acid (graphene-1h, blue line) and after 1.5h of milling (graphene-1.5h, red line).

XRD was also used to optimize the time of the milling process. As observed in Figure 1, the intensity of the graphitic signal at  $2\theta = 26^\circ$ , very intense for the parent sample (Figure 1, green line) drastically decreases at 1h of milling (Figure 1, blue line). This decrease is much less intense in the case of using 1,5h (Figure 1, red line), suggesting no more than 1h of milling time is required to produce the graphene-like materials.

The as-obtained graphene-like samples are tested as active electrode materials in sensing, starting from their electrochemical performance for detecting traditional redox probes as potassium ferricyanide. The obtained results allow to determine the effect of the characteristics of the as-prepared graphene like materials (i.e. size of graphene layer, graphenic defects or surface functional groups at the basal planes of graphene layers and edges) on their resulting electrochemical behavior.

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### References:

Sierra, U., Álvarez, P., Blanco, C., Granda, M., Santamaría, R., Menéndez, R. New alternatives to graphite for producing graphene materials. *Carbon*, 2015, 93, 812-818.

Chang, Y., Venton, B. J. Optimization of graphene oxide-modified carbon-fiber microelectrode for dopamine detection. *Analytical Methods*, 2020 12(22), 2893-2902.

Sierra U., Mercado A., Cuara E., Barriga Castro E., Cortés A., Gallardo C., Fernández S. Coke-derived few layer graphene-like materials by mild planetary milling exfoliation. *FUEL*, 2020, 262, 1-10.