Resolving the complex structure of molecular networks

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Abstract
The arrangement of molecules in molecular networks determines their physical and chemical properties. Addressing this fundamental issue requires proper structural characterization tools. Due to an overlap, interdigitation, tilting or stacking of molecules revealing the structure of the networks is challenging. Tebi et al (2015 Nanotechnology 27 025704) developed a clever approach that enables accessing the arrangement of individual molecules in complex chemical networks. The proposed method utilizes imaging and manipulation with scanning tunneling microscopy.

Keywords: molecular network, atomic structure, corrole, STM, manipulation

Often we see parts of reality, but cannot identify what they are. Perhaps the most representative example of this issue is complex molecules and molecular networks formed on crystal surfaces. To take advantage of such structures and make significant progress in various areas of science and nanotechnology, like molecular electronics, catalysis, sensors, and biomedicine [1–4], the understanding of structural and electronic properties of complex molecular networks is required. The molecular packing and the arrangement of individual molecules with respect to each other and relative to the substrate’s atomic structure, dominated by the delicate balance between intermolecular and molecule–substrate interactions, determine the physical and chemical properties of such nanostructures [5–7]. This is a fundamental concept in chemistry and in the molecular sciences.

To characterize the structure of molecular networks advanced experimental methods must be employed. Usually, these include diffraction, optical and scanning probe techniques. In particular, scanning tunneling microscopy (STM) [8] and atomic force microscopy (AFM) [9] are the most widely used for the structure characterization. The development of these tools has provided us with the remarkable ability to observe nanoscale objects at the atomic level, manipulate and shape them [10–12].

Although imaging of single atoms and molecules adsorbed on crystal surfaces with STM is today a common practice, STM suffers from a serious drawback—it cannot resolve complex chemical structures. The major barrier to accessing detailed information on the structure results from the nature of tunneling phenomena and probing by STM the local density of states in the vicinity of the Fermi level, while details of a chemical structure are determined by bonding utilizing low-lying energy states. Thus the imaged molecules usually appear as blurred blobs. In this respect, AFM is superior to STM, as it probes the total electron density, and indeed, the inner structures of molecules have been demonstrated [13, 14]. Nevertheless, many attempts to cure the problem of STM have been made, and a better ability to resolve the internal structure of molecules has been achieved. It turns out that functionalization of the tip apex by single atoms or simple molecules substantially improves the STM resolution of chemical structures [14–17].
When individual molecules are packed densely into more complicated structures, like molecular arrays or networks, the resulting objects feature the next level of complexity, and additional difficulties arise. Due to a partial overlap, interdigitation, tilting or stacking of molecules, their arrangement within the networks often becomes complex and highly non-trivial. Attempts to determine the geometry of individual molecules within the networks using a standard STM technique are extremely challenging and most often fruitless. At best, STM topography can reveal the size and shape of the surface unit cell, like for example in the case of self-assembled monolayers of molecules [18, 19]. Of course, using functionalized tips may circumvent the limitations of the standard STM method. However it also has several drawbacks, for example the instability of tunneling junctions or very long acquisition time, which somewhat limits the applicability of this approach to structural investigations.

In issue 2 of Nanotechnology, Tebi et al presented an alternative method that resolves the structure of molecular networks readily [20]. As an example, they studied a network composed of a monolayer of 5, 10, 15-tris(pentafluorophenyl)-corrole (TpFPC) molecules adsorbed on Ag(111) surface. They were able to determine the size and shape of the surface unit cell as well as the relative positions and orientations of individual corrole molecules within this cell.

Their method is very clever, elegant, and at the same time as simple as one could imagine. It combines constant current STM imaging and lateral manipulation. In the first step of their method, the constant current STM topography of the surface containing the TpFPC network was recorded. Then the manipulation procedure was launched. The STM tip was moved over a selected molecule, and switched to manipulation parameters (higher tunneling current). Next the tip was displaced along a defined trajectory to the region outside the network, i.e. where the bare, uncovered Ag(111) surface exists. This procedure allows one to detach and displace a single molecule at a time, and its success rate is around 75%. The moved molecule remained intact, but its final orientation was not controlled. After manipulation the STM imaging parameters were restored and the topography of the same region of the surface was recorded again. In the next step, a pixel-to-pixel subtraction of the STM topography images before and after manipulation was performed. In this way a topography image of the individual corrole molecule within the network, before its removal, was obtained. Thus, the difference image allows one to precisely identify the position and orientation of the individual molecule within the network and relative to the substrate.

As a result of their study, the crystal basis of the primitive lattice cell of the molecular network of TpFPC on Ag(111) surface was revealed. The basis consists of two molecules with different orientations. The obtained results have been confirmed by their density functional theory calculations, and the agreement is very satisfactory. The present study shows that the arrangement of TpFPC molecules on the Ag(111) surface is non-trivial, and features partial overlap, tilting and stacking of the molecules.

The work by Tebi et al develops a new method to access the structure of individual molecules arranged into complex chemical networks. The authors expect that their technique can successfully be applied to other nanostructures composed of various molecules that are interesting from the point of view technological applications. Indeed, knowledge of the structure of such molecular networks is crucial for several research areas in the field of nanotechnology, including molecular electronics, catalysis, sensors, biomedicine, and others. To achieve a substantial progress in such imaging, however, further investigations are required. In particular, the measurements by Tebi et al were performed at cryogenic temperatures, since the problem of the thermal drift is crucial for this approach, and getting a reliable pixel-to-pixel difference image at higher temperatures may be an issue.
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References