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Progress in Physics (37)

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Bottom-up Fabrication of Atomically Precise Graphene Nanostructures**

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Conventional top-down structuring is reaching its limitations and is currently hampering the investigation of specific graphene nanostructures where quantum confinement and hence structural variations on the atomic level govern the electronic properties. On the other hand, bottom-up approaches relying on the colligation of suitable molecular precursors allow for the fabrication of prototypical graphene nanostructures with atomic precision and make them accessible for investigation of their physical properties.

A prominent system exemplifying the intimate relation between electronic and atomic structure is given by graphene. The electronic properties of graphene, a single atomic layer of graphite, are marked by some highly intriguing values such as a high charge carrier velocity (10^6 m/s), ballistic transport properties in the micrometer range at room temperature. Together with its structural stability, chemical inertness and optical properties (graphene absorbs only 2.3% of the light in very large spectral range while offering extraordinary electrical conductance properties [1]), this is currently motivating an impressive number of investigations that seek for possibilities on how to take advantage of these properties in various application fields. From a fundamental point of view, the Dirac-like equation describing the electronic properties of graphene where the carbon atoms are arranged in a honeycomb lattice gives access to the investigation of relativistic quantum phenomena in a benchtop experiment [2].

The whole richness of possible physical properties, however, is only accessible when considering specific nanostructures of graphene, i.e. when exploring the intimate relation between structural and electronic properties on a length scale where extreme confinement and interactions govern the properties of the charge carriers. Figure 1 shows two examples of graphene nanostructures: (i) specific shapes of graphene flakes with an imbalance between the number of carbon atoms belonging to the A and B sublattices, respectively, and (ii) narrow stripes of graphene, so-called graphene nanoribbons, that are described by a specific width and direction with respect to atomic lattice. For the first example, Lieb's theorem predicts a characteristic spin S that is relying on an imbalance between the occupation of the two structural sublattices: $S=1/2(N_A-N_B)$ [3]. The ability to structurally define such an imbalance thus holds promise for the design of pure hydrocarbons with a net magnetic moment. However, it requires the ultimate, namely atomic, resolution in their structure definition. The second example, graphene nanoribbons (GNRs), reveals that for low-dimensional systems, one of the major shortcomings of graphene, the missing electronic band gap, can be created when confining the electronic states to a very narrow width. Both examples show, however, that the atomic precision is needed in order to get predictable electronic or magnetic properties. For armchair GNRs (AGNRs), for instance, the band gap disappears when extending the width of a 7-AGNR (arm-

chair ribbons with 7 carbon dimers across the width) by a single additional carbon dimer (Fig. 1c).

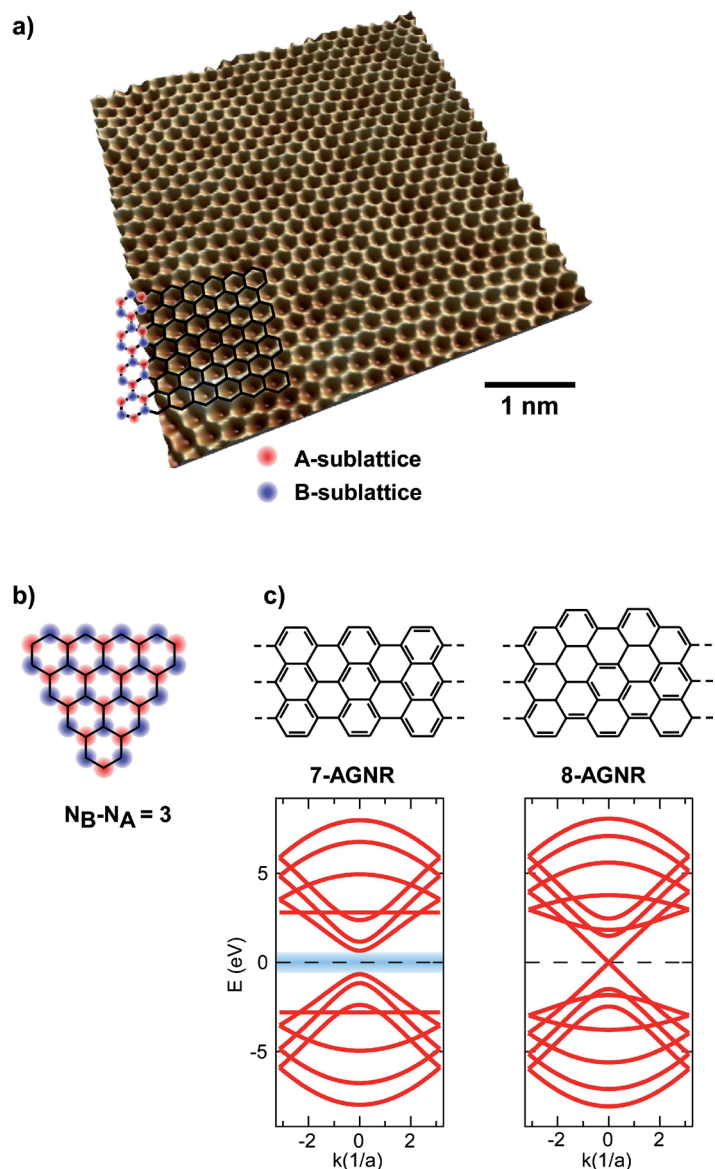


Fig. 1: Graphene-related structures. (a) Small-scale STM image of extended graphene grown on Pt(111) revealing the honeycomb-like atomic lattice. (b) Graphene nanostructure with a predicted magnetic moment due to the imbalance in the occupation of A- and B-sublattices. (c) Graphene nanoribbon structures and their respective electronic band structure (tight binding) revealing semiconducting and metallic properties for 7-AGNRs and 8-AGNRs, respectively.

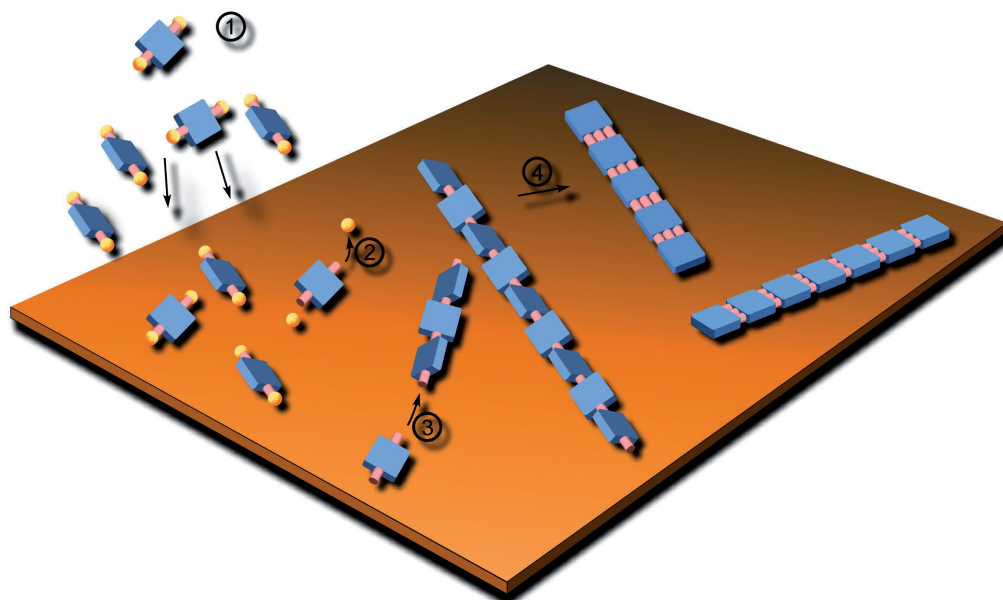


Fig. 2: Bottom-up fabrication concept for Graphene Nanoribbons: (1) Vacuum sublimation of precursor monomers on clean metal surface. (2) Surface-assisted monomer activation. (3) Oligomer formation by radical addition of diffusing monomers. (4) Planarization of the oligomer by intramolecular cyclodehydrogenation forming the final GNR.

Such resolution is, however, not accessible for traditional top-down structuring approaches. Comparing today's available resolution of e-beam lithography (10 nm) to the needed atomic precision (0.1 nm) is very much like trying to fabricate toothpicks with a motor saw. There is a factor of ~ 100 separating the actually needed and currently available structural resolution.

Bottom-up approaches, on the other hand, intend to fabricate such structures by using atomically precise building blocks, i.e. molecules or atoms, which then couple together to form extended structures with properties that are fully

dictated by the properties of the precursor monomer. In order to do so, molecular building blocks furthermore need to have specific coupling sites that can be activated by an external stimulus in order to specifically colligate to the next structural subunits. Polymer chemistry has elaborated the needed chemical tools with great success and allows nowadays for the solution-based synthesis of organic materials with a vast range of properties. In view of graphene-related structures, such as carbon nanotubes, fullerenes and graphene itself, the solution-based bottom-up approach was until now not successful. Typically, graphene-related materials are fabricated by high temperature processes where a multitude of structural variants are produced, which then need, in a second step, to be separated in order to yield the desired structure.

In 2007, the Grill group presented new concepts [5] allowing for the covalent assembly of molecular building blocks on surfaces. The work is based on the ability of introducing defined connection points onto the molecular building blocks that can be efficiently activated as soon as the molecules are adsorbed on a well-defined surface. The ability of organic chemistry to synthesize molecular building blocks with different number and relative position of predefined connection points allows for the construction of various topologies such as molecular dimers, linear molecular chains as well as two-dimensional arrays. This seminal work proved that the concept of 'molecular Lego' can be used for the fabrication of stable (since covalently bonded) and precise nano-architectures. Furthermore, this work has triggered numerous studies exploring possibilities to control specific chemical reactions on surfaces. Yet, this newly established research field of *on-surface chemistry* is not just about replicating known solution-based chemical reactions on the surface but much more about i) exploring the catalytic properties of the surface hosting the molecular species for the low-temperature activation of specific chemical reactions and ii) using the well defined conformation of molecular species adsorbed on atomically flat surfaces to get control on the activation of specific functional groups that are in close proximity to the surface, while others with larger distances remain unaffected. In a recent study [4], we have explored the possibilities of surface-assisted reactions for the bottom-up fabrication of GNRs. The main steps of the related on-surface synthesis protocol are sketched in Fig. 2. Experiments are conducted under ultra-high vacuum (UHV) conditions in order to be able to prepare and maintain clean surfaces and in order to be able to exclude reactions of the deposited molecular species with residual gas. The fundamental steps include (1) deposition of the molecular precursor on the metal surface by vacuum sublimation, (2) surface-assisted precursor activation by a first

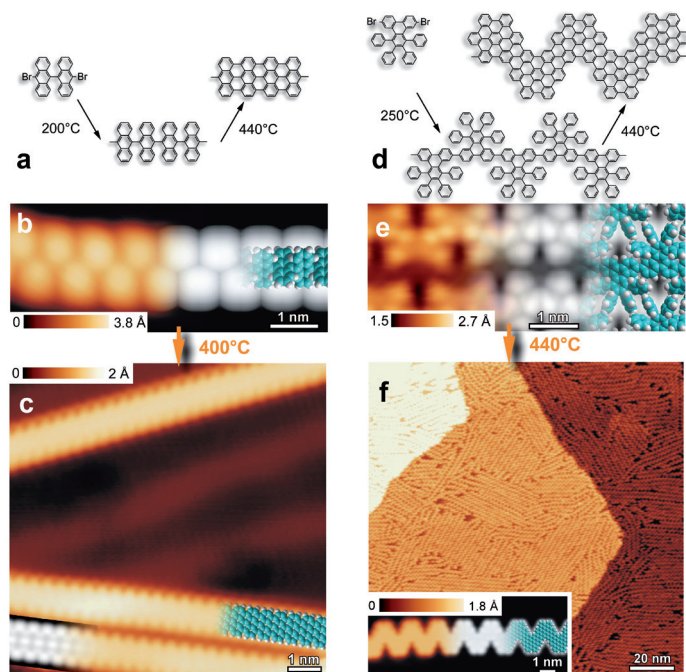


Fig. 3: STM images of the intermediate (top) and final step (bottom) during the bottom-up synthesis of two different types of GNR. (left) Fabrication of 7-AGNRs using a bianthryl-based precursor monomer. (right) Synthesis of chevron GNRs. Greyscale inserts are DFT-based simulations of STM images of the polymer and ribbon structures [4].

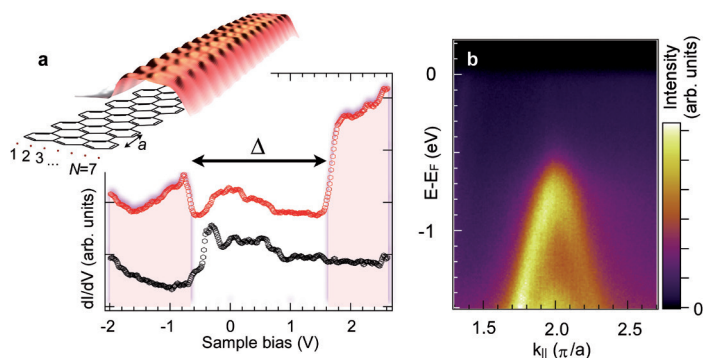


Fig. 4: Electronic structure determination of as-grown 7AGNRs. (a) Scanning tunneling spectra taken on the metal substrate (black) and on a GNR (red) revealing an electronic band gap Δ of 2.3 eV. (b) Angle-resolved photoemission spectroscopy of aligned 7-AGNRs. The highest occupied band is characterized by a low effective mass of $0.21 m_0$ and large slopes (and hence large charge carrier speeds of $8 \cdot 10^5$ m/s) in the linear band segments [6].

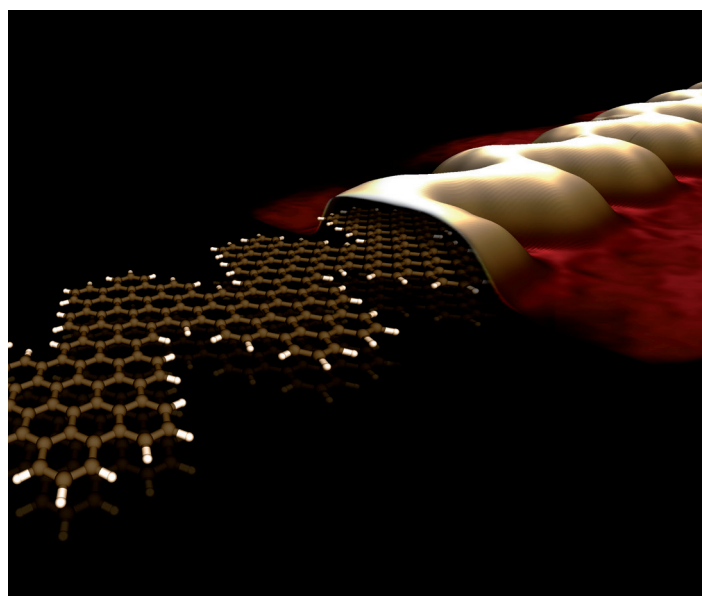
annealing step producing biradical species that (3) by diffusion along the surface covalently couple to each other by a radical addition process to form extended one-dimensional oligomers. For GNRs, an additional dehydrogenative step is necessary in order to transform the oligomers with single C-C bonds between the building blocks into the flat GNRs (4). It is clear that in order to follow and characterize the individual bottom-up fabrication steps, a method capable of resolving molecular conformations and separations with atomic resolution is needed. Scanning Tunneling Microscopy (STM) is ideally suited to give the needed insights in order to address possible unwanted reactions by changing reaction parameters or monomer design in order to get the desired GNR structure. STM images of intermediate and final structure of two different types of GNR [4] are shown in Fig. 3 and reveal that the bottom-up approach indeed allows for the targeted atomic precision of GNR fabrication. Accordingly, some prototypical GNR structures are now available for investigation of their electronic properties and to compare them to theoretical predictions. In a recent study [6], we determined the electronic structure of 7-AGNRs by means of Scanning Tunneling Spectroscopy and Angle-Resolved Photoelectron Spectroscopy (Fig. 4) and find a sizable band gap of 2.3 eV and a band dispersion that is in excellent agreement with theoretical predictions.

It is clear that similar fabrication strategies can also be used for the design of two-dimensional nanostructures. Examples along this direction are porphyrin-based nanoarchitectures [7], the synthesis of porous graphene [8] and triphenylamine-related macromolecular structures [9] that are all based on the activation and colligation of halogen-substituted precursor monomers. In order to reach even more diverse and complex bottom-up grown nanostructures, new types of on-surface reactions are currently investigated in different labs. These reactions include various dehydrogenation steps, imide and amide bond formation as well as Sonogashira coupling (for an overview see Refs. [10-12]) and show promise to establish a toolbox allowing for the surface-assisted fabrication of a rich variety of precise nano-architectures.

Future studies will furthermore have to tackle the problem of the metallic substrate that is currently needed as a catalyst for most of the used reactions. For the fabrication of prototypical devices relying on electronic or optoelectronic properties of the fabricated nanostructures it will thus be crucial to develop efficient but yet gentle process protocols allowing for their transfer onto insulating substrates.

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Bottom-up fabrication of atomically precise graphene nanoribbons. 3D representation of a scanning tunneling microscopy image and chemical structure of a chevron graphene nanoribbon. © Empa.