Covalent modification of graphene and graphite using diazonium chemistry: tunable grafting and nano-manipulation

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Abstract

We shine light on the covalent modification of graphite and graphene substrates using diazonium chemistry under ambient conditions. We report on the nature of the chemical modification of these graphitic substrates, the relation between molecular structure and film morphology, and the impact of the covalent modification on the properties of the substrates, as revealed by local microscopy and spectroscopy techniques and electrochemistry [1]. By careful selection of the reagents and optimizing reaction conditions, a high density of covalently grafted molecules is obtained - a result that is exposed in an unprecedented way by scanning tunneling microscopy (STM) under ambient conditions. By nano-manipulation, *i.e.* nano-shaving using STM, surface structuring and functionalization at the nanoscale is achieved [2]. This mechanical manipulation leads to the removal of the covalently anchored molecules, regenerating pristine sp² hybridised graphene or graphite patches, as proven by space-resolved Raman microscopy and molecular self-assembly studies.

References

[1] Greenwood, J.; Phan, T. H.; Fujita, Y.; Li, Z.; Ivasenko, O.; Vanderlinden, W.; Van Gorp, H.; Frederickx, W.; Lu, G.; Tahara, K.; Tobe, Y.; Uji-i, H.; Mertens, S. F. L.; De Feyter, S., ACS Nano, **9 (5)** (2015) 5520-5535.

[2] Mali, K. S.; Greenwood, J.; Adisoejoso, J.; Phillipson, R.; De Feyter, S., Nanoscale, **7** (2015) 1566-1585.

Figures



Nano-shaving of 3,5-TBD grafted on HOPG, creating 'Nano-man', and STM image of *n*-pentacontane (n-C₅₀H₁₀₂) self-assembly within nano-trenches of bare HOPG produced by nano-shaving of grafted 3,5-TBD, forming lamellar structures.