Correlative chemical imaging to reveal the nature of different commercial graphene materials

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1. Introduction

Since Novoselov and Geim's seminal report in 2004[1], Graphene has attracted immense attention owing to its extraordinary properties[2]. Over the last two decades, the synthesis and functionalization of graphene have significantly advanced[3]. Various synthesis methodologies have emerged, giving rise to the development of related materials such as graphene oxide (GO) or elemental-doped graphene[4]. Additionally, chemical functionalization of the material surface can augment or modify specific graphene properties. Accurate physico-chemical characterization using diverse analytical techniques is indispensable for elucidating the nature of these materials[5]. Particularly those analytical methods equipped with imaging capabilities can derive greater analytical insights from these specific 2D materials. Nevertheless, a dedicated sample preparation is the prerequisite for a meaningful outcome.

2. Well-defined monolayer Graphene Oxide in µm range

Single-layer GO flakes, generously provided by Graphenea (Spain), were meticulously prepared for systematic imaging analysis. These flakes were carefully arranged on an alignment-marked SiO_2 substrate and sequentially imaged using scanning electron microscopy (SEM), atomic force microscopy (AFM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), Raman spectroscopy, and additionally analysed with X-ray photoelectron spectroscopy (XPS). The exceptional lateral resolution and surface sensitivity of these techniques was crucial for accurate imaging of single-layer GO flakes. The ToF-SIMS images exhibited strong correlation with the SEM and AFM images (Figure 1a, c and d), offering valuable insights into the chemical composition. Employing 2D Raman spectroscopy, the number of overlapping single-layer flakes could be distinguished. Such structures were further visualized by Raman microscopy in a 3D image (Figure 1b). These GO flakes are good candidates for reference materials not only for imaging graphene-like structures, but also for exploring other types of 2D materials.

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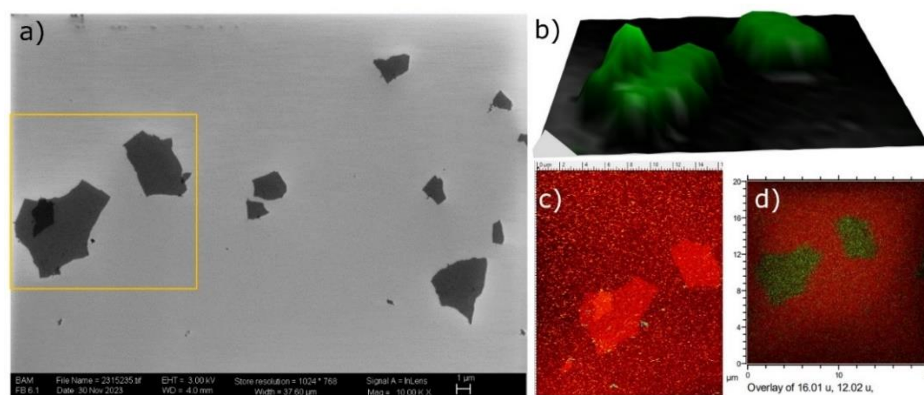

Figure 1: Correlative images of GO flakes a) SEM image, b) Raman intensity of G peak scanned over the area in (a) marked with yellow, c) AFM image and d) ToF-SIMS overlay image of C^- (green) and O^- (red) fragments.

3. Suspensions and Inks containing commercially fluorinated and nitrogenated GO Powder

In addition to the clearly defined monolayer graphene oxide (GO) flakes, we also examined commercial GO-containing suspensions and inks (from Haydale) with a more complex morphology, by using correlative imaging techniques. The basis of the inks and suspensions is GO powder which was functionalized e.g. with fluorine and nitrogen. To identify the source of various chemical fragments, ToF-SIMS and Auger electron spectroscopy (AES) were combined with SEM images of the same analysis area on the sample. Interestingly, not all GO flakes from the powder were homogeneously functionalized suggesting that the functionalization reaction takes place preferably on specific sites. It was also shown that the fluorine functionalization is a more effective process than the nitrogenation.

To obtain the inks, carbon black was mixed with functionalized GO powder and resin. SEM imaging showed that, based on morphological information, the GO sheets seem to be uniformly embedded into the resin/carbon black matrix (Figure 2a). The final confirmation proving a homogenous distribution of functionalized GO flakes was found by ToF-SIMS imaging and Energy-Dispersive X-ray Spectroscopy (EDX) elemental mapping. The results align closely with the nominal distribution of 10 % of specific functionalizations (marked by fluorine) solely associated to the graphene flakes, as indicated in the SEM images. While fluorine and oxygen signals are only visible on GO flakes, signals for carbon clusters (e.g. C_2^-) are noticeable on the whole surface as expected (see Figure 2). EDX mapping of Fluorine operated at low energy values could be correlated with these findings, albeit with lower resolution compared to ToF-SIMS, as EDX analysis probes deeper regions in the sample (roughly 1 µm) and ToF-SIMS only analyzes the outermost layer. Notably, AES on the same region could not identify the fluorine since the concentration is near the detection limit and the functionalized GO flakes “lie” mostly unparallel at the sample surface but rather being embedded deeper in the ink matrix. On one hand the GO powder is diluted by an order of magnitude with carbon black/resin and on the other hand the powder used for this specific ink was not as highly fluorinated as others according to XPS and EDX bulk analyses.

Besides the functionalization, traces of elements such as Na, K and Fe coming from the production process could be found and localized at the flakes sites when measuring ToF-

SIMS in positive mode. Intriguingly, as in the case of different functionalizations, the impurities were also detected on different areas/locations of graphene flakes.

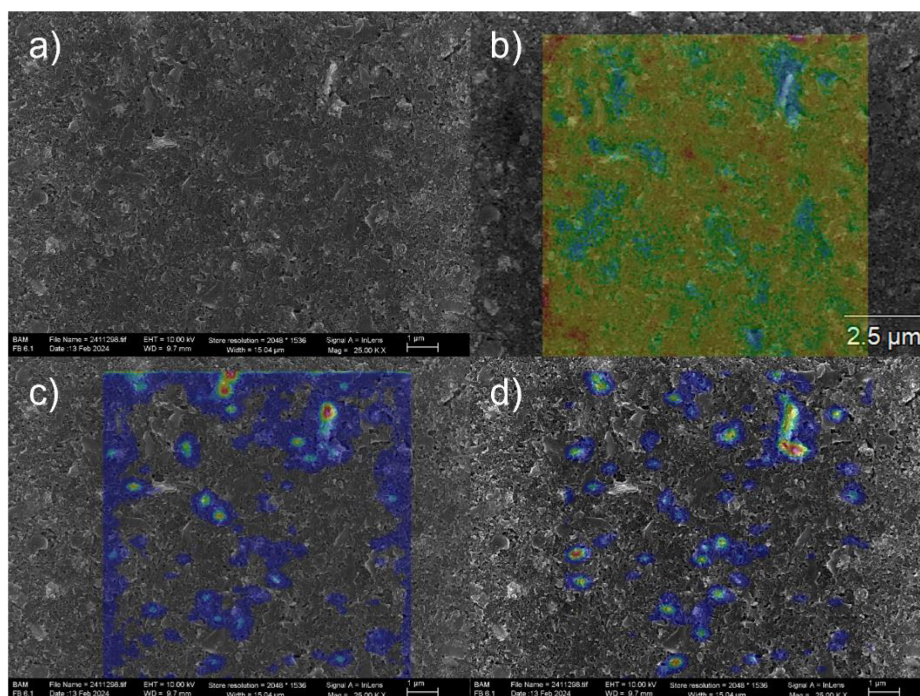

Figure 2: Correlative images of an ink containing fluorinated GO flakes: a) SEM micrograph, b) C_2^-, c) O^- and d) F^- SIMS maps overlayed on the SEM image in thermal colour representation (blue= low intensity, red=high intensity).

4. Conclusions

GO flakes and GO flakes containing commercial materials were chemically imaged at high resolution with different analysis techniques. In a first case study, single layer and overlapping sheets could be precisely visualized after dedicated preparation on a substrate. As these sheets have a highly defined structure, their potential exploitation as a reference material is considered.

Chemical imaging on functionalized GO flakes of commercial grade showed different fragments from surface functionalization, but also residual elements from the production process. The distribution of the functionalization over the flakes is rather inhomogeneous. Within the inks as the final product, the flakes were homogeneously distributed in accordance with the manufacturer specifications.

These findings demonstrate that ToF-SIMS is a powerful method in regard to surface sensitivity and detection sensitivity with excellent lateral resolution (well below 100 nm) making it an optimal method for imaging monolayer and few-layer graphene 2D materials.

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6. References

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