

Chemical Analysis of Functionalized Graphene along the Production Chain

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1. Introduction

In 2004 Geim and Novoselov successfully isolated and characterized graphene, which was proven to be groundbreaking discovery [1]. Graphene is a two-dimensional (2D) material consisting of a single layer of carbon (C) atoms arranged in a hexagonal lattice structure. It has attracted significant attention in the scientific and industrial communities due to its exceptional mechanical, thermal, electrical, and optical properties. Hence, graphene applications are immense, including electronics, energy storage, composites, and sensors. Its extraordinary electrical conductivity and high carrier mobility make it a prime candidate for next-generation electronic and optoelectronic devices, potentially overcoming limitations of traditional silicon-based technologies [2]. The material's strength, coupled with its lightweight nature, opens up new possibilities in the development of advanced composite materials for automotive, aerospace, and structural applications, where enhanced performance with reduced weight is constantly sought. Graphene shows significant promise, yet there is still much to uncover about its properties and industrial applications through ongoing research.

In this study, we characterize graphene materials with different types of functionalization, in form of powder, suspension, and inks, using various characterization techniques such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and Auger electron spectroscopy (AES).

2. Experimental

In this study, we first analyze the chemical composition of starting material for commercial functionalized graphene (FG) that is in powder form. We then analyze the powders after functionalization (at Haydale) in various versions; dispersed in water forming suspensions. Finally, we investigate the behavior of this functionalised powders when inks are formed. The FG samples under investigation are functionalized using four different functionalization groups: fluorine (F), oxygen (O), ammonia (NH₃), and carboxylic acid (COOH). Pure graphene (G) was also investigated as the reference sample.

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XPS is a cornerstone technique in chemical surface analysis. Through the interaction of X-rays with material surfaces and emission of photoelectrons, it accurately identifies elemental composition, chemical states, and electronic structures. EDX excels in rapidly analyzing elemental analysis and mapping of materials. It also gives a valuable insight about the materials bulk (in the range of 1 micron). This is enabled by detecting characteristic X-rays emitted from the sample upon interaction with high-energy electrons of a SEM (or TEM). It is worth mentioned that EDX was carried out at 5 keV and 15 keV which gives a balanced insight about the near-surface as well as the bulk regions of the samples. SEM is a powerful analytical tool that has the capability to show the intricate details of surface morphology and structure with high resolution and clarity. The images created by SEM enables visualization of surface features down to nanoscale dimensions, such as the topographical characteristics, particle size distributions, and surface roughness or porosity. Finally, ToF-SIMS offers an unparalleled sensitivity for detecting trace amounts of surface composition (including contamination).

For the XPS analysis the powders were deposited onto a Tesa tape that is stuck on an aluminum substrate before entering the ultra-high vacuum chamber. The same samples were later investigated by SEM, EDX, and ToF-SIMS in that order. The suspensions, which are graphene powders dissolved in water with approximately 50 mg/mL concentration, were let to sediment then using a micropipette, 6 μ L from the sediment (i.e., bottom) suspension were deposited onto polished silicon wafers. The drop-casted samples were put into vacuum desiccator to dry overnight, then the samples were used for investigation in the same order as the powders. The inks were “spread” over silicon wafers and left to dry in vacuum overnight before analysis.

3. Results and Discussions

XPS analysis for the graphene powders showed presence of fluorine in the F-functionalized sample (F-FG) as well a high oxygen-to-carbon concentration ratio in the COOH and O functionalized samples. EDX analysis results – as bulk analysis - are in agreement with the surface-sensitive XPS results. The XPS analysis of the graphene suspensions also showed existence of F in the F-functionalized sample. The oxygen-to-carbon concentration ratio for the COOH- and O-functionalized samples were high as well. When compared to the powders, the oxygen -to-carbon ratio for all suspensions are higher than the ratios of the powder samples. For the inks, the EDX and ToF-SIMS showed the presence of F in the F-functionalized sample in certain areas of the sample. However, detection of the oxygen-to-carbon ratios proved to be very challenging. This is because the abundance of C in the resin and carbon black that are mixed with the graphene powders. Figure 1 shows a representative SEM micrograph and the corresponding EDX mapping of F result for the F-functionalized ink.

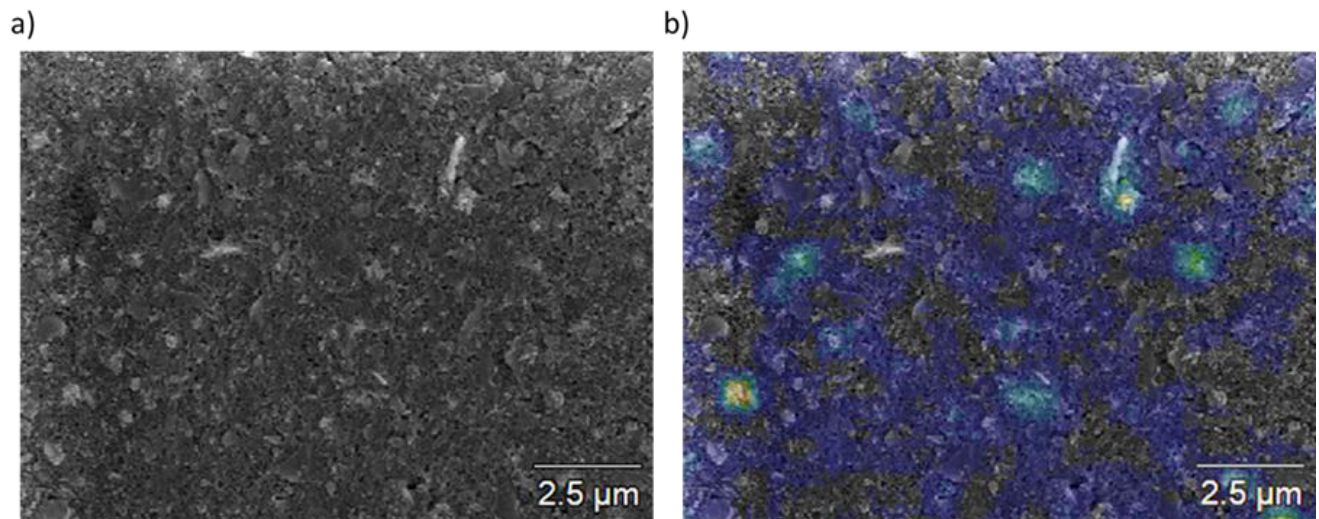


Figure 1: SEM image (a) and corresponding 5 kV EDX elemental map (b) of fluorine for an ink containing fluorine-functionalized-graphene within ink, after deposition of ink on silicon wafer, overlaid on (a)

4. Conclusions

Our results suggest a significant effect of water and commercial resins on the presence of graphene and associated functionalized group. For example, XPS analysis shows some significant differences between the chemical compositions of the solutions and the starting materials (powders). These changes can be explained by the location of the functionalization at the outermost surface as indicated by Chemello et al [3].

5. Acknowledgement

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6. References

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