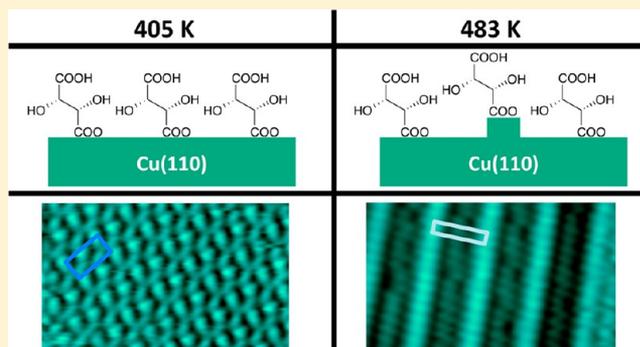


Long Range Chiral Imprinting of Cu(110) by Tartaric Acid

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ABSTRACT: Restructuring of metals by chiral molecules represents an important route to inducing and controlling enantioselective surface chemistry. Tartaric acid adsorption on Cu(110) has served as a useful system for understanding many aspects of chiral molecule adsorption and ordering on a metal surface, and a number of chiral and achiral unit cells have been reported. Herein, we show that given the appropriate annealing treatment, singly deprotonated tartaric acid monolayers can restructure the Cu metal itself, and that the resulting structure is both highly ordered and chiral. Molecular resolution scanning tunneling microscopy reveals that singly deprotonated tartaric acid extracts Cu atoms from the Cu(110) surface layer and incorporates them into highly ordered, chiral adatom arrays capped by a continuous molecular layer. Further evidence for surface restructuring comes from images of atom-deep trenches formed in the Cu(110) surface during the process. These trenches also run in low symmetry directions and are themselves chiral. Simulated scanning tunneling microscopy images are consistent with the appearance of the added atom rows and etched trenches. The chiral imprinting results in a long-range, highly ordered $\left(\frac{2}{6} \frac{-1}{7}\right)$ unit cell covering the whole surface as confirmed by low energy electron diffraction. Details of the restructuring mechanism were further investigated via time-lapse imaging at elevated temperature. This work reveals the stages of nanoscale surface restructuring and offers an interesting method for chiral modification of an achiral metal surface.



■ INTRODUCTION

The enantioselective production of chiral compounds and enantiospecific separation of the enantiomers of chiral compounds are of critical importance to the pharmaceutical, agricultural, and food industries that require enantiopure materials.^{1–3} To generate chiral compounds without the use of costly resolving agents, enantioselective catalysts or separators, ideally being heterogeneous versus homogeneous, are required. Even though the benefits of heterogeneous asymmetric catalysts are clear, few examples exist in the literature, and the mechanism for enantioselectivity is not well understood, therefore, further study of chiral catalysts themselves, in parallel with study of enantiospecific surface chemistry on well-defined model systems is warranted.^{1,4–17} One method for obtaining well-defined enantioselective surfaces involves preparation of intrinsically chiral metal surfaces.^{8,18–21} Intrinsically chiral metal surfaces are formed when a single crystal is cut along a low symmetry, high Miller index plane exposing terraces, step edges, and chiral kink sites. Studies have shown that these surfaces are enantiospecific because chiral molecules have different reaction rates, desorption temperatures, and adsorption energies on the two surface enantiomers.^{19,20,22} While these surfaces demonstrate

the possibility for chiral surface chemistry and are ideal for understanding enantiospecific molecule-surface interactions, it would be a challenge to synthesize intrinsically chiral metal surfaces with a high surface area. A second very common method for rendering a surface chiral, with potentially easier scale-up, involves the adsorption of chiral molecules onto achiral metal surfaces.^{6,8,13,23–41} However, while adsorbing molecules onto a surface can produce asymmetry by creating a chiral surface template exposing chiral pockets, these layers require large flat areas of the metal surface to support ordered arrays which may not be formed on metal nanoparticles. A related approach of using molecules to chirally modify the structure of the metal substrate itself offers a potentially more practical method for inducing chirality in a catalytic substrate. Despite this advantage, there are few examples of this type of restructuring of the underlying metal surface, called chiral imprinting.^{32,33,42–47} Some key studies of the chiral imprinting

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of well-defined single crystal surfaces include the adsorption of L-lysine on Cu(100)^{32,33,44} and HtBDC on Cu(110).⁴⁶ Upon adsorption, the enantiopure amino acid L-lysine reorganizes the achiral Cu(100) surface to form chiral Cu(3 × 1 × 17)^R facets of a single handedness. On Cu(110), HtBDC molecules self-assemble into rows and in doing so pull Cu atoms from the surface layer. This was verified by removal of the molecules with the scanning tunneling microscope (STM) tip to reveal chiral trenches in the surface underneath the molecules. A few tantalizing examples of chiral imprinting of metal nanoparticles also exist.^{42,43,45,47–49} In a recent study by Pachón et al., it was demonstrated via photoelectron emission that it was possible to synthesize Pd nanoparticles in the presence of a chiral modifier and render the nanoparticles chiral. It is thought that the modifier imprints its chirality onto the nanoparticle because the metal nanoparticles retain their chirality after extraction of the chiral modifier.⁴⁵

In the present study we have investigated the chiral imprinting of Cu(110), an achiral surface, by (R,R)-tartaric acid (TA), a molecule with two chiral centers. Interest in TA's surface chemistry is motivated by its use as a chiral modifier in the enantioselective hydrogenation of β -ketoesters on heterogeneous Ni catalysts.^{6,27} Previous STM studies have shown that codepositing TA and methyl acetoacetate (MAA) on Ni(111) leads to a highly ordered array that contains both molecules. From STM images it appeared that the TA and MAA form intermolecular bonds, orienting the MAA parallel to the surface, thus exposing only one face to the surface.^{6,50} TA has also been investigated on Cu surfaces and was shown to form well-ordered domains that run in low symmetry directions on the Cu(110) surface yielding arrays of chiral pockets.^{29,30} TA forms a variety of ordered phases on the Cu(110) surface that are typically referenced by their matrix notation $\begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$ to relate the overlayer vectors (**a** and **b**) to the substrate vectors (**a_s** and **b_s**):

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} \begin{pmatrix} \mathbf{a}_s \\ \mathbf{b}_s \end{pmatrix} \quad (1)$$

TA phases include chiral monotartrate $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ and bitartrate $\begin{pmatrix} 1 & -2 \\ 8 & 2 \end{pmatrix}$ structures.^{30,51} While some of the phases have chiral unit cells, the effect of TA chemisorption on the structure of the Cu(110) surface itself has not been shown to date. Herein, we describe how TA restructures the Cu(110) surface, pulling Cu atoms out of the surface and incorporating them in highly ordered arrays within the adsorbate layer. These molecule-atom complexes appear in our molecularly resolved STM images as raised atomic rows and atomic trenches that run parallel to one another across the surface in a low symmetry direction, characteristic of chiral imprinting. Given sufficient thermal annealing the whole surface becomes restructured and the added atom structures form a long-range repeating chiral $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell. This configuration was interrogated by both low energy electron diffraction (LEED) and STM and was modeled using density functional theory (DFT).

■ EXPERIMENTAL SECTION

The Cu(110) single crystal surface was cleaned by Ar⁺ sputtering and annealing at 750 K. STM experiments above room temperature were carried out in the STM stage using a

pyrolytic boron nitride (PBN) heater embedded behind the sample. The sample temperature was monitored via a chromel-alumel thermocouple mounted in the STM stage. Heating to temperatures between 300 and 500 K (± 1 K of the desired set point) for multiple hours was possible with this setup. The Cu(110) crystal used for LEED experiments was spot-welded between two Ta wires at the end of an UHV manipulator. It could be heated or cooled over the temperature range 80 to 1000 K with the temperature measurement being made by a chromel-alumel thermocouple spot-welded to the edge of the crystal.

TA was purchased from Aldrich Chemical Co. in an enantiomerically pure form as D- or L-TA, (S,S)- or (R,R)-TA, respectively. TA was deposited on the surfaces of the single crystals by exposing them to TA vapor emanating from heated glass vials mounted in the UHV chambers. Saturation coverage of TA was formed by depositing multilayers on a room temperature crystal followed by annealing to 405 K for 1 min (STM studies) or by exposing TA to a crystal held at 405 K (LEED studies). Coverage is quoted in monolayers where 1 ML equals 1 TA molecule per 1 Cu surface atom. The saturation coverage of TA in this case is 0.28 ML, which is adsorbed in a $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ overlayer.

The TA/Cu(110) system was imaged with molecular scale resolution using an Omicron NanoTechnology variable-temperature ultrahigh vacuum scanning tunneling microscope (VT-UHV-STM). Imaging was performed with etched W tips from Bruker and Omicron NanoTechnology. The base pressure in the STM chamber was $< 1 \times 10^{-10}$ mbar. Typical scanning conditions to image TA molecules on Cu(110) were -0.5 V – 0.5 V and $5 - 100$ pA. Bare Cu(110) was imaged at -0.01 V and 50 nA.

LEED patterns were obtained from the TA modified Cu(110) surfaces held at 90–110 K using an OCI Vacuum Microengineering optics with 77° solid angle view and a 75 mm diameter dual microchannel-plate for image intensification. This allowed LEED patterns to be obtained with an electron beam current of a few nanoamps, thereby minimizing damage to the TA overlayer. Because the microchannel plates and the phosphorus screen are flat, the reciprocal space image of the LEED pattern is slightly distorted from the one obtained with a spherical screen. This has not complicated the assignment of the LEED patterns.

Density functional theory calculations were performed with the Vienna ab initio simulation package^{52–55} using the PBE-GGA functional^{56,57} with a plane wave expansion cutoff of 500 eV. All calculations used smearing with the first order Methfessel–Paxton method with a width of 0.2 eV. Structural optimization was conducted via a conjugate gradient algorithm with a force stopping criterion of 0.03 eV/Å. Cu(110) was simulated as a four-layer slab with the bottom two layers immobilized. The $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ chiral imprint was created by adding Cu adatoms to the Cu(110) surface. Calculations on this 35.7 Å by 5.0 Å surface unit cell sampled the reciprocal space with $1 \times 4 \times 1$ *k*-points. Test calculations indicated that this reciprocal space sampling was sufficient to give well-converged results. The partial charge density was evaluated at $-0.20 - 0.00$ eV with respect to the Fermi-energy level. STRender⁵⁸ used the partial charge density file to generate the constant charge density interface. The charge density value of 3.4×10^{-4} e/Å³

was found to provide the best clarity for the simulated STM images.

RESULTS AND DISCUSSION

TA overlayers observed on Cu(110) have structures that depend on the amount of TA deposited and the temperature of the surface upon adsorption.^{24,29,30,41,51,59} At low coverage and low temperature, TA exists in the bi-acid form that is the fully protonated, neutral form. Upon increasing temperature, TA exists in a bitartrate or doubly deprotonated form and at higher coverage a variety of monotartrate or singly deprotonated forms have been reported.^{34,51,60} The binding structure of the bitartrate species, in which both carboxylate groups bind to the surface, has been previously elucidated using X-ray photoelectron diffraction showing the molecular bond angles relative to the substrate lattice.⁶¹ All packing arrangements in this work arise from dense monolayers and feature the monotartrate phase. The monotartrate phase is characterized by having one carboxylate group bound to the Cu surface, the protonated carboxylic acid group pointing upward away from the surface, and the two hydroxyl groups within the layer participating in hydrogen bonding with adjacent molecules. Since the hydroxyl groups are bound to the chiral centers in the TA molecule the hydroxyl groups can bind to one another leading to the formation of overlayers with chiral unit cells.²⁹ Of the known packing arrangements for TA on Cu(110), several are chiral including $\begin{pmatrix} 1 & -2 \\ 8 & 2 \end{pmatrix}$ and $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$, which are formed by the bitartrate and monotartrate species, respectively.

The starting point of our chiral imprinting experiments was the formation of the dense $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ monolayer structure of TA on Cu(110). Although previous literature denotes the most dense unit cell as $\begin{pmatrix} 4 & 1 \\ 2 & 5 \end{pmatrix}$, to be consistent with matrix rules outlined by Ernst,⁶² we will identify the $\begin{pmatrix} 4 & 1 \\ 2 & 5 \end{pmatrix}$ unit cell as $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$, $\begin{pmatrix} 4 & 0 \\ 2 & 1 \end{pmatrix}$ as $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$, and $\begin{pmatrix} 9 & 0 \\ 1 & 2 \end{pmatrix}$ as $\begin{pmatrix} 1 & -2 \\ 8 & 2 \end{pmatrix}$. Figure 1A shows a room temperature STM image of the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell of TA on Cu(110), which has the highest reported coverage among TA overlayers on Cu(110) (0.28 ML).⁶⁰ For STM experiments, the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ TA structure was prepared by adsorbing multilayers of TA onto the Cu(110) surface at room temperature then annealing to 405 K for 1 min in the STM stage to leave the saturated monolayer. The blue rectangle in Figure 1A highlights the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell, which measures 1.5 ± 0.2 nm by 1.1 ± 0.1 nm and has been previously shown to contain five molecules per unit cell, yielding a coverage of 0.28 ML.^{24,60} Figure 1B is a Fourier transform (FT) image of the STM image in Figure 1A. The FT image is similar to a LEED pattern in that it is presented in reciprocal space. The FT of the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell highlights the rectangular symmetry of the overlayer and can be used for comparison to other unit cells, especially $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ that is elongated hexagonal in packing.⁶³ A schematic of the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell can be seen in Figure 1C where the underlying Cu(110) lattice has been rotated to have the same lattice directions as the Cu(110) single crystal lattice in the STM images. The blue circles in Figure 1C are used to

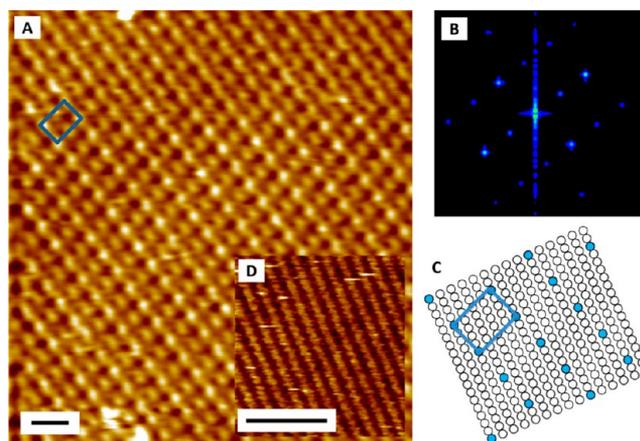


Figure 1. STM image of the highest density $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell of TA on Cu(110). (A) STM image of $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ taken at 300 K after annealing the monolayer at 405 K. The blue rectangle highlights the unit cell. Scale bar is 2 nm. (B) Fourier transform of the STM image highlighting the symmetry of this overlayer. (C) Schematic of the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell where blue circles represent the corners of the unit cell. (D) Atomic resolution STM image of bare Cu(110) in which the direction of the atomic rows is visible. Scale bar is 2 nm.

highlight the corners of the unit cell and are assigned to atop binding sites for simplicity. The Cu(110) lattice in the schematic was aligned so that the $[\bar{1}10]$ direction overlapped with the single crystal as shown by atomic resolution of the atomic rows of the clean Cu(110) surface in Figure 1D. From the schematic in Figure 1C, and comparing the overlayer directions in Figure 1A with the atomic rows in Figure 1D, it becomes clear that the close-packed rows of TA molecules are rotated $21 \pm 6^\circ$ counterclockwise with respect to the close-packed Cu atoms, a low symmetry direction that renders the unit cell chiral.^{51,60} This angle corresponds to the $[221]$ direction (19° counterclockwise rotation from close-packed direction) of the (110) surface.⁶⁰ This chiral $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell has been confirmed by LEED and is only observed when enantiomerically pure TA is deposited on the surface.^{24,60} The $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ overlayer structure is proposed to contain a mixture of TA dimers and monomers in the standing up, monotartrate phase, which accounts for the high density in this phase.^{30,60}

Previous studies have shown that it is possible to induce new packing arrangements of TA with thermal treatments.⁵¹ In our prior work on TA/Cu(110) we observed the progression of TA packing structures with annealing time from $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ to $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ to $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ before undergoing rapid decomposition in what is known as a surface explosion.⁶³ This progression of unit cells is interesting because it begins with a chiral unit cell, $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$, changes to an achiral unit cell, $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$, and finishes with another chiral unit cell, $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$. The $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell was formed by annealing the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ unit cell at 445 K for 430 s. The progression of TA packing structures is caused by the irreversible loss of molecules from the surface, decreasing the density, and allowing the molecules to spread farther apart. It is

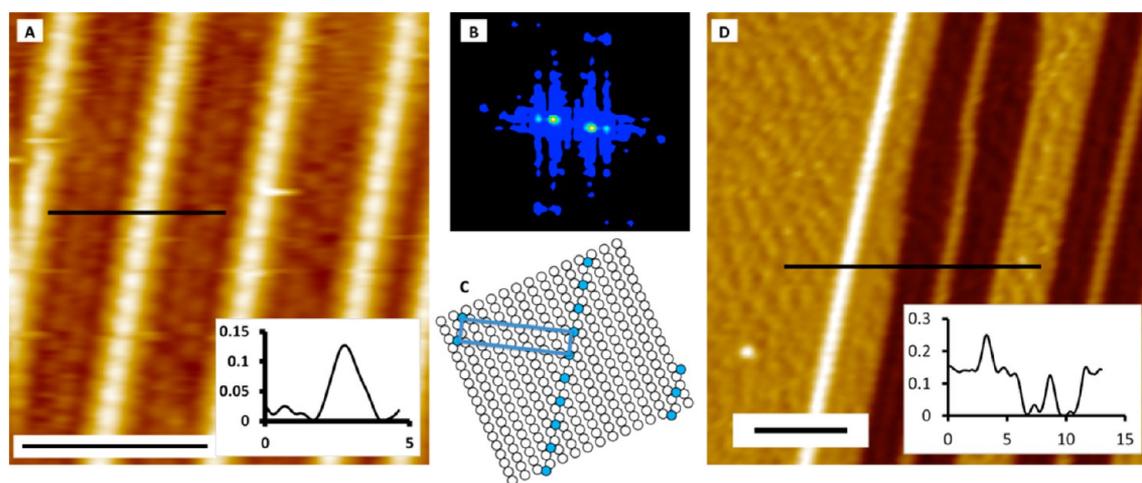


Figure 2. STM images and schematic of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell formed after chiral imprinting of the Cu(110) surface by TA. (A) STM image of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ structure formed after annealing the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ TA overlayer at 445 K for 430 s. Scale bar is 5 nm. The inset is a topographic line scan along the black line in the STM image revealing that the bright rows are one atomic layer high. Both axes have units of nanometers. (B) Fourier transform of the STM image in panel A showing intense central spots corresponding to the added row spacing of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell. (C) Schematic of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell in which the blue circles indicate the corners of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell. Note that despite their linearity, the added rows do not lie along a high symmetry direction. (D) STM image of an added row next to trenches formed after Cu atoms are removed from the Cu(110) surface. The trenches are one atomic layer deep, and the added row is one atom high. Scale bar is 5 nm. Both axes in the inset are in units of nanometers and indicate that the added rows are as high as the trenches are deep.

important to note that while the density of molecules has decreased from the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ packing density of 0.28 ML to ~ 0.25 ML in $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$, the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell still consists of tightly packed TA molecules in the monotartrate phase because more loosely packed TA in the bitartrate $\begin{pmatrix} 1 & -2 \\ 8 & 2 \end{pmatrix}$ phase is known to decompose at temperatures below 445 K.^{41,60}

Figure 2A is a representative STM image of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell. This unit cell is very different from the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ and $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ structures and is characterized by parallel bright rows running across the surface covered by a continuous array of adsorbed TA molecules. Our previous X-ray photoelectron spectroscopy (XPS) results describe the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell as having a TA coverage similar to $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$.⁶³ The bright rows are spaced 3.0 ± 0.4 nm and are rotated $36 \pm 2^\circ$ clockwise from the Cu close-packed direction. The STM image of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ structure looks drastically different from that of the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ in Figure 1A, and the Fourier transform in Figure 2B supports this. In Figure 2B, the spacing of the central spots with highest intensity in the Fourier transform pattern corresponds to the spacing of the bright rows in the STM image in Figure 2A. Based on measurements, a proposed schematic is shown in Figure 2C, which corresponds to a $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell. In the schematic, the blue circles are used to represent the corners of the unit cell and were arbitrarily placed on 4-fold sites for clarity. Due to the corrugation of the row structures in the

$\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell, it is difficult to assign the absolute positions of the molecules, but from high resolution images like that shown in Figure 2A, it appears that the molecular packing arrangement is very similar or identical to that of the $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ structure. The bright rows are very regular, and from the schematic it is clear that they run in a low symmetry direction, making $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ a chiral unit cell. XPS and STM observations suggest that $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ and $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ have roughly the same TA coverage and spacing. The elongated hexagonal $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ unit cell has one row of molecules that runs in the same direction as the bright rows in $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$. It therefore seems likely that the inter-row spacing in $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ is dictated by the spacing of the molecules in $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$, the major difference being that the molecules in this direction are now brighter than the surrounding ones. While this could help explain the inter-row spacing, there is nothing obvious that dictates a row-row spacing of 3 nm, except that this happens to be equivalent to the spacing of five molecules in the $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ unit cell. The topographic linescan shown in the inset in Figure 2A is taken along the black line in the image. The heights of the bright rows measure 120 ± 30 pm, which is very close to the height of a monatomic step edge on Cu(110); 128 pm. This points to a restructuring of the underlying Cu(110) surface by TA molecules, which pull Cu atoms from the surface layer onto the surface. The fact that monolayer deep trenches are simultaneously formed in the Cu surface as shown in Figure 2D supports our hypothesis that the bright rows are formed by

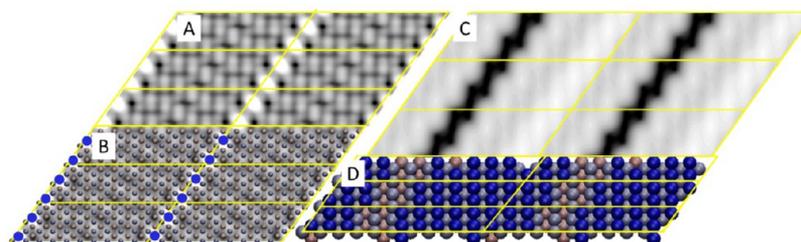


Figure 3. Simulated STM image of rows of Cu atoms pulled out of the surface and the resultant vacancy trenches in the surface. (A) Simulated STM image of rows of Cu atoms in the $\left(\frac{2}{6} \bar{1}\right)$ structure. (B) Same simulated image with superimposed atoms; dark blue circles are added Cu on the surface, light blue circles are the upper rows of Cu(110) and the gray circles are the valleys. (C) Simulated STM image of trenches in the Cu(110) surface that are 2 atoms wide and 1 atom deep. (D) Schematic of the atomic structure of trenches used to simulate STM images. Thin yellow lines mark the supercell used to generate the STM images. Simulated bias is in (A) -0.10 V, (C) -0.20 V.

Cu adatoms removed from the surface. The trenches are on average 1.9 ± 0.4 nm wide and 113 ± 20 pm deep, again consistent with atom removal. Notably, the trenches are very linear and run parallel to the adatom rows rendering them also chiral. This restructuring of Cu(110) upon TA adsorption provides more evidence that the underlying metal surface is not always static and can change upon adsorption of molecules.⁶⁴

While direct observation of the chiral imprinting of a Cu(110) surface induced by TA adsorption has not been reported before, it has been shown that: (i) lateral surface stress exists upon bitartrate adsorption,⁵⁹ (ii) adsorption of a similar molecule (malic acid) can induce restructuring of the underlying Cu(110) surface, pulling out Cu adatoms that then align in a chiral manner,^{31,65} and (iii) TA can induce stress upon adsorption on a Ni(110) surface.^{66,67} A similar release of Cu atoms has previously been seen during formic acid oxidation on Cu(110).⁶⁸ It has also been proposed that Ni atoms incorporated in a formate overlayer participate in the decomposition of formate on Ni(110).⁶⁹ On a related note, other systems, such as benzoic acid and alkane thiol self-assembled monolayers (SAMs), have been observed to restructure the underlying metal surface.⁷⁰ The alkane thiol molecules deprotonate upon adsorption, and the strong Au–S bonding results in Au atoms being pulled up from the surface, creating monolayer deep etch pits.^{71,72} Significantly, we have shown here that in the case of TA, the underlying achiral Cu(110) surface is restructured in a chiral manner since the added rows and trenches are oriented along a low symmetry direction ($36 \pm 2^\circ$) with respect to the close-packed Cu surface direction.

We simulated STM images using DFT to support our proposed model of the $\left(\frac{2}{6} \bar{1}\right)$ chiral imprinting of Cu(110). In Figure 3A, the bright spots associated with the raised row of Cu atoms in the simulated STM image are consistent with the STM image from Figure 2A. We carried out similar calculations for the monolayer deep trenches. The trench in Figure 3C is two atoms wide in the $\left(\frac{2}{6} \bar{1}\right)$ direction. The bright line between two neighboring trenches is the result of periodic boundary condition in DFT; a similar feature would not be observed in experiment. Figure 3D illustrates the atomic position for the monolayer trench. The resemblance between simulated and experimental STM images supports our proposed model for the $\left(\frac{2}{6} \bar{1}\right)$ chiral imprinting for both the adatom and the monolayer trench.

Zooming out to image larger areas of the partially reconstructed surface resulted in STM images like those shown in Figure 4. From this perspective, it is evident that the

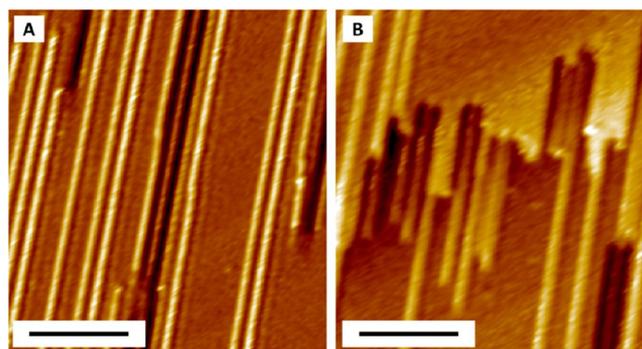


Figure 4. (A) Large scale STM image of the partially formed $\left(\frac{2}{6} \bar{1}\right)$ surface with rows and trenches running parallel to one another over long length scales. (B) In addition to the added atom rows running in a low symmetry, chiral direction, the step edges appear to be faceted. Both scale bars are 20 nm.

adatom rows are the dominant feature of the chiral imprinting and that they run straight and parallel for many tens of nanometers (Figure 4A). While it is difficult to elucidate the local structure of the underlying Cu(110) surface before adsorption of TA molecules, it appears that after restructuring by TA, there are step edges that run parallel to the bright rows on the surface as opposed to the more randomly oriented steps present on bare Cu(110), further highlighting the chiral imprinting of the metal surface. Figure 4B shows one particular step edge that appears to have been reconstructed, with parts of the step edge etched away in the low symmetry direction parallel to the added atom rows.

In order to examine the global ordering of the $\left(\frac{2}{6} \bar{1}\right)$ imprinted Cu(110) surface, LEED was employed. The Cu(110) surface was saturated with either (*R,R*)- or (*S,S*)-TA by adsorption at 405 K and then heated to 483 K at 1 K/s and quenched to ~ 100 K. 483 K is ~ 15 K below the temperature at which explosive decomposition leads to complete removal of the adsorbed TA.⁶³ Heating to 483 K does not result in the detectable desorption of any of the decomposition products such as CO₂; however, it does result in some loss of adsorbed TA as the adsorbed overlayer changes from the $\left(\frac{4}{-2} \frac{1}{4}\right)$ to

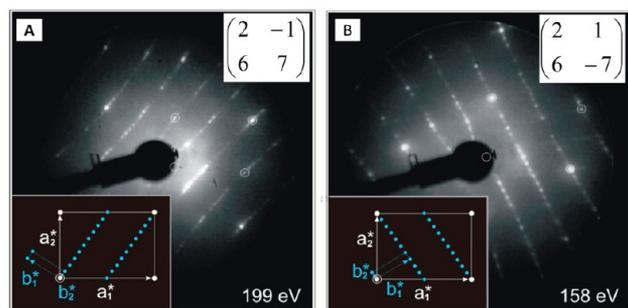


Figure 5. LEED patterns resulting from the adsorption of (A) (*R,R*)- and (B) (*S,S*)-TA on Cu(110) after annealing to 483 K. The LEED patterns highlight the long-range order seen in the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell.

$\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ and then $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$. In Figure 5A, the sharp $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ LEED pattern generated by the surface with adsorbed (*R,R*)-TA is indicative of long-range well-ordered restructuring of the Cu(110) surface. The fact that this enantiomeric $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ overlayer LEED pattern is observed across the whole surface indicates that the imprinting of chirality by the adsorbed (*R,R*)-TA occurs uniformly across the entire surface and not just in the small regions imaged with the STM. The fact that the chirality of the reconstructed Cu(110) surface is dictated by the chirality of the adsorbed TA was confirmed by preparing the surface with adsorbed (*S,S*)-TA using a procedure identical to that used with (*R,R*)-TA. The LEED pattern from the overlayer generated by heating to 483 K is shown in Figure 5B. This is the $\begin{pmatrix} 2 & 1 \\ 6 & -7 \end{pmatrix}$ overlayer, the enantiomer of the $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ overlayer generated by (*R,R*)-TA. The enantiomeric relationship between the overlayers is clearly demonstrated by the

mirror image relationship between the two LEED patterns in Figure 5.

In order to further investigate the restructuring process, we performed time-lapse STM imaging of TA on Cu(110) at elevated temperature. Starting with the $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ packing structure, we annealed the sample to 420 K, a temperature at which the conversion of $\begin{pmatrix} 4 & 1 \\ -2 & 4 \end{pmatrix}$ to $\begin{pmatrix} 2 & 1 \\ -2 & 1 \end{pmatrix}$ to $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ occurred over ~ 1.5 h.⁶³ This enabled us to image the surface in real time as the chiral imprinting occurred. Figure 6 shows a sequence of STM images recorded at 420 K where the time in each image indicates the time elapsed after the sample reached 420 K. The drawbacks of imaging at elevated temperature include both thermal drift in each image location and lower resolution. However, as Cu atom removal leads to rows and trenches >0.1 nm high/deep, the imprinting process could be followed in real time.

Figure 6 reveals that the initially disordered step edges found on Cu(110) are etched away, leaving parts of them very linear. Figure 6A–C shows a step edge being etched, as indicated by the arrows. Isolated adatom rows appear on the terrace (Figure 6D) and grow denser over time as more Cu atoms are etched out of the surface. After ~ 1.5 h at 420 K, the whole surface is converted to a regular row structure with a global $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ unit cell (Figure 6F). The fact that trenches are only seen at the intermediate stages of $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ growth indicates that these are mobile enough to diffuse and annihilate at step edges. Therefore, the very long-range, highly ordered $\begin{pmatrix} 2 & -1 \\ 6 & 7 \end{pmatrix}$ structure left at the end of the imprinting process requires a high degree of Cu surface atom mobility during its formation.

CONCLUSIONS

We report experimental evidence for large-scale, highly ordered chiral imprinting of a Cu(110) surface by TA. Although many

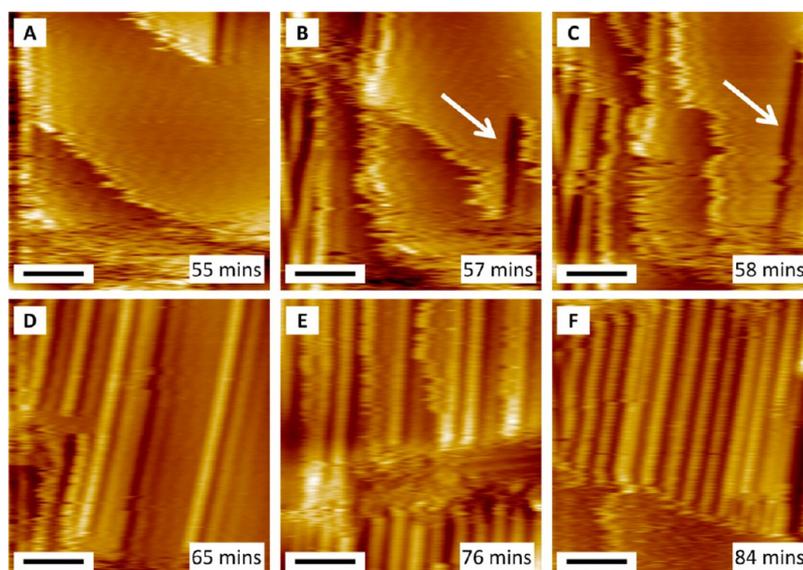


Figure 6. Sequence of STM images of 0.28 ML (*R,R*)-TA on Cu(110) taken at 420 K showing the evolution of the surface structure over time. The time spent at 420 K is shown in each image. (A–C) Images showing the restructuring of a step edge (white arrow) as it becomes straighter and longer. (D) Added atom rows begin to appear, isolated at first but increasing in density (E) until their spacing becomes very regular (F). All scale bars are 10 nm.

studies of TA overlayers on Cu(110) have been performed and have revealed the presence of chiral TA overlayers, this is the first to report restructuring of the metal surface by adsorbed TA. Our data indicates that gently annealing a saturated monolayer of singly deprotonated TA leads to the removal of Cu atoms from the surface and their ordering on the surface in long, linear, and evenly spaced rows. Evidence for these rows being composed of Cu adatoms comes from the simultaneous appearance of one atom deep trenches in the Cu surface and step edge etching. Most interestingly, these adatom rows and trenches run in a low symmetry direction and hence are chiral. While it is obvious how long linear rows and trenches could form in high symmetry directions epitaxial with the rectangular Cu(110) substrate lattice, the degree of long-range order of the chiral imprinting that we observe is surprising. This indicates a thermodynamic preference for TA to bind adatoms in a chiral, asymmetric fashion that drives the restructuring process. This work reveals the importance of considering surface restructuring in the adsorption of strongly interacting chiral molecules on metals and indicates that achiral metal surfaces can be rendered chiral by choice of the appropriate molecule. The interesting implication is that once restructured, they can induce enantioselective surface chemistry.

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Notes

The authors declare no competing financial interest.

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