Atomically precise graphene nanoribbons through on-surface synthesis

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Graphene nanoribbons (GNRs) are a new class of materials that have promising applications in next-generation nanoelectronic, photonic and spintronic devices. GNRs have been predicted to show interesting electronic properties that depend strongly on their width and edge structure. However, the required precision cannot be achieved by top-down approaches, including e-beam lithography on a sheet of graphene or unzipping carbon nanotubes. Recently, bottom-up synthesis using molecular precursors has been shown to provide precise control over the width and edge geometry of GNRs [1]. By changing the monomer design, fabrication of a wide range of different GNRs can be achieved with engineered chemical and electronic properties.

In the typical picture of the on-surface synthesis, the substrate does not play a big role in the chemical reaction. Using low-temperature scanning tunneling microscopy (STM) and atomic force microscopy (AFM), I will show that the substrate is not always an innocent bystander in these reactions. On Au(111) surface, the prototypical precursor dibromo-bianthryl (DBBA) polymerizes via an Ullmann route to form straight GNRs with armchair edges. However, on Cu(111), the DBBA precursor forms chiral (3,1)GNRs. In contrast, dibromo-perylene (DBP) precursors do form armchair GNRs via Ullmann coupling, in close analogy to recent results on Au(111). The reaction intermediates highlight the role of the precursor shape, molecule-molecule interactions and substrate reactivity as decisive factors in determining the reaction pathway [2]. Our findings help to realize new routes for previously unattainable covalently bonded nanostructures.

The armchair GNRs can be divided into three families based on their width N: GNRs with N=3m or N=3m+1, where m is an integer, are semiconducting. On the other hand, GNRs with a width of N=3m+2 are predicted to be nearly metallic with a very small bandgap. We have synthesized N=5 armchair GNRs and studied their electronic properties in detail using low-temperature scanning probe techniques [3]. Scanning tunneling spectroscopy demonstrates that N=5 ribbons show nearly metallic behavior with much smaller bandgap than the wider N=7 GNRs belonging to the N=3m+1 family. These narrow armchair GNRs with a small bandgap would form ideal molecular wires to be used as interconnects in molecular scale circuitry. In addition mono-component GNRs, we have realized metal-semiconductor heterostructures by

joining armchair GNRs belonging to the metallic (5-atom wide) and semiconducting (7-atom wide) families through on-surface synthesis. These structures constitute the first steps towards enco ding more functionality into a single GNR for electronic applications.

[1] L. Talirz, P. Ruffieux, R. Fasel, *Adv. Mater.* **28**, 6222 (2016).
[2] F. Schulz et al., *submitted* (2016).
[3] A. Kimouche et al., *Nat. Commun.* **6**, 10177 (2015).