

Improving amine-functionalised biosensors through understanding the bonding mechanisms for CVD-grown graphene

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Due to graphene's desirable properties, such as the ease of chemical functionalisation, high electrical conductivity, and high surface area, graphene biosensors are a rapidly growing area of research. To achieve high selectivity, graphene must be functionalised with appropriate molecules, such as amine groups which are required to bind to antibodies then used for the detection of biomarkers. However, there are a range of possible methods to functionalise graphene with amine, and the optimal method is still unclear. Typically, covalent functionalisation is more durable, due to the greater bond strength, but this can disrupt the sp^2 -hybridised carbon structure and thus degrade the electrical conductivity. Non-covalent functionalisation is expected to be less durable but maintains the sp^2 lattice and electrical conductivity. We have investigated the differences between a covalent functionalisation, with phenyl amine groups bound to graphene, and a non-covalent functionalisation, with poly(1,5-diaminonaphthalene) (pDAN) layers on graphene. The I_D/I_G ratio from the Raman spectra of graphene can be used as an indication of the level of disorder, and therefore can approximate the level of sp^3 defects due to molecules bound to the graphene. Consequentially, it is typically used to confirm the success of a functionalisation process. However, Bissett, M. A *et al.* [1] and Knirsch, K. C. *et al.* [2] both previously reported unexpected changes in the I_D/I_G , where the I_D/I_G increased with functionalisation, but decreased again after an external force, due to strain and a chemical process respectively. Greenwood, J. *et al.* [3] also reported changes in the Raman spectra after scanning tunnelling microscopy (STM) on functionalised highly oriented pyrolytic graphite (HOPG). The work presented here on amine-functionalised, chemical vapor deposition (CVD) graphene shows that while covalent functionalisation is usually the method of choice, it is not necessarily preferable over non-covalent alternatives. Removal of functional groups from CVD graphene with contact-mode atomic force microscopy (AFM) explains unexpected changes in the Raman spectra and suggests the durability of covalent functionalisation can be similar or worse than non-covalent functionalisation. Utilising a combination of imaging techniques, we demonstrate some imaging challenges and the importance of using different analytical techniques to investigate the physicochemical properties of biosensors. Our characterisation combines the use of contact-mode and tapping-mode AFM, Raman spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS). We have also shown how different functionalisation processes affect the operation of a pH sensor, showing a higher sensitivity for the non-covalent process compared to the covalent process.

References

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