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Analysis of Industrial Graphene-Based Flakes – First Results on Morphological Characterization, Sample Preparation and Chemical Composition

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Graphene is a carbon allotrope arranged in a 2D single atom layer structure where the carbon atoms are packed in a hexagonal honeycomb structure. The carbon covalent bonds are sp2 hybridized in which the σ bond (in-plane) is responsible for the high mechanical properties of graphene, while the π bond (out-of-plane) contributes to the electron delocalization of graphene. This latter mechanism is responsible for the extraordinary electrical and thermal properties [1].

Since its isolation in 2004, graphene is worldwide recognized as a wonder material because of its outstanding and unique properties. However, graphene has not yet reached the expected role in real-life application and its large-scale production is still quite limited. Before industrial grade graphene could reach comparable quality to the controlled laboratory scale material, many challenges must be overcome. In order to bridge the gap between lab-scale and industrial-scale production is necessary to develop processes, equipment and measurement procedures to control the material features [2]. One of the most crucial reasons of graphene's limited commercialization is the lack of standard procedures to properly characterize and define the material chemical and structural properties down to the nanometer level. This leads to many issues regarding material synthesis repeatability, inappropriateness choice of measurands and measurement reproducibility which heavily affect the consistency of the material performance [3]. For example, among all the different industrially produced real-world graphene, it is crucial to determine how many layers of graphene build the material. Products that are built by more than 10 layers should be more correctly referred as nanosized graphite, a problem that is often regarded as the "fake graphene" issue [4].

In our study, a comparative analysis is performed on two different series (G5 and G6) of industrial graphene powders, each series produced with four types of functionalization: raw graphene, oxygen-functionalized, nitrogen-functionalized and fluorine-functionalized. All the 8 sample variants were analyzed from a chemical and morphological point of view in the form of powders prepared as slightly pressed in metallic sample holders.

The morphology of the flake powders was evaluated through Scanning Electron Microscopy (SEM), using both conventional and InLens secondary electrons detectors at a 10 keV excitation energy.

A comparative characterization of the chemical composition was performed through X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersive X-ray Spectroscopy (EDS) with a SEM. XPS depth resolution is in the order of 10 nm, while for EDS the analysis was carried out at two different excitation energies, i.e. 5 keV and 15 keV, and thus varying the analysis depth from ~200 nm to ~2 µm. The XPS measurement area is 300x700 µm², while the EDS measurement was performed by measuring a grid of 5 locations of 150 x 150 μm^2 area, covering the whole sample surface @ 5 mm diameter. A

standardless quantification has been applied for each area and the mean of the elemental concentration for each sample has been finally calculated.

The results of the comparative chemical analyses XPS and EDS show a good agreement in the concentration values for all the elements present in the samples, despite the different analysis volumes addressed by the two techniques. For this reason, the samples can be considered homogeneous in both lateral and vertical direction.

The SEM analysis highlights that the two series of graphene, G5 and G6, possess two different morphologies. In fact, one presents large, jagged flakes packed with relatively low density, while the other is characterized by smaller, rounded flakes packed in a higher density structure. The quantitative chemical analyses of the atomic concentration values, show a marked difference among the two series, both with XPS and with EDS. The difference between the measured concentration of atoms in the two series is higher for the functionalization elements N and F than for the C/O ratio. It may seem that a correlation exists between the measured chemical composition and the morphology of the powder. If so, it must be clarified whether this difference comes from the material or from the measurements. Given that the two techniques, EDS and XPS, showed comparable results, it is reasonable to assume that the difference comes from the material itself. In fact, the morphology of the flakes could have affected the functionalization process, for example due the different surface specific areas. The quantified results obtained by standardless EDS and XPS have been verified by applying the same quantification procedure to an ionic liquid sample containing the elements C, N, O, F and S in a well-defined stoichiometry as a reference sample. Both methods, XPS and EDS perform very good, apart from an overestimation of S and underestimation of N by EDS. The understanding and correction of these deviations are in progress.
A clear influence of the morphology on the composition is evident. Therefore, such correlative measurements of morphology and composition are necessary for a comprehensive characterization of industrial graphene flakes. Protocols for reliable characterization of industrial graphene flakes are in progress [5].

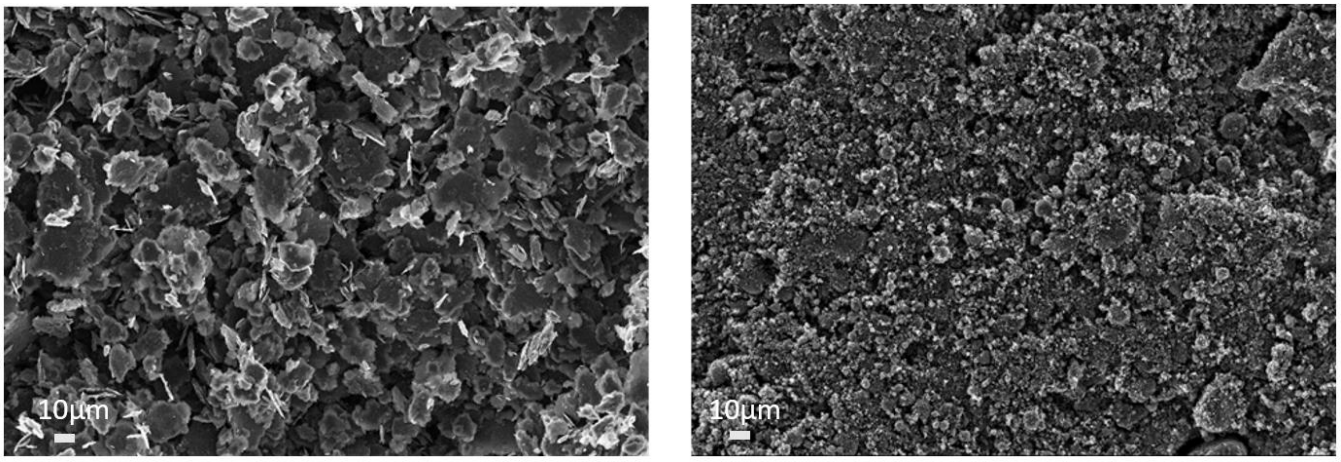

Figure 1. SEM (SE InLens) micrographs of G6 powder morphology (left) and G5 powder morphology (right)

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