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## Synthesis of pure graphene and graphene/carbon nanotubes hybrid by atmospheric pressure plasma

Since the discovery of carbon nanotubes (CNTs) in 1991 [1] and, more extensively, after the isolation of graphene in 2004 [2], the development of new procedures for the synthesis of these one- and two- dimensional nanostructures has been in the spotlight due to their suitability to be utilized in many applications in different fields as electronics or biomedical [3,4] as well as in the development of new improved materials [5]. In addition, it has been demonstrated that graphene-CNTs hybrid nanomaterials exhibit the virtues of both graphene and CNTs which make them to be of special interest in energy storage [6] or the fabrication of supercapacitors [7].

Among other techniques, Chemical Vapour Deposition (CVD) or Liquid Phase Exfoliation (LPE) are presented as suitable technologies for these carbon-based nanomaterials synthesis. However, both procedures present several limitations such as (i) the need of complementary treatment to extract graphene from the substrate or the solvent or (ii) the use of harmful catalyzers which increase the number of defects of the synthesized material. Therefore, CVD and LPE can be hardly considered as potential techniques for the synthesis of high-quality graphene and graphene-CNTs hybrids at large scale.

To overcome these major drawbacks, the use of non-thermal microwave plasmas working at atmospheric pressure for the synthesis of graphene or graphene-CNTs hybrids using aliphatic alcohols as precursors has been successfully proven [8-10]. Microwave atmospheric-pressure plasmas are extraordinarily energetic media which allow some reactions to take place. For instance, organic compounds such as alcohols are decomposed into their fundamental entities, *e.g.* carbon atoms, which are the departure point for the synthesis of graphene and graphene-CNTs hybrids. Finally, the use of atmospheric-pressure plasmas enables the development of online high-throughput processes, which is crucial for industrial applications.

Concerning the formation of high quality few-layers graphene by ethanol decomposition, an argon microwave plasma torch: Torche à Injection Axiale sur Guide d'Ondes (TIAGO) was used with an ethanol flow rate of 2 g/h [11], whereas graphene-CNTs hybrid was successfully obtained from the decomposition of the aforementioned alcohol (0.22 g/h) by means of a surface wave discharge sustained by a surfatron device [12]. Among others, X-ray photoelectron spectroscopy and energy dispersive X-ray analysis were performed in the material synthesized by the TIAGO torch plasma and SWD, respectively. In both cases, the results showed the presence of carbon atoms as unique element of graphene flakes and graphene-CNTs hybrids.

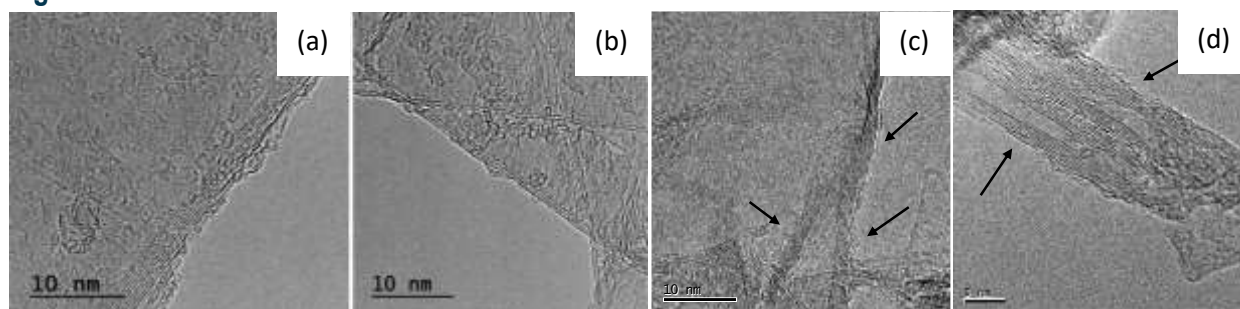
Concerning the study of high-resolution transmission electron microscopy (HRTEM) images (Figure 1), less than 7 layers-graphene sheets without CNTs or graphitic particles are observed in the images from the powder created by the TIAGO torch (Figure 1 a, b) whereas the material synthesized by a SWD contains both multilayer graphene sheets (Fig 1c) and short carbon nanotubes (Fig 1d). The analysis of Raman spectra (Figure 2) confirms the presence of  $sp^2$  hybridized carbon atoms by the so-called G and 2D band in the solid synthesized by both microwave plasmas. Moreover, the location of G band in both spectra at  $\approx 1580\text{ cm}^{-1}$  discard the formation of graphene oxide. The intensity ratio of D and G band is, in both cases, lower than the unity, which points out the existence of small defects in the material synthesized ( $I_D/I_G$  (TIAGO) = 0.24 and  $I_D/I_G$  (surfatron) = 0.60).

As far as the production rate is concerned, plasmas sustained with the TIAGO torch can generate 1.33 mg/min of few-layers graphene, whereas 0.07 mg/min of graphene-CNTs hybrid is synthesized by a SWD. These two catalyst-free methods are carried out in a single step and offer the possibility of scaling it to industrial level.

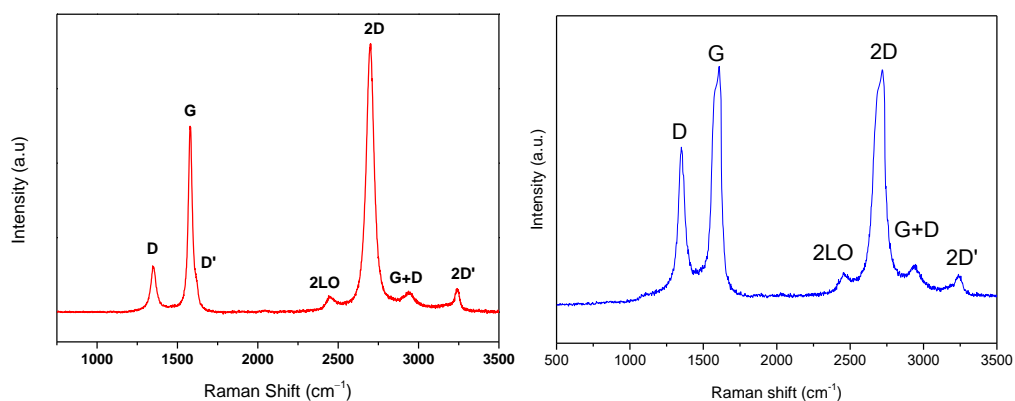
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## Figures



**Figure 1:** High-resolution TEM images of solid matter synthesized by TIAGO torch (a,b) and SWD (c,d)



**Figure 2:** Raman spectra of solid matter synthesized by TIAGO torch (a) and SWD (b)