August, 27th 2013 - “The paper by Angelova et al. has demonstrated that, starting from a library of broadly similar self-assembled monolayer molecules, it is possible to tailor the properties of carbon nanomembranes, for example, to produce ultrathin films with or without nanopores. The cross-linking between the molecules in the SAM derives from the selective breaking of molecular bonds under low-energy electron-beam irradiation. Instructive insight is provided into how researchers are pulling together complementary strands from a quarter century of nanoscience research to develop novel, hybrid processing schemes” (Ref. 1).

A novel method to form CNMs and graphene sheets

Graphene from self-assembled monolayers of aromatic molecules: How nanoscience translates into technology

Researchers from University of Bielefeld have extended the investigation of 1,1'-biphenyl-4-thiol (BPT) by Eck et al. 2005 (Ref. 3) to numerous aromatic molecules. They have been self-assembled on a surface - laterally cross-linked by low-energy electrons - and partially removed from the surface leaving 1 nm thick Carbon Nanomembranes (CNMs). The thickness, homogeneity, presence of pores and surface chemistry of...
the CNM are determined by the nature of the initial molecular monolayer. When these CNMs are pyrolized at ~1000 K, they transform into graphene, see for example Figure 1a-c. For a detailed analysis of the transformation of the precursor BPT, which belongs to group (1) in Fig. 1d, into atomically perfect graphene, see (Ref. 4-6).

Researchers from University of Ulm have imaged the atomic structure of the CNMs by aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) at 80 kV, after annealing at 900 °C, see Figure 2. Figure 2a shows one of the thinnest CNMs (0.8 nm, see Fig. 1d, molecule-type 3a) after annealing. Most of the sheet area consists of single-layer graphene (~50%, light blue color coded) with the clearly recognizable hexagonal arrangement of carbon atoms; randomly oriented graphene nanocrystallites are connected with each other via the typical heptagon-pentagon grain boundaries (see inset to Fig. 2a). A small fraction of the sheet (~20%, light green color coded) consists of graphene double-layers, which reveals the respective moiré pattern (Ref. 7).

Grey and light red areas correspond to the disordered carbon and holes, (green) and heptagons (blue) are marked, respectively. The thickness of the formed graphene sheets depends on the structure of precursor molecules, their abilities to form SAM and to be cross-linked into CNMs. As seen in Fig. 2b-g, graphene sheets from various precursors have the same nanocrystalline morphology as in Fig. 2a; however, their thickness varies by a factor of ~3 depending on the precursor. This visual impression was confirmed by measuring the film thickness by quantitative Electron energy loss spectroscopy (EELS) at the carbon K absorption edge (Ref. 8). See for more detail Table S2 from the Supplementary Information.

Researchers from the MPI Mainz concern themselves with the chemistry and the nature of graphene in general (Ref. 9), while Andreas Terfort from the University of Frankfurt has a special focus on SAMs and their spontaneous formation and property change on surfaces (substrates). In this study, the synthesizing of the molecules took place at these two workgroups. They have synthesized three types of thiolbased molecular precursors with different chemical structures: (1) non-fused oligophenyl derivatives; (2) condensed polycyclic precursors; and (3) "bulky" molecules. The different chemical structures of the molecules are shown in Fig. (1d): 2c-f and 3a-c, MPI Mainz, Fig. (1d): 1c and 2b, University of Frankfurt, Germany.

References:
6. Note that the publication by Matei et al. 2013, Ref. 4 has been selected as the front cover of Advanced Materials, 25, 2013.