

**Atomic-scale Origin of the Enantioselective Decomposition of Tartaric Acid on Chiral
Copper Surfaces**

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Experimental Methods

To prepare the Cu(110) \pm 14° S⁴C, a Cu(110) single crystal (Monocrystals Inc.) that was ~10 mm in diameter and 2 mm thick was sent to a nanomachining service (Empire Precision Plastics, Rochester, NY) where a single-point diamond tipped lathe fabricated the single crystal into a spherical dome with a radius of curvature of 21 mm. Vacuum braising was used to mount the Cu(110) \pm 14° S⁴C onto a 14x14x3 mm³ Cu block. For STM, Ta screws drilled through the Cu block secured the sample to a Ta sample plate.

The XPS experiments are discussed in detail in a previous manuscript.¹ Briefly, experiments were conducted in a ThermoFisher ThetaProbe spatially resolved XPS instrument. The coverage of TA was measured as a function of isothermal heating time at 433 K at 169 different points on the S⁴C. The O 1s signal was used to determine the TA coverage. At each collection point, the coverage of TA was calculated by taking the ratio of the O 1s signal at that time divided by the initial O 1s signal and corrected for the remaining O 1s signal when the reaction was complete. In this way, time-dependent maps of location-specific TA coverage were constructed.

STM experiments were conducted in an Omicron Nanotechnology variable-temperature (VT) ultra-high vacuum (UHV) STM with a separate preparation chamber (base pressure <1.0 x 10⁻⁹ mbar) and STM chamber (base pressure <2.0 x 10⁻¹¹ mbar). The Cu(110) \pm 14° S⁴C was cleaned by repeated cycles of Ar ion bombardment with a cold cathode sputter gun (~5 μ A drain current and 1.0 keV beam energy) and ~700 K thermal annealing. A saturated monolayer of L- or D-TA acid was deposited using an organic material dual cluster source solid doser (MBE-Komponenten), heating the crucible to ~400 K, depositing L or D-TA for 30 min on the Cu(110) sample held at room temperature, and then annealing to 405 K for 1 min to desorb any TA multilayers. To reproducibly approach the STM tip to a given spot on the Cu(110) \pm 14° S⁴C, the computer screen that displays the sample for tip approach was equipped with a grid that was constructed with polar coordinates and fit to the optical image of the Cu sample. More details on this procedure can be found in our previous manuscript.² STM images were acquired at room temperature with an Omicron Nanotechnology etched W tip. For the clean Cu(110) \pm 14° S⁴C images, typical scanning conditions were 200 mV bias and 200 pA tunneling current. Typical scanning conditions for L- or D-TA overlayers on the sample were 500 or -500 mV and 10 – 100 pA.

S.I. 1. Characterization of the Clean Cu(110) \pm 14° S⁴C

To ensure that the Cu(110) \pm 14° S⁴C was properly fabricated, STM images of the clean surface were acquired at multiple positions across the sample as shown in Figure S.I. 1.

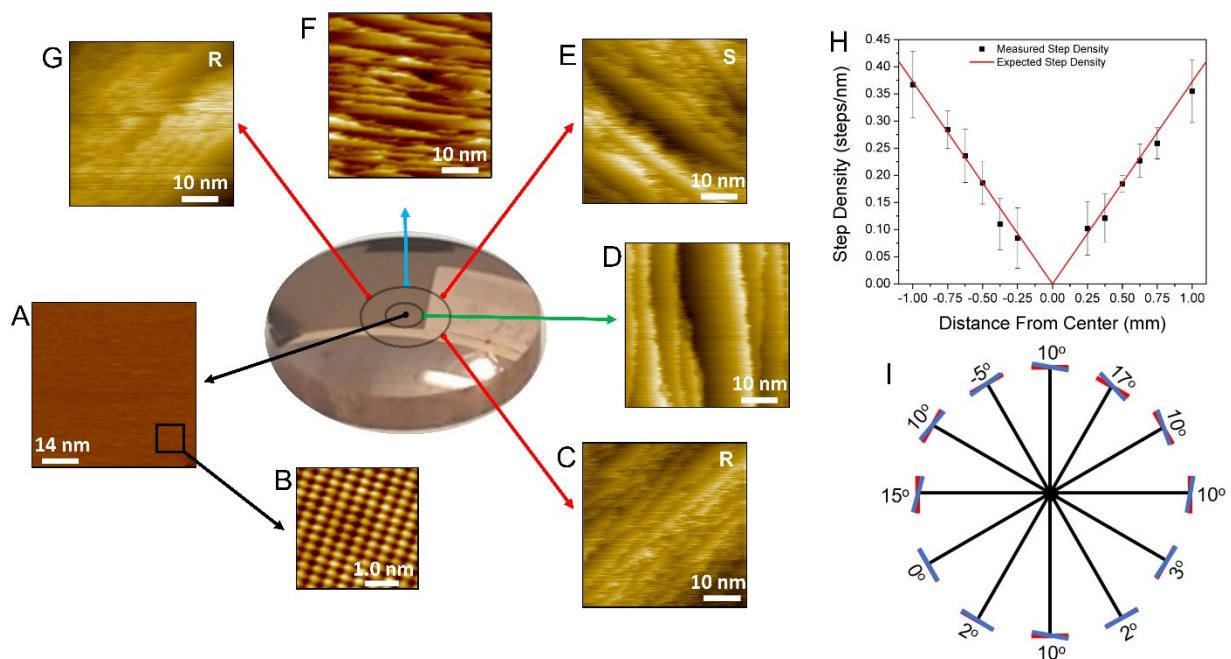


Figure S.I. 1 – Characterization of the clean Cu(110) S^4C . A & B) Large scale and small scale STM images at the center of the S^4C , respectively, where the flat 110 terraces are largest and atomic resolution imaging of the surface revealed the Cu(110) facet. C-G) STM images at various locations about the center of the sample where step density increases with increasing distance from the center of the sample and the surface step edge orientation follows the curvature of the S^4C . H) Measured step density vs. expected step density as a function of distance from the crystal pole with error bars being the standard deviation of the step density at a given location. I) Surface step edge orientation at various positions 0.5 mm from the pole where red and blue bars represent the expected and measured step edge orientation, respectively, and the numbers indicate the error between expected and measured step edge

These data demonstrate that the center of the Cu(110) S^4C exhibits the largest terraces and atomic resolution of the Cu(110) facet is observed. Figure S.I.1H shows how the surface step edge density increases further from the flat (110) pole. Figure S.I.1I demonstrates the step edge orientations (angles) run at a tangent to the line from the center of the sample to that step edge. Together these data indicate that the surface step edge density and their orientation in the regions of interest to this study are as would be expected from the doomed shape of the S^4C .

S.I. 2. Large Scale STM imaging at 2.0 mm from the center of the sample and TA unit cell at 1.5 mm from the center of the sample

While the most enantiospecific facet of the S^4C , Cu(14 17 2) is 2.75 mm from the center of the sample, STM images shown in the manuscript were acquired at 1.5 mm from the center of the sample. This allowed for better resolution of the surface step edges. However, the following STM image demonstrates that restructuring of the surface occurs around the enantiospecific region of the sample. Additionally, to ensure the TA overlayer persisted further out on the

sample, molecular resolution imaging of the surface revealed that the same unit cell for a saturated monolayer of TA still persists at 1.5 mm from the center of the sample.

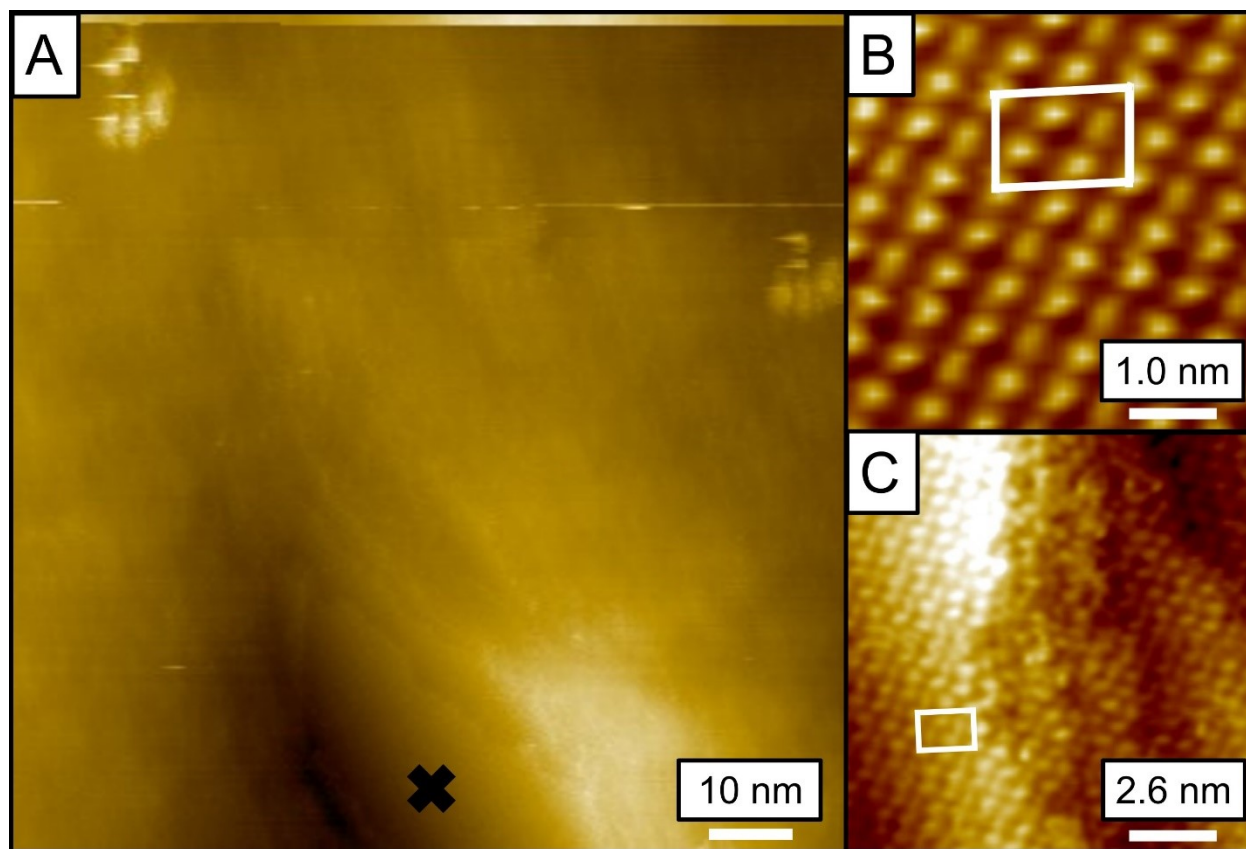


Figure S.I. 2 – A) Large scale STM image of the L-TA overlayer on S chirality quadrant 2.0 mm from the center of the sample where large terraces (black cross) are still seen as a result of step bunching. B) Molecular resolution of L-TA overlayer as shown in Figure 2F. C) Molecular resolution of L-TA overlayer 1.5 mm from the center of the sample. White rectangle indicates the unit cell.

References

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