

Synchrotron and STM studies of bottom-up synthesised graphene nanoribbons.

In recent years graphene nanoribbons (GNRs) have received much attention due to their remarkable structural and electronic properties. These properties vary dramatically with changes in the atomic structure of the GNR in terms of width, edge termination, dopant heteroatoms, and crystallographic symmetry. Moreover, the electronic properties can be modulated even further by the appropriate design of GNR heterostructures or by additional functionalisation. This enormous tunability of the electronic properties is thus extremely promising for next-generation nanoelectronic and optoelectronic devices. The high susceptibility of these properties to small changes in the GNR structure also indicates the need for atomic precision in GNR synthesis. To date, the bottom up synthesis, first demonstrated by Cai *et al.* [1], is the only technique offering the required level of precision. While a large range of precursor molecules have been synthesised for the bottom up synthesis of GNRs with different edge orientations, widths, or heteroatoms, only a few GNRs have been successfully synthesised with the required precision. To date, the most widely studied nanoribbon is the armchair oriented GNR with seven dimer lines across its width (7-AGNR) grown from 10,10'-dibromo-9,9'-bianthracene precursor in a multistep reaction, including dehalogenation, polymerization and cyclodehydrogenation. In this talk I discuss the effect of the structure and chemistry of the underlying metal substrate on the GNR growth process. The growth of GNRs has been followed in detail by combining core level and x-ray absorption spectroscopies, scanning tunnelling microscopy, and density functional theory calculations, thus providing a clear correlation between the spectroscopic fingerprints and the different reaction processes [2,3]. For the fabrication of functional multicomponent nano-systems the covalent bonding of organic molecules within the GNR is desirable. In this talk we also discuss an on-surface synthesis method for functionalization of GNRs with porphyrin molecules. These novel porphyrin-functionalised graphene-nanoribbons (Py-fGNRs), are expected to exhibit significantly different electronic, chemical, transport and optical properties than the GNR or Py. The versatile chemical functionality of the different transition metals within the integrated-porphyrin macrocycle (TM-Py), determines much of these electronic, optical, and chemical properties, as well as defining the transport and spin-transport properties. With STM we determine the possible distinct configurations that occur when the porphyrin couples to the GNR. These configurations are explored by DFT calculations which reveal a large reduction in the HOMO-LUMO band-gap on the porphyrin molecule.

[1] J. Cai et al., **Atomically precise bottom-up fabrication of graphene nanoribbons.** *Nature* **466**, pages 470–473 (2010). doi:10.1038/nature09211

[2] K.A. Simonov et al., **Synthesis of armchair graphene nanoribbons from the 10,10'-dibromo-9,9'-bianthracene molecules on Ag(111): the role of organometallic intermediates.** *Scientific Reports*, **8** Article 3506 (2018)

[3] K.A. Simonov et al., **From Graphene Nanoribbons on Cu(111) to Nanographene on Cu(110): Critical Role of Substrate Structure in the Bottom-Up Fabrication Strategy.** *ACS Nano*, **9**, 9 8997 (2015)