Investigation of the Wagonwheel Effect in Graphene via atomic resolution HAADF and EELS

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Here we present an investigation into the so called "wagonwheel effect" in Nitrogen and Boron doped Graphene and present the first direct experimental observation of the effect by High Angle Annular Dark Field (HAADF) imaging. Furthermore we demonstrate its importance as we investigate the local effects to the electronic structure of Nitrogen and Boron atoms substitutionally doped into graphene via monochromated Electron Energy Loss Spectroscopy (EELS).

The "Wagonwheel Effect" occurs in many physical systems but as predicted by *Lawlor et al* [1] , in Graphene it should manifest as substitutional dopants preferentially occupying one sub-lattice over another. Some attempts have been made to verify this but all of these have involved chemical vapour deposited (CVD) graphene sitting on substrates such as copper and never via electron microscopy, all of which could have unknown consequences on the sample and the dopants within it. For our experiments the graphene has been prepared via manual exfoliation, doped via low energy ion implantation, is free standing over a vacuum and imaged directly via HAADF in a scanning transmission electron microscope (STEM).

This is important to verify as a physical effect but also has strong implications for the development of graphene for industrial applications. When introducing Nitrogen to n-dope graphene and Boron to p-dope it, the sub-lattice sites of the dopants are predicted to have a critical effect on the electronic structure of the modified material; if both dopants occupy the same sub-lattice, no band gap appears, whereas if they occupy opposite sub-lattices a bandgap is created in the doped graphene [2]. In our experiments we investigate the conditions under which the wagonwheel effect occurs, the strength of the effect and the area over which it dominates, the electronic structure of graphene doped with both Nitrogen and Boron, and the effects of dopants in different sub-lattice positions on the local electronic structure of the material.

[1] J. A. Lawlor and M. S. Ferreira, Beilstein J. Nanotechnol. **5**, 1210 (2014).

[2] H. Park, A. Wadehra, J. W. Wilkins, and A. H. Castro Neto, Phys. Rev. B - Condens. Matter Mater. Phys. **87**, 85441 (2013).