

THEORETICAL ANALYSIS OF GRAPHENE FLUORINATION

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There exist few techniques to date that allow selective modification of regions of a graphene surface, or variation of the properties of single carbon nanotubes along their length in a controlled manner. Of the different chemical modification techniques available, fluorination takes a special place as it can provide for full outer wall functionalisation up to CF for graphene and C₂F for nanotubes,[1] and a range of functionalisation methods is available.[2] In particular radio-frequency (RF) plasma functionalisation is easy, fast, and upscalable to industrial levels with good control over the fluorination degree [3]. There has been a long-time interest in graphite fluorination for lubricant applications [4]. For carbon nanotubes, fluorination is used for debundling and dispersion, enabling their solubilization in e.g. alcohols, and potential applications for fluorinated nanotubes include the use in Lithium-ion batteries, supercapacitors and as lubricants [5].

In this work, the reaction mechanisms and electronic properties for graphene fluorination are explored, and compared to carbon nanotube fluorination using Density Functional Theory calculations. Also, the transport properties of hetero-structures containing various domains (pure C, C₂F and C₄F stoichiometry) are determined. These *ab initio* studies have been carried out with the Gaussian and SIESTA codes, and the conductance has been calculated using the usual Green functions formalism. For F₂ gas-phase and HF catalysed graphene fluorination, both (1,2) and (1,4) addition mechanisms can occur, whereas for carbon nanotubes fluorine pairs add at (1,4) spacing, naturally leading to a self-organised C₄F coverage.[5] The latter addition pattern can subsequently rearrange into dense axial C₂F lines by fluorine diffusion upon solubilisation or heat treatment. Contrary to graphene, fluorine banding on carbon nanotubes are thus not formed by fluorine addition in bands directly but by fluorine arranged in a spaced (1,4) addition pattern followed by migration over the surface.

Controlling the fluorination process and subsequent processing results in fluorinated material types with unexplored electronic and chemical properties. Partially fluorinated graphene and banded nanotubes should have many interesting properties, since the fluorinated regions will have a different electronic structure than the pristine segments, raising the intriguing possibility of introducing quantum wells on the graphene surface or along the nanotube length via fluorine banding.

References

- [1] C.P. Ewels, G. Van Lier, J.-C. Charlier, M.I. Heggie, P.R. Briddon, *Phys. Rev. Lett.*, 96 (2006) 216103.
- [2] L. Bulusheva, Yu. Fedoseeva, A. Okotrub, E. Flahaut, I. Asanov, V. Koroteev, A. Yaya, C. P. Ewels, A. Chuvilin, A. Felten, G. Van Lier, D. Vyalikh, *Chem. Mater.*, 22 (14), 4197 (2010).
- [3] A. Felten, C. Bittencourt, J.-J. Pireaux, G. Van Lier, J.-C. Charlier, *J. Appl. Phys.*, 98 (2005) 074308.
- [4] R.L. Fusaro, H.L. Sliney, *ASLE Trans.*, 13 (1970) 56.
- [5] M. Glerup, V. Krstic, C.P. Ewels, M. Holzinger, G. Van Lier, *Doping of Carbon Nanotubes in Doped Nanomaterials and Nanodevices*, W. Chen ed., American Scientific Publishers, Stevenson Ranch, CA, 2007.
- [6] S. Osuna, M. Torrent-Sucarrat, M. Sola, P. Geerlings, C.P. Ewels, G. Van Lier, *J. Phys. Chem. C*, 114 (2010) 3340.