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TWO GOOD THINGS THAT ARE BETTER TOGETHER: STM AND X-RAY SYNCHROTRON MICROSCOPY

Over the past three decades, scanning tunneling microscopy (STM) has rapidly become a major component of the condensed matter physics toolbox. While STM can provide vast quantities of data about the electronic, structural, and magnetic properties of materials at atomic resolution, its Achilles heel is its inability to characterize elemental species. But a team from Argonne and Ohio University has found a way around this limitation by combining STM with the spectroscopic versatility of synchrotron x-rays, achieving chemical fingerprinting of individual nickel clusters on a copper surface at a resolution of 2 nm (Fig. 1), creating a powerful and versatile nanoscale imaging tool with exciting promise and potential for the materials and biological sciences.

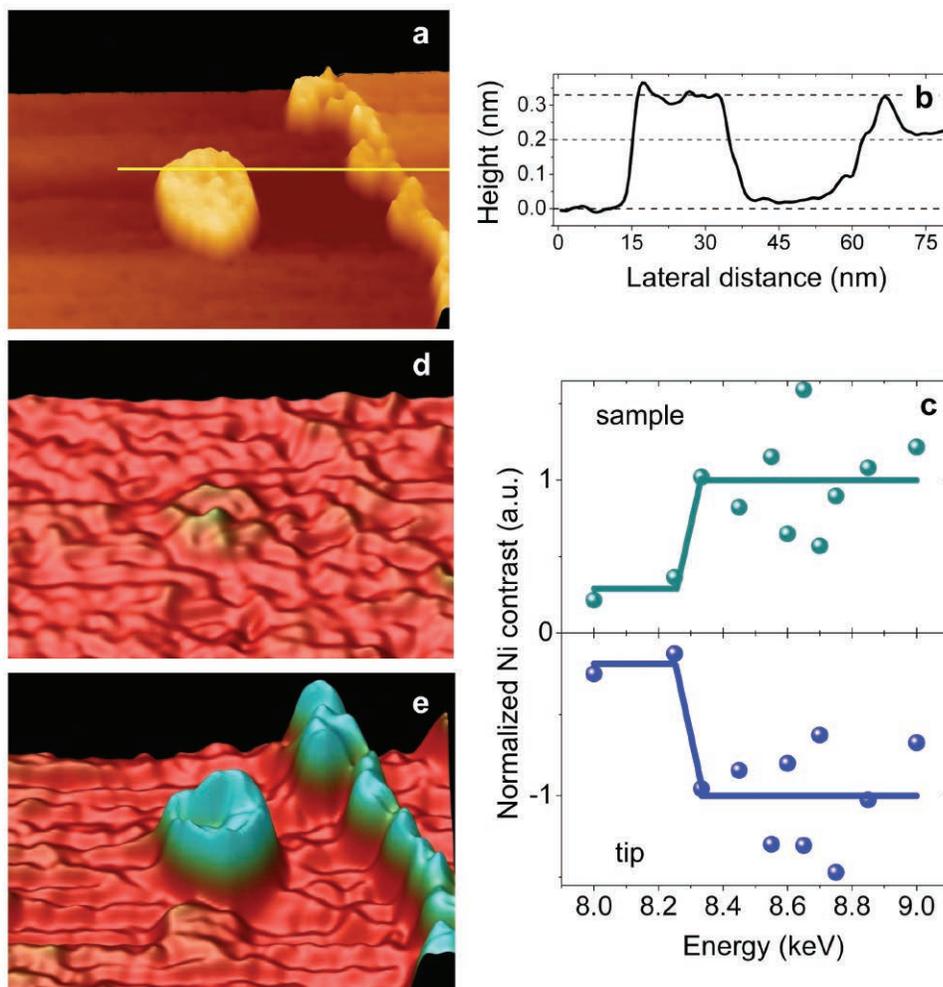


Fig. 1. Localized x-ray cross-section of a Ni island. (a) Perspective three-dimensional view of a STM topography scan ($110 \times 60 \text{ nm}^2$, -1 V , 1 nA). (b) Height profile of the line shown in the topography scan. (c) X-ray cross section of a single Ni island obtained from $I^{x\text{-ray}}_{\text{sample}}$ (top) and $I^{x\text{-ray}}_{\text{tip}}$ (bottom). (d) Sample current $I^{x\text{-ray}}_{\text{sample}}$ does not provide chemical contrast, when the x-ray energy ($E = 8.25 \text{ keV}$) is below the Ni K-edge (8.33 keV). (e) The Ni island on the Cu(111) terrace and islands along the Cu step edge become clearly visible for photon energies above the Ni K-edge, here $E = 8.55 \text{ keV}$. Figures from N. Shirato et al., *Nano. Lett.* **14**(11), 6499 (2014). © 2014 American Chemical Society

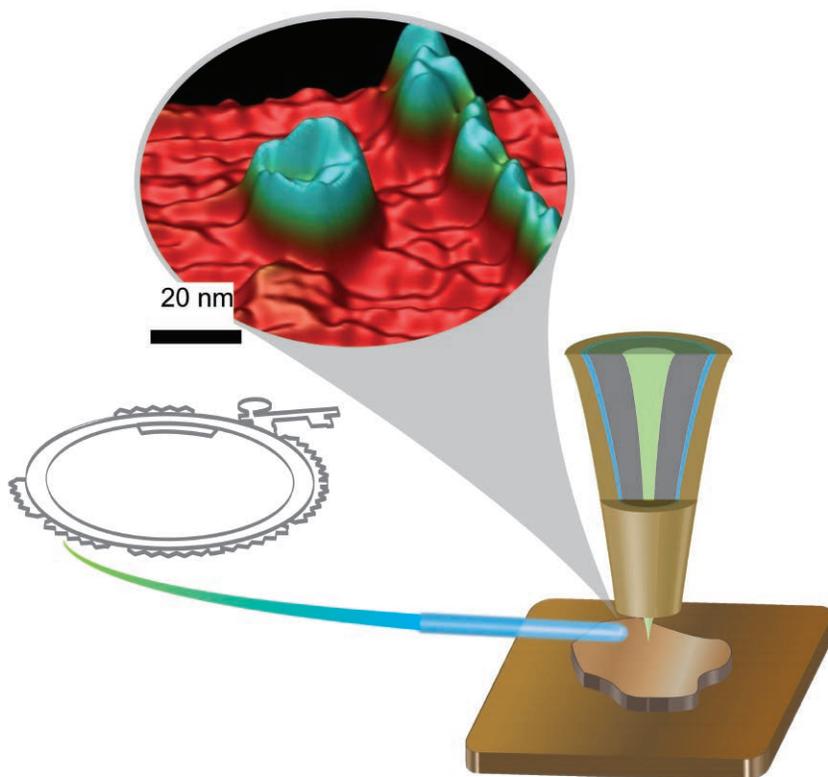


Fig. 2. A diagram of the imaging setup, featuring the STM “smart tip” and an image of Ni clusters (green) on the Cu surface (red).

Working at the CNM/XSD 26-ID-C beamline at the APS, the researchers took advantage of some new technological innovations developed by Argonne researchers.

However, the team had to overcome some experimental hurdles to combine STM with synchrotron x-rays. The resolution and sensitivity of STM can be adversely affected by photoejected electrons from the sample interfering with the measurement of tunneling effects. The Argonne researchers invented and patented a nanofabricated “smart tip” for the scanning tunneling microscope that sharply focuses detection of electrons solely to those collected at the scanning tip where it interacts with the sample, ignoring the background electrons from the side-walls of the tip (Fig. 2). The various coatings for the smart tip were grown at the Center for Nanoscale Materials (CNM) at Argonne. Then, focused ion beam milling at the CNM Electron Microscopy Center at Argonne was used to expose the tip apex.

The team also developed a filter circuit that separates the chemical and magnetic data from the x-ray-induced currents and topographical data from

conventional tunneling effects into two channels, allowing them to be recorded separately without mutual interference.

Using the markedly enhanced resolution and sensitivity made possible with these advances in synchrotron x-ray tunneling microscopy (SX-STM), the Argonne/Ohio University experiment team analyzed nickel clusters deposited on a copper surface. Usually, because chemical fingerprinting using x-rays is based on photoionization cross sections, such measurements are averaged over a rather wide surface area and depth. But the new technique was able to image and obtain a photoionization cross section of a single nickel cluster on the sample surface with 2-nm resolution.

The team demonstrated a world record in the spatial resolution of chemical imaging using synchrotron x-ray scanning tunneling microscopy, with tremendous impact for many scientific areas including materials science, chemistry, and energy materials.

Both that remarkable resolution and the precise chemical fingerprinting of individual nickel nanoclusters were also clearly evident in the topographic images of the sample surface, even

down to the height of a single atom. The experimenters note that the thickness of individual clusters appears to have no effect on the contrast intensity of their chemical signature. They suggest that because tunneling is a local effect sensitive only to the topmost layer of materials, this phenomenon as observed topographically results from the tunneling of x-ray excited photoelectrons from states between the Fermi level and the work function.

While the current experiments were conducted at room temperature, the researchers anticipate achieving the same resolution of SX-STM at far lower temperatures.

Even in its present form, the techniques demonstrated here can revolutionize nanoscale imaging in realms far beyond materials science, including electronics and biology. By overcoming the inherent limitations of both STM and x-ray microscopy, this new work has also combined the strengths of each to create a powerful and versatile imaging tool with an exciting promise and potential. — *Mark Wolverton*

See: Nozomi Shirato¹, Marvin Cummings¹, Heath Kersell², Yang Li², Benjamin Stripe¹, Daniel Rosenmann², Saw-Wai Hla^{1,2**}, and Volker Rose^{1*}, “Elemental Fingerprinting of Materials with Sensitivity at the Atomic Limit,” *Nano Lett.* **14**(11), 6499 (2014). DOI: 10.1021/nl5030613

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