

# Large scale production of graphenic materials by Grupo Antolin and their applications development

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Graphene oxide is mainly produced from graphite although other graphitic materials have also been employed. The major disadvantage of graphite, as starting material, is the low efficiency of the oxidation process due to the high number of stacked layers present in its structure. As an alternative route, we present an industrial process to obtain few layer sheets of graphene oxide (GRAnPH®) by using GANF® carbon nanofibers as starting material and the Hummers' method as oxidation procedure.

GANF® presents a singular helical ribbon graphitic structure, composed by a graphitic ribbon of approximately five graphene layers rolled along the fiber axis. This structure makes them very attractive as starting material for graphene production, Fig 1-2[1].

The low number of stacked graphene layer in GANF® allows the achievement of a highly effective oxidation. Thus, whereas GRAnPH® can be used without further purification, several centrifugation steps are absolutely necessary to remove non oxidized graphite when the oxidation was carried out from graphite as starting material.

In order to analyze the quality of GRAnPH® graphene oxide the following techniques were used X-Ray Diffraction, UV-Vis, XPS and Raman spectroscopy. The most representative results are collected in table 1. For comparative purposes, results corresponding to graphite oxide (GO) also have been included.

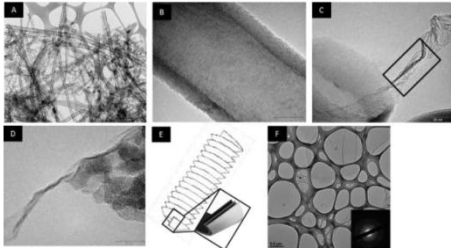
Table1. GRAnPH® and GO characterization.

Technique	Results	
	GRAnPH®	GO (Graphite)
UV-Vis	$\lambda_{max}=235\text{nm}$	$\lambda_{max}=230\text{ nm}$
	O/C=0.61	O/C=0.62
XPS	60% C-C	49% C-C
	26% C-O	45% C-O
	14% C=O	6% C=O
XRD	$d_{(002)}=0.77\text{ nm}$	$d_{(002)}=1.02\text{ nm}$
Raman	$I_D/I_G = 1.03$	$I_D/I_G = 1.4$

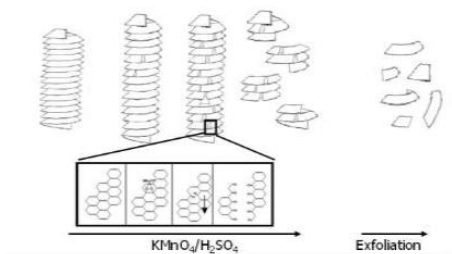
As it can be observed in table 1, the position of the maximum of GRAnPH® UV-Vis spectrum is five nanometers red-shifted respect to the maximum corresponding to GO. The red- shift of this band can be related to the higher amount of sp<sup>2</sup> carbons in the graphene network. This result is consistent with the information obtained from the XPS measurements. Finally, the size of the sp<sup>2</sup> domains was evaluated by means of the I<sub>D</sub>/I<sub>G</sub> ratio obtained from the Raman spectra. The results show lower ratio for GRAnPH® than for GO. This fact means that the size of the Csp<sup>2</sup> domains is larger for GRAnPH® than for graphite oxide.

The chemical composition of GRAnPH® graphene oxide allows the preparation of stable suspensions in different polar solvents. Moreover, it can be deposited over a wide variety of substrates by different methods and be used for diverse applications.

## Figures



**Figure 1:** TEM micrographs of: A) HR-CNFs; B) GANF<sup>®</sup> HR-CNF, it can be observed its high graphitic structure; C) Unraveled ribbon from the HR-CNF; D) Detail of the ribbon; E) Scheme of the structure of the HR- CNFs; F) Large single graphene oxide sheets derived from GANF<sup>®</sup>.



**Figure 2:** Scheme of the graphene oxide sheets derived from GANF<sup>®</sup> HR-CNFs. First step is an oxidation reaction by a modified Hummers method; second step is an exfoliation.

## References

- [1] Vera-Agullo J, Varela-Rizo H, Conesa JA, Almansa C, Merino C, Martín-Gullón I. Carbon. **45** (2007) 2751-8