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ATOMIC FORCE MICROSCOPY

A high-resolution molecular photo-shoot

> The next natural step was to try our more rigid CuOx tip to solve some of the fundamental problems in sub-molecular imaging

Atomic force microscopy (AFM) is one of the most popular techniques for imaging molecules. However, the atomic-scale resolution of the images is highly affected by the atomic composition and structure of the microscope's tip. Although it is important to passivate a metallic tip in order to scan a surface safely, sometimes the flexibility of the tip may give rise to artefacts such as spurious bonds. Obtaining highly realistic molecular images is important to probe surface chemical reactions or molecular self-assembly driven by weak molecular interactions. In a study published in *Nature Nanotechnology*, Harry Mönig and co-workers use an oxygen-terminated copper tip (CuOx tip) to image organic molecules at high resolution, which enables the previously elusive quantitative measurements of molecular interactions.

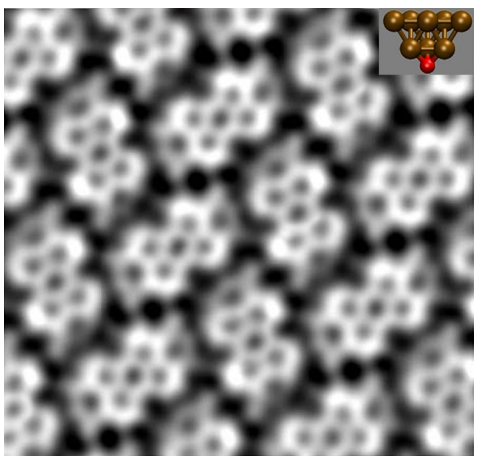
The central component of an atomic force microscope is the atomically sharp tip, which scans a surface while attached to an oscillating cantilever. The forces between the tip and the surface are affected by the nature of the tip and cause the cantilever to experience variations in its oscillations, which are converted into images. One cannot bring a pure metallic tip too close to a surface because the molecules on the surface could be displaced or become attached to the tip. If a metallic tip is passivated with a CO or Xe molecule, it can safely come nearer to the surface, thereby enabling organic molecules to be imaged at unprecedented resolution. "However, the weak bond between the CO molecule and the tip makes the assembly flexible. This flexibility can distort images, lead to overestimation of bond lengths and, in some cases, bond artefacts," says Mönig.

Previous work by Mönig and co-workers involved simulating AFM and standard tunnelling microscopy (STM) images assuming tips of different atomic compositions and structures. Oxygen-terminated copper tips were found more frequently when comparing simulations and experiments. "The trigonal pyramidal nature of the O–Cu bonds makes the CuOx tip relatively inert and mechanically stable," clarifies Mönig. "The next natural step was to try our more rigid CuOx tip to solve some of the fundamental problems in sub-molecular imaging."

The CuOx tip was first tested on a C_{60} molecule, giving sub-ångstrom agreement between predicted and experimental C–C bond lengths. These data represent a remarkable improvement on previous measurements using more flexible tips, which overestimated the bond lengths by 80% with respect to predictions. Furthermore, the more flexible tips gave rise to a spurious bond-like feature not observed in images obtained with the CuOx tip. Bond artefacts have also been observed between the two S atoms of the dibenzo[*a*,*h*]thianthrene molecule when AFM measurements were performed using a CO-terminated Cu tip. In contrast, the two S atoms appear as two individual maxima when a CuOx tip is used. Finally, the CuOx tip also gave rise to surprisingly good contrast for weak intermolecular interactions, such as hydrogen bonds between the perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) molecules. "Although the CuOx tip is at least one order of magnitude more rigid than a CO-terminated tip, the hydrogen bonds between PTCDA molecules appear at a similar or even slightly higher intensity compared to images acquired using CO tips, excluding tip flexibility as origin of these features," explains Mönig.

Despite these impressive results, several aspects of the imaging mechanism remain unclear. "It is surprising that the very small charge redistribution associated with a hydrogen bond formation leads to relatively strong AFM contrast," points out Mönig. "I believe that further studies could provide fundamental insights into the complexity of hydrogen bonds, which involve electrostatic effects, covalent contributions, electron correlation effects, directionality and polarizability effects, some of which are challenging to be described theoretically."

Gabriella Graziano



Credit: Adapted from Monig, H. et al. (2018), Macmillan Publishers Limited

ORIGINAL ARTICLE Mönig, H. et al. Quantitative assessment of intermolecular interactions by atomic force microscopy imaging using copper oxide tips. *Nat. Nanotechnol.* https://doi.org/10.1038/s41565-018-0104-4 (2018)
FURTHER READING Mönig, H. et al. Understanding Scanning Tunneling Microscopy Contrast Mechanisms on Metal Oxides: A Case Study. *ACSNano*. https://doi.org/10.1021/nn4045358 (2013)