

STM identification of N-doped nanoarchitectures formed by on-surface (cyclo)dehydrogenation of heteroaromatics

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Abstract

Surface-assisted cyclodehydrogenation and dehydrogenative polymerisation of polycyclic (hetero)aromatic hydrocarbons (PAH) are among the most important strategies for bottom-up assembly of new nanostructures from their molecular building blocks [1]. Although diverse compounds have been formed in recent years using this methodology, a limited knowledge on the molecular machinery operating at the nanoscale has prevented a rational control of the reaction outcome. By controlling the diffusion of N-heteroaromatic precursors, the on-surface dehydrogenation can either lead to monomolecular triazafullerenes [2] and diazahexabenzocoronenes (N-doped nanographene), to N-doped oligomeric or polymeric networks, or to carbonaceous monolayers [3]. Governing the on-surface dehydrogenation process is a step forward towards the tailored fabrication of molecular 2D nanoarchitectures distinct to graphene and exhibiting new properties of fundamental and technological interest.

A significant progress in this area has been enabled by ultra-high vacuum scanning tunneling microscopy (UHV STM), which is a suitable technique for imaging nano-objects with ultimately intramolecular resolution. In this work we combine advanced in-situ surface characterization techniques as STM, near edge x-ray adsorption fine structure (NEXAFS) and high-resolution x-ray photoemission spectroscopy (XPS) with theoretical ab-initio calculations including van der Waals (vdW) forces to yield a complete understanding of the self-assembling of molecular precursors on surfaces.

Particularly, in this contribution we show that an adequate combination of STM experimental images with theoretical ones calculated using a Keldysh–Green function formalism, together with the first-principles tight-binding Hamiltonian obtained from the local-orbital DFT-Fireball method allow us to present a chemical route for the transformation of a molecule upon dehydrogenation. The theory-experiment agreement in the apparent height determination of STM features from different molecular nanostructures can be a valid methodology for identification at the nanoscale.

References

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Figures

