Effect of nanoparticles on the material properties of graphene-based nanocomposites.

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Graphene-based nanocomposites (NCs) consist of a matrix -graphene- in which nanometer-size particles are included. These particles should not compromise the intrinsic properties of graphene but rather enhance the overall characteristics of the NC. Such nanostructures are of special interest in the field of energy storage. For example, using graphene-Cu, graphene-TiO_2 or graphene-Au nanocomposites as electrode materials has improved the performance of batteries [1]. Among other NC production techniques, microwave plasmas at atmospheric pressure stands out. This process offers numerous benefits in contrast to chemical methods, making it a compelling option for industrial-scale nanostructures production: does not require vacuum equipment since it can operate at atmospheric pressure and no hazardous or contaminating products are produced during the synthesis process. Furthermore, surplus products from various industries or pollutant emissions can serve as precursors, which are substances that could be introduced into plasma and used for synthesis of nanostructures and/or formation of nanocomposites.

In this research, graphene and graphene-Cu NCs are synthesized by using a TIAGO (*Torche à injection Axiale sur Guide d'Ondes*) and the effect of Cu NPs on graphene properties is deeply studied by Raman spectroscopy, X-ray photoelectron spectroscopy, Transmission electron microscopy (TEM) and thermal-gravimetric analysis. As reported in [2-4], graphene and graphene-Cu NCs can be obtained by introducing ethanol molecules into an argon plasma and acting on input microwave energy. Since the discharge is generated on the tip of the field applicator, which is made of copper, Cu NPs can be sputtered during the synthesis the graphene thus resulting in the formation of graphene-Cu NCs. Low-magnification TEM image of graphene sample (Figure 1a) shows the distinctive structure of graphene in the absence of any other nanostructured carbon material or carbonaceous particles. Furthermore, the structure exhibits homogeneity, evident in transparent zones representing extended sheets and darker zones indicating folded graphene sheets. In contrast. Low-magnification TEM image of graphene-Cu NC (Figure 1b) shows graphene sheets with the presence of few nanometer units Cu NPs, as evidenced in the compositional analysis (Figure 1c) with C (marked in red) and Cu (marked in green) signals originating from graphene and the particles observed in the TEM image, respectively.

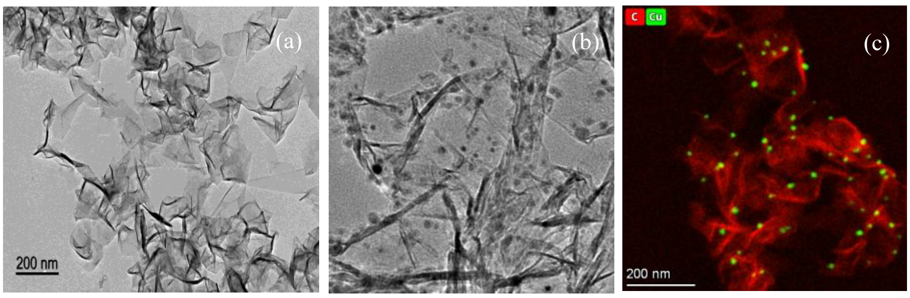

Fig. 1: Low-magnification TEM images of (a) graphene and (b) graphene-Cu NC samples. (c) compositional analysis of graphene-Cu NC by energy dispersive spectroscopy.

To assess the influence of larger Cu NPs on graphene properties, Raman spectra of both graphene and graphene-Cu NCs were measured and are shown in Figure 2.

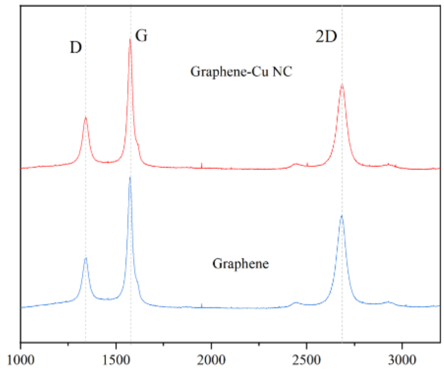

Fig. 2: Raman spectra of graphene and graphene-Cu NCs.

Regardless of the presence of Cu NPs, G and 2D bands characteristic of graphene are observed. Indeed, similar I_D/I_G and I_{2D}/I_G ratios from the Raman spectra indicate similar number of defects and thickness in both samples, *i.e.*, graphene quality remains uncompromised when larger Cu NPs are included. Nevertheless, as it was reported previously in [4], the presence of Cu NPs on graphene has an impact on graphene oxidation resistance as evidenced by thermogravimetric analysis (TGA). The graphene sample exhibits exceptional thermal stability (Figure 3), peaking at ~700°C, which is typical for graphene materials. This stands in contrast to graphene-Cu NC, where copper (Cu) may serve as a catalyst for oxidative reactions during thermal stability assessments. The first derivative of the TGA curve (dTG curve) and its characteristics varied significantly between the two materials, with graphene showing typical GNS behavior and graphene-Cu NPs displaying a fast onset of oxidation followed by a gradual decrease in oxidative reaction speed.

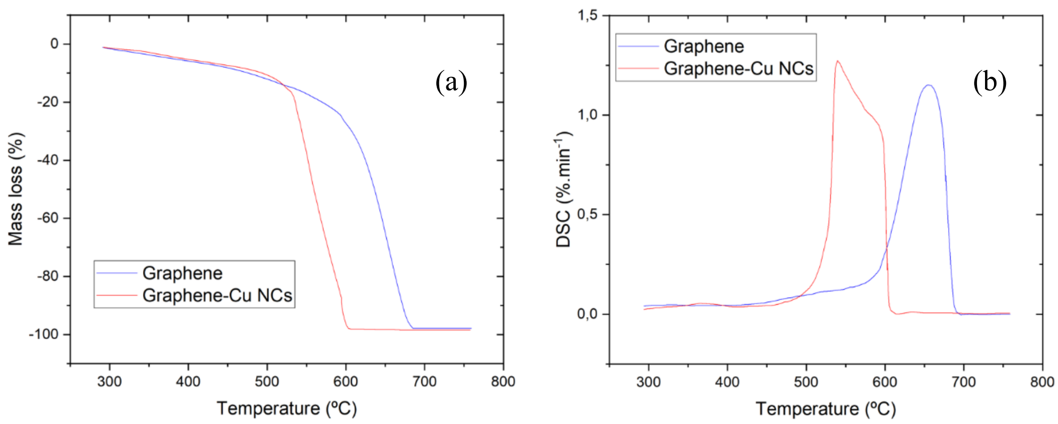

Fig. 3: TGA (a) and dTGA (b) analyses of prepared Graphene and Graphene-Cu NPs

In conclusion, using microwave plasmas at atmospheric pressure, graphene-based NCs can be synthesized which might exhibit different characteristics while keeping high quality graphene properties.

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