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Templated Growth of a Homochiral Thin Film Oxide

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7 ABSTRACT: Chiral surfaces are of growing interest for 8 enantioselective adsorption and reactions. While metal surfaces 9 can be prepared with a wide range of chiral surface orientations, 10 chiral oxide surface preparation is more challenging. We 11 demonstrate the chirality of a metal surface can be used to 12 direct the homochiral growth of a thin film chiral oxide. 13 Specifically, we study the chiral "29" copper oxide, formed by 14 oxidizing a Cu(111) single crystal at 650 K. Surface structure 15 spread single crystals, which expose a continuous distribution of 16 surface orientations as a function of position on the crystal, 17 enable us to systematically investigate the mechanism of 18 chirality transfer between metal and the surface oxide with



19 high-resolution scanning tunneling microscopy. We discover that the local underlying metal facet directs the orientation and 20 chirality of the oxide overlayer. Importantly, single homochiral domains of the "29" oxide were found in areas where the Cu 21 step edges that templated growth were ≤ 20 nm apart. We use this information to select a Cu(239 241 246) oriented single 22 crystal and demonstrate that a "29" oxide surface can be grown in homochiral domains by templating from the subtle chirality 23 of the underlying metal crystal. This work demonstrates how a small degree of chirality induced by slight misorientation of a 24 metal surface (~1 sites/20 nm²) can be amplified by oxidation to yield a homochiral oxide with a regular array of chiral oxide 25 pores (~75 sites/20 nm²). This offers a general approach for making chiral oxide surfaces via oxidation of an appropriately 26 "miscut" metal surface.

27 KEYWORDS: chiral amplification, thin film oxide, oxidation, copper oxide, "29" oxide, scanning tunneling microscopy

hirality plays an important role in areas ranging from 28 the structure of biomolecules, such as amino acids and 29 DNA, to pharmaceuticals.^{1–3} The efficacy of many of 30 31 the highest valued drugs is dependent on their chirality and 32 enantiomeric purity.⁴ Synthesis often involves making a 33 racemic mixture of the drug and then separating the two 34 enantiomers, which can be a time-consuming and expensive 35 part of this \$1.2 trillion industry.⁵ This has led to great interest 36 in enantioselective reactions that eliminate the need for 37 product separations and most recently the potential for 38 enantioselective heterogeneous processes.^{6–10} Toward this 39 goal, surface science has played a crucial role in developing our 40 understanding of enantioselective surfaces and the interactions 41 between molecules and surfaces, which enables a more 42 complete understanding of the fundamental connection 43 between surface structure and enantiospecific behavior.¹⁰⁻²⁰

This approach has been used to study the transfer of surface ⁴⁴ chirality to adsorbates, or *vice versa*, as well as using chiral ⁴⁵ arrays of molecules to impart enantioselectivity to achiral ⁴⁶ surfaces. ^{21–30} 47

While the atomic-scale structure of chiral metal surfaces and 48 their enantiospecific interaction with molecules is fairly well 49 understood, only a handful of chiral oxides are known and their 50 preparation and structural determination is challeng- 51 ing.^{15,19,31-35} Work by Switzer *et al.* demonstrated that a 52

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Figure 1. The "29" oxide has a chiral pore structure with long-range order. DFT-based structures are given in panels A and D, showing the two different chiralities of the "29" oxide with the unit cells highlighted. The black spheres indicate oxygen adatoms, and the red and gray spheres represent O anions and Cu cations, respectively. The pink spheres represent the Cu atoms on the underlying Cu(111) surface. The black rings in A highlight the six hexagonal rings that comprise the unit cell. The computational details of this structural model are described in our previous work.³⁸ STM images B and E correspond to the chiralities depicted in A and D. The dotted line represents the mirror plane and corresponds to the vertical close-packed direction of the Cu(111) lattice. The scale bars in B and E are 2 nm in length. C and F display LEED patterns of surfaces that are predominantly single and opposite chiralities of the "29" oxide.



Figure 2. STM images of all six rotational orientations and enantiomers of the "29" oxide structure that are found on the Cu(111) surface. Marked with green arrows are the angles of the long side of the unit cell, relative to the close packed [101] direction of the Cu(111) surface: A 22°, B 142°, C 262°, D -22°, E -142°, F -262°. The close-packed direction is consistent across all images. The scale bars are 10 nm in length. The two enantiomers of the "29" oxide are defined by the sign of the angle formed between the unit cell and one close-packed direction.

⁵³ chiral oxide can be obtained by electrochemically depositing a⁵⁴ copper oxide film from solutions containing chiral species such⁵⁵ as tartaric acid. The chirality of the deposited film depends on

the chirality of the tartrate ions in the deposition solution.^{34–36} 56 Other templating work includes pulsed laser deposition 57 experiments performed by Salvador *et al.* in which a chiral Pt 58 ⁵⁹ film was grown over a chiral $SrTiO_3$ (621) surface. The ⁶⁰ chirality of the substrate surface was imparted to the Pt layer ⁶¹ by the underlying $SrTiO_3$ substrate, rendering the Pt film ⁶² surface chiral.³⁷

Herein we describe a system in which oxidation of a metal 63 64 surface with a low density of chiral kink sites exhibits direct 65 and robust chirality transfer and amplification during the 66 formation of a homochiral surface oxide film. This effect is 67 demonstrated with the well-defined "29" surface oxide, which 68 is intrinsically chiral.^{38–41} High-resolution scanning tunneling 69 microscopy (STM) enables us to correlate the chirality of the 70 "29" surface oxide with its position on a surface structure 71 spread single crystal (S^4C) and hence its relationship to the 72 underlying Cu(hkl) facet.⁴² These S⁴C crystals have spherically 73 shaped surfaces that expose a continuous distribution of step 74 and kink combinations, or microfacets, as described else-75 where.⁴² In order to expose these microfacets, single crystals 76 are purchased and then polished to have a shape that mimics 77 the top of a sphere. The preparation of these crystals allows for 78 exposure of all possible face centered cubic crystallographic 79 surface orientations with just a few single-crystal samples. This 80 approach allows us to probe how the subtle chirality of the step 81 edges on a Cu(111)-S⁴C templates homochiral growth of the "29" surface oxide. We go on to demonstrate that by selecting a 82 83 subtly "miscut" crystal vicinal to Cu(111), it is possible to grow 84 a single homochiral domain of the "29" oxide.

85 RESULTS AND DISCUSSION

Structure and Orientation of the "29" Copper Oxide 86 87 Film. The unit cell of the $Cu_2O/Cu(111)$ -like layer consists of 88 six hexagonal oxide rings made up of O-Cu-O bonded 89 networks (see Figure 1A), with five of the six rings having an 90 oxygen adatom in the center, and forms in large well-ordered domains when the Cu(111) crystal is exposed to a saturation 91 92 (900 L) dose of oxygen at 650 K.³⁸ This oxide is known as the "29" oxide because it has a unit cell 29 times larger than that of 93 94 a clean Cu(111) unit cell. Full details of the STM appearance 95 and structure of the "29" surface oxide have been described in 96 detail elsewhere.³⁸ Because the lattice vectors of the "29" oxide 97 do not coincide with the high-symmetry direction of the 98 Cu(111) substrate, the oxide can grow in two different 99 enantiomeric forms with respect to the underlying Cu(111)100 lattice. Figure 1A and D show the DFT-derived unit cell model 101 of the "29" oxide, with the dotted line between the two images 102 representing the mirror plane of the "29" oxide, parallel to a 103 close-packed direction of the Cu(111) substrate. STM images 104 taken of this surface, Figure 1B and E, show examples of the 105 two different enantiomers of the oxide that match the DFT-106 based unit cells. The LEED patterns in Figure 1C and F show 107 the corresponding LEED patterns for these enantiomers. Both 108 the DFT-based and the STM data reveal that the long axis of 109 the "29" oxide unit cell is rotated 22° from the close-packed 110 Cu(111) lattice rendering it chiral.

111 Due to the 3-fold symmetry of the underlying Cu(111) 112 surface, each chirality (+22° and -22°) of the oxide exhibits 113 three rotational domains. Figure 2 shows STM images of all six 114 different orientations of the "29" oxide that can form on a flat 115 Cu(111) surface due to the two enantiomers (denoted +, -) 116 of the "29" oxide aligned with the three equivalent directions 117 on the 3-fold symmetric substrate. Each chiral unit cell is 118 rotated 22° from the close-packed directions of Cu(111). The 119 different orientations of the oxide are classified by the angle 120 formed between the oxide and the [101] close-packed direction. We refer to one chirality of the oxide as the $+22^{\circ}$, $_{121}$ $+142^{\circ}$, and $+262^{\circ}$ oxides, and the opposite chirality as the $_{122}$ -22° , -142° , and -262° oxides. The positive (counter- $_{123}$ clockwise) and negative (clockwise) angles are enantiomers of $_{124}$ each other.

Templated Growth of Chiral Oxides on the Curved 126 Cu(111) Single Crystal. In order to determine whether the 127 orientation and chirality of the "29" oxide domains are related 128 to the structure and chirality of the underlying Cu surface, we 129 performed STM measurements to determine how each oxide 130 domain on the S⁴C was related to the local facet orientation of 131 the underlying Cu surface. Because all terraces on the Cu(111) 132 S⁴C surface are flat (111)-oriented planes, and are hence 133 achiral, the step edges, most of which contain chiral kinks, are 134 the only features that can play a role in templating the 135 orientation and chirality of the "29" oxide film. Therefore, we 136 acquired STM images at a number of positions spanning the 137 S⁴C crystal in order to probe the impact of all step and kink 138 combinations (i.e., local orientations of the underlying Cu 139 surface) on the orientation and chirality of the "29" oxide. 140 Figure 3 shows STM images obtained at 12 different points 141 f3



Figure 3. Local orientation of the copper S⁴C dictates the local orientation and chirality of the "29" oxide. A chart in the center shows the different oxide orientations and chiralities at different locations around the S⁴C. The inner circle shows the step type of that area of the crystal with A and B steps and the superscript (R/S) denoting the kink type in that area. The chirality of the oxide is denoted with blue (+) and with red (-) angle values. STM images of the 12 representative areas are displayed on the outer circle. All white scale bars are 5 nm. The inset table emphasizes the relationships between step type and oxide chirality. The unit cell is shown for each STM image.

around the central (111) pole of the S⁴C. The inner circle of 142 Figure 3 lists the type of step edges found on the bare Cu 143 crystal.^{42,43} Because the Cu(111) S⁴C surface is polished in a 144 dome shape to expose a continuous distribution of surface 145 orientations, straight, close-packed step edges aligned with the 146 high-symmetry directions of the crystal are either (100) 147 (referred to as A type steps) or (110) oriented steps (B type 148

f4

149 steps). For steps to run in a low-symmetry direction they must 150 incorporate *R* or *S* kinks and hence expose chiral microfacets. 151 The combination of step type and kink type alternate around 152 the crystal as seen in Figure 3. The outer circle of Figure 3 153 shows representative STM images of the "29" oxide taken at 154 multiple locations around the (111) pole ranging from 0.5 to 155 1.5 mm from the center with terrace widths between 5 and 20 156 nm. The 3-fold symmetry of the S⁴C leads to three equivalent 157 locations any given facet, for example A type step, that 158 incorporates kinks of a particular chirality, *i.e.*, *R*, denoted A^R as 159 seen in Figure 3.

The column at the center of Figure 3 reveals the correlation 161 between the step type (A vs B), the chirality of the step (R vs162 S), and the chirality of the oxide (+vs -). If, for example, one 163 changes the kink type (R to S) of an A-type step edge, the 164 oxide will flip its chirality (+ to -). Perhaps slightly less 165 intuitively, if one compares an A-type step with R kinks with a 166 B-type step with R kinks, the chirality of the oxide in each 167 region will be opposite (see the center of Figure 3). The origin 168 of this direct templating effect can be understood if one 169 considers the orientation of the step edges in these different 170 regions. After oxidation, the step edge orientation always 171 matches the orientation and chirality of the oxide formed in 172 that region.

Local Step Edge Refaceting during the Formation of 174 the "29" Oxide. In an attempt to further understand the 175 templated growth of the "29" oxide, the local structures of the 176 step edges were studied before and after oxidation, as displayed 177 in Figure 4. Figure 4A shows step edges on the clean Cu(111)



Figure 4. During oxidation, the Cu steps refacet to run along directions $\pm 22^{\circ}$ from the high-symmetry direction of the (111) lattice with an orientation closest to original step direction. This leads to transfer of net step chirality to the chirality of the oxide. A derivative STM image taken of the step edges of the S⁴C crystal before (A) and after (B) the oxidation process. The scale bars in A and B are 20 nm. The bottom panel represents a terrace and step edge before oxidation (left) and after oxidation (right). The step edge on the right is refaceted by the formation of the "29" oxide.

178 substrate that correspond to the schematic below the STM 179 image. The steps in the STM image in Figure 4A run roughly 180 parallel to each other and in the direction dictated by the local 181 surface orientation. The steps themselves, however, meander, 182 which is typical for clean metal surfaces that undergo thermal 183 roughening during the annealing step of their preparation.⁴⁴ In contrast, after oxidation, STM imaging reveals that the steps 184 straighten after the "29" oxide formation (Figure 4B). While 185 we cannot image during oxidation, previous work on the room-186 temperature oxidation of Cu(111) surfaces^{39,42,45} has shown 187 that oxidation starts at step edges and significantly refacets the step edges, in our case into low-symmetry directions that are aligned with the unit cell of the chiral "29" oxide. The exact 190 mechanism of this step refaceting is unclear, but we 191 hypothesize that it could be driven by the "29" Cu oxide if it 192 has larger penalties for variations in the stepped-kinked 193 structure than the Cu metal surface.

Analysis of Step Density on Oxide Templating. While 195 the above conclusions are valid for areas of the S⁴C in which 196 the step density was somewhat high (terraces widths ~10 nm), 197 we systematically studied other areas of the S⁴C crystal in order 198 to investigate the effect of step density on chiral oxide 199 templating. Imaging the very large terraces (<20 nm) at the 200 (111) pole of the S⁴C after oxidation yielded areas that have 201 long-range (>50 nm) order of a single oxide orientation/ 202 chirality, as well as areas with several different oxide 203 orientations. Figure 5C shows a large STM image that covers 204 fs 200 × 200 nm², comprising just one large, flat 160 nm terrace, 205 and no step edges. This area contains two different orientations 206



Small Terraces Medium Terraces Large Terraces

Figure 5. Effect of local Cu surface facet on the orientation and chirality of the Cu₂O film. The histogram shows the percent match of the "29" oxide orientation and chirality with local facet as a function of terraces width. The scatter plot above shows the number of times each terrace width was observed. The inset shows a side view photo of the S⁴C crystal. (A) "Small" (terrace widths >5 nm) STM image taken at a radius of 1 mm from the (111) pole. (B) Derivative "medium" (terrace widths between 5 and 20 nm) STM image taken at a radius of 0.5 mm. (C) Derivative "large" (terrace widths <20 nm) STM image of a single terrace, obtained at the(111) pole of the crystal. The scale bars are 5 nm in A and 20 nm in B and C. The white arrows in the STM images denote monatomic steps, whereas the green arrows show step bunches.

207 of the "29" oxide. Farther from the (111) center of the S^4C , the ²⁰⁸ step density increases, leading to smaller terraces (>10 nm).⁴² 209 In most of the STM images taken at similar distances from the 210 center of the crystal to the area in Figure 5B, smaller terraces 211 (20 nm) of single oxide domains exist. Not all the step edges, 212 however, have the same orientation of the oxide. Figure 5B 213 shows examples in which an oxide domain is surrounded by 214 steps of different orientation, and hence it can only align with 215 one of the steps. By moving farther from the center of the S^4C_1 216 the terrace width continues to decrease and regions of oxide 217 and step edges orientated in the same direction become more 218 common. These terraces, shown in Figure 5A, are between 5 219 and 10 nm wide, and the oxides on adjacent terraces almost 220 always have the same orientation and chirality. The histogram 221 in Figure 5 quantifies the influence of step density on oxide 222 templating; >700 STM images were analyzed, and the oxide 223 orientation with respect to the step edges is plotted as a 224 function of terrace width. Figure 5 shows a strong oxide 225 templating effect for terraces ≤ 20 nm. Increasing terrace width 226 above 20 nm leads to more random oxide orientations.

In order to demonstrate that the chiral templating effect can 227 228 be used to direct the macroscopic growth of just one chirality 229 and orientation of the "29" surface oxide film, we selected a Cu(239 241 246) single crystal that is oriented 0.7° from the 230 [111] axis and has step edges running parallel to the 231 232 orientation of the oxide with terrace widths of 18 nm. Due to the slight miscut of the crystal, this surface has only ~ 1 233 234 chiral kink per 20 nm² (1D kink density of 2 kinks/1.6 nm 235 along the step edge), while the "29" surface oxide has 75 chiral 236 pores per 20 nm². To test our hypothesis that control of the 237 facet of the underlying Cu metal surface would direct the 238 macroscopic growth of just one orientation and chirality of the 239 "29" oxide, we used LEED to examine the oxide orientation ²⁴⁰ and chirality of the oxide over the whole $\sim 1 \text{ cm}^2$ single crystal. 241 Figure 6 shows that only one chirality and orientation of the oxide is present at most points on the crystal. 242

Unfortunately, the center of the crystal produced LEED 243 244 patterns consisting of multiple orientations/chirality of the 245 oxide as seen in Figure 6. This became progressively worse 246 over time, and the results are consistent with an inhomoge-247 neous flux of Ar⁺ ions during sputter cleaning treatments that 248 lead to the center of the crystal being sputtered away 249 preferentially, as can be seen visually in the inset of Figure 6. 250 Given that the Cu(239 241 246) single crystal is only a 0.7° 251 miscut from the achiral (111) orientation, very little material 252 needs to be removed to destroy the homochirality of the Cu 253 crystal, as is observed in our experiments. For example, in order to transition from the 0.7° miscut crystal surface that 254 255 exposes just one chirality of kink to a surface that exposes the 256 opposite chirality kink, one must reorient the Cu(239 241 246) surface by 1.4° . The width of the misoriented area in the 257 258 center of the crystal is ~5 mm wide; so to expose an 259 appreciable number of kinks of opposite chirality, geometrically one would have to sputter ~0.14 mm into the crystal at 260 this point. Assuming a sputter yield of 3.41 Cu atoms ejected 261 262 per Ar⁺ under our typical cleaning conditions of 2 μ A at 1.5 263 keV, we estimate that it would take ~1587 h of sputtering to ²⁶⁴ create such a defect.⁴⁶ This equates to \sim 2 h per day of cleaning 265 and is in agreement with the total duration of the cleaning 266 treatments used over the past 2 years.

Nonetheless, this growth of a homochiral "29" surface oxide on the Cu(239 241 246) surface serves as a proof of principle of our hypothesis that controlling the subtle chirality of a metal



Figure 6. Oxidation of a vicinal Cu(239 241 246) crystal (18 nm terrace widths) showing predominant formation of a just one rotational orientation of the homochiral "29" oxide. The LEED images are from different areas across the oxidized Cu(239 241 246) crystal and show a single orientation of the "29" oxide across the surface with the exception of the center and one edge. This is due to Ar^+ ion sputtering induced damage of the center of the crystal during cleaning. A photograph of the Cu(239 241 246) crystal is inset in the top right of the figure.

surface with nanoscale chiral facets can be used to template the 270 growth of oriented, homochiral oxides at the macroscale. 271

CONCLUSION

We have demonstrated that the orientation and chirality of a 273 single-layer thin film "29" surface oxide can be controlled by 274 the local orientation and structure of the underlying Cu surface 275 before oxidation. The "29" surface oxide exists in two 276 enantiomeric forms, with each chirality having three equivalent 277 orientations due to the 3-fold rotational symmetry of the 278 Cu(111) crystal. Using a S⁴C allowed us to systematically 279 investigate how the local Cu surface orientation influenced the 280 oxide growth. We discovered that the chirality of the 281 underlying Cu surface could be used to template fairly long- 282 range homochiral growth of the oxide film with terraces up to 283 20 nm wide showing a predominance of just one enantiomer 284 and rotational orientation of the oxide. Our data also revealed 285 that the chiral templating effect can be understood in terms of 286 the direction of the local step edges which align with the 287 orientation of the "29" oxide on the associated terrace. 288

Given that oxidation starts at step edges on the Cu surface 289 and that they become significantly refaceted during oxidation 290 in a direction that aligns exactly with the oxide orientation, it 291 follows that the oxide forms in the orientation that is closest to 292 the original direction of the step edge.⁴² Previous studies have 293 demonstrated the existence of different chiral domains on a 294 "29" oxide surface. However, the driving force behind the 295 formation of these domains was not understood.^{39,45} Our 296 systematic study lends insight into this process by emphasizing 297 the direct correlation between local underlying metal surface 298 facet and homochiral oxide domain orientation. We demon- 299 strate that the relatively small number of chiral kink sites on 300 the steps of a Cu(239 241 246) crystal are enough to direct the 301

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302 homochiral growth of the oxide. This chirality transfer between 303 metal surface and thin film oxide may in fact be general and 304 therefore enable a range of oriented homochiral thin film 305 oxides to be grown in a straightforward manner without the 306 difficulty of cutting and polishing oxide single crystals.

307 EXPERIMENTAL SECTION

308 All of the STM work presented in this study was performed on a 309 Cu(111) ±11° S⁴C crystal prepared at Carnegie Mellon University. 310 The S⁴C crystal was cleaned by consecutive cycles of Ar⁺ sputtering 311 (1.5 keV/17 μ A) and annealing (800 K) in the preparation chamber 312 (base pressure of 1 \times 10⁻¹⁰ mbar) of an Omicron Technology 313 variable-temperature ultra-high-vacuum (VT-UHV) STM. The same 314 experiments were performed in an Omicron Technology low-315 temperature ultra-high-vacuum (LT-UHV) STM. In order to make 316 the surface oxide layer, the surface was exposed to 900 L of O_{2} , 317 through a collimated leak valve, while the crystal was held at 650 K. 318 Once the oxide was formed, the crystal was transferred to the STM 319 chamber (base pressure $<1 \times 10^{-10}$ mbar) and imaged using a W tip 320 from Omicron Technology. Typical imaging conditions in the 321 presented VT-STM images are a bias of -0.4 V, with respect to the 322 sample, and current of 0.7 nA with all images being recorded at 298 K. 323 LT-STM images were collected at 80 K with typical imaging 324 conditions of -0.5 V, with respect to the sample, and 0.5 nA 325 tunneling current. All low-energy electron diffraction patterns were 326 generated using an OCI Vacuum Microengineering Digital LEED and 327 AES system model LPS300-D with a filament current of 2.64 A, a 328 focus of 88 V, a screen voltage of 5 kV, and a beam energy of 66 eV. 329 The images were captured using a Samsung Galaxy S9 smartphone. 330 The STM images used to generate the chart in Figure 5 were 331 processed with SPIP software and analyzed by measuring the width of 332 every terrace imaged and separating each terrace into one of two 333 categories: (1) the oxide rows are formed in an orientation matching 334 the upper and lower step edges, or (2) the oxide rows are formed in 335 an orientation not matching the step edges. These data are plotted on 336 the chart in Figure 5 as a function of terrace width.

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Notes	387

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- REFERENCES
- (1) Kyriakou, G.; Beaumont, S. K.; Lambert, R. M. Aspects of 400 Heterogeneous Enantioselective Catalysis by Metals. *Langmuir* 2011, 401 27, 9687–9695. 402
- (2) Lennard, M. Clinical Pharmacology through the Looking Glass: 403 Reflections on the Racemate vs Enantiomer Debate. Br. J. Clin. 404 Pharmacol. **1991**, 31, 623. 405
- (3) Nugent, W.; RajanBabu, T. V.; Burk, M. Beyond Nature's Chiral 406
 Pool: Enantioselective Catalysts in Industry. *Science* 1993, 259, 479–407
 483.
- (4) Rouhi, M. A. Chiral Chemistry. *Chem. Eng. News* **2004**, 47–62. 409 (5) IQVIA Institute for Human Data Science: https://www.IQVIA. 410 com/institute/reports/the-global-use-of-medicine-in-2019-and- 411 outlook-to-2023, accessed Nov 19 2019; *Institute Report*; The Global 412
- Use of Medicine in 2019 and Outlook to 2023; p 75. 413 (6) Knowles, W. S. Asymmetric Hydrogenation. Acc. Chem. Res. 414
- **1983**, 16, 106–112.
- (7) Kacprzak, K. M.; Maier, N. M.; Lindner, W. Highly Efficient 416 Immobilization of Cinchona Alkaloid Derivatives to Silica Gel *via* 417 Click Chemistry. *Tetrahedron Lett.* **2006**, 47, 8721–8726. 418
- (8) Jacobsen, E. N. Asymmetric Catalysis of Epoxide Ring-Opening 419 Reactions. Acc. Chem. Res. 2000, 33, 421–431. 420
- (9) Orito, Y.; Imai, S.; Nguyen-Gia-Hung. Asymmetric Hydro- 421 genation of Methyl Benzoylformate Using Platinum-Carbon Catalysts 422 Modified with Cinchonidine. J. Soc. Org. Synth. Chem. 1979, 37, 173- 423 174.

(10) Mallat, T.; Orglmeister, E.; Baiker, A. Asymmetric Catalysis at 425 Chiral Metal Surfaces. *Chem. Rev.* **200**7, *107*, 4863–4890. 426 427 (11) Jenkins, S. J.; Pratt, S. J. Beyond the Surface Atlas: A Roadmap 428 and Gazetteer for Surface Symmetry and Structure. *Surf. Sci. Rep.* 429 **2007**, *62*, 373–429.

430 (12) Gellman, A. J.; Tysoe, W. T.; Zaera, F. Surface Chemistry for 431 Enantioselective Catalysis. *Catal. Lett.* **2015**, *145*, 220–232.

432 (13) Mahjoub, B.; Hamouda, A. B.; Einstein, T. L. Role of Step 433 Stiffness and Kinks in the Relaxation of Vicinal (001) with Zigzag 434 [110] Steps. *Surf. Sci.* **2017**, *662*, 74–81.

435 (14) Rampulla, D. M.; Gellman, A. J. Enantioselective Decom-436 position of Chiral Alkyl Bromides on Cu(643) R & S: Effects of 437 Moving the Chiral Center. *Surf. Sci.* **2006**, *600*, 2823–2829.

438 (15) Sedghamiz, T.; Bahrami, M.; Ghatee, M. H. Enantiospecific
439 Adsorption of Propranolol Enantiomers on Naturally Chiral Copper
440 Surface: A Molecular Dynamics Simulation Investigation. *Chem. Phys.*441 2017, 487, 48–58.

442 (16) Reinicker, A. D.; Therrien, A. J.; Lawton, T. J.; Ali, R.; Sykes, E. 443 C. H.; Gellman, A. J. Influence of Step Faceting on the 444 Enantiospecific Decomposition of Aspartic Acid on Chiral Cu 445 Surfaces Vicinal to Cu{111}. *Chem. Commun.* **2016**, *52*, 1–4.

446 (17) Gellman, A. J.; Huang, Y.; Koritnik, A. J.; Horvath, J. D. 447 Structure-Sensitive Enantiospecific Adsorption on Naturally Chiral

448 Cu(hkl) R & S Surfaces. *J. Phys.: Condens. Matter* **2017**, *29*, 034001. 449 (18) Hazen, R. M.; Sholl, D. S. Chiral Selection on Inorganic 450 Crystalline Surfaces. *Nat. Mater.* **2003**, *2*, 367–374.

451 (19) Sholl, D. S.; Asthagiri, A.; Power, T. D. Naturally Chiral Metal 452 Surfaces as Enantiospecific Adsorbents. *J. Phys. Chem. B* **2001**, *105*, 453 4771–4782.

454 (20) Baber, A. E.; Gellman, A. J.; Sholl, D. S.; Sykes, E. C. H. The 455 Real Structure of Naturally Chiral Cu{643}. *J. Phys. Chem. C* 2008, 456 *112*, 11086–11089.

457 (21) Iski, E. V.; Tierney, H. L.; Jewell, A. D.; Sykes, E. C. H. 458 Spontaneous Transmission of Chirality through Multiple Length 459 Scales. *Chem. - Eur. J.* **2011**, *17*, 7205–7212.

460 (22) Weng, Z.; Zaera, F. Increase in Activity and Selectivity in 461 Catalysis *via* Surface Modification with Self-Assembled Monolayers. *J.* 462 *Phys. Chem. C* **2014**, *118*, 3672–3679.

463 (23) Lawton, T. J.; Pushkarev, V.; Wei, D.; Lucci, F. R.; Sholl, D. S.;
464 Gellman, A. J.; Sykes, E. C. H. Long Range Chiral Imprinting of
465 Cu(110) by Tartaric Acid. *J. Phys. Chem. C* 2013, *117*, 22290–22297.
466 (24) Shukla, N.; Bartel, M. A.; Gellman, A. J. Enantioselective
467 Separation on Chiral Au Nanoparticles. *J. Am. Chem. Soc.* 2010, *132*,
468 8575–8580

469 (25) Kühnle, A.; Linderoth, T. R.; Hammer, B.; Besenbacher, F. 470 Chiral Recognition in Dimerization of Adsorbed Cysteine Observed 471 by Scanning Tunnelling Microscopy. *Nature* **2002**, *415*, 891–893.

472 (26) Karakalos, S.; Lawton, T. J.; Lucci, F. R.; Sykes, E. C. H.; Zaera, 473 F. Enantiospecific Kinetics in Surface Adsorption: Propylene Oxide 474 on Pt (111) Surfaces. *J. Phys. Chem. C* **2013**, *117*, 18588–18594.

475 (27) Therrien, A.; Lawton, T. J.; Mernoff, B.; Lucci, F. R.;
476 Pushkarev, V. V.; Gellman, A.; Sykes, E. C. H. Chiral Nanoscale Pores
477 Created during the Surface Explosion of Tartaric Acid on Cu(111).
478 Chem. Commun. 2016, 52, 14282–14285.

479 (28) Cheong, W. Y.; Gellman, A. J. Energetics of Chiral Imprinting 480 of Cu(100) by Lysine. *J. Phys. Chem. C* **2011**, *115*, 1031–1035.

481 (29) Jewell, A. D.; Tierney, H. L.; Zenasni, O.; Lee, T. R.; Sykes, E.
482 C. H. Asymmetric Thioethers as Building Blocks for Chiral
483 Monolayers. *Top. Catal.* 2011, *54*, 1357–1367.

484 (30) Liriano, M. L.; Carrasco, J.; Lewis, E. A.; Murphy, C. J.; 485 Lawton, T. J.; Marcinkowski, M. D.; Therrien, A. J.; Michaelides, A.; 486 Sykes, E. C. H. The Interplay of Covalency, Hydrogen Bonding, and 487 Dispersion Leads to a Long Range Chiral Network: The Example of 488 2-Butanol. *J. Chem. Phys.* **2016**, *144*, 234701–241506.

(31) Horvath, J. D.; Gellman, A. J. Enantiospecific Desorption of Rand S-Propylene Oxide from a Chiral Cu(643) Surface. *J. Am. Chem.*Soc. 2001, 123, 7953–7954.

(32) Horvath, J. D.; Gellman, A. J. Enantiospecific Desorption of
Chiral Compounds from Chiral Cu(643) and Achiral Cu(111)
Surfaces. J. Am. Chem. Soc. 2002, 124, 2384–2392.

(33) Gudavarthy, R. V.; Burla, N.; Kulp, E. A.; Limmer, S. J.; Sinn, 495 E.; Switzer, J. A. Epitaxial Electrodeposition of Chiral CuO Films from 496 Copper(II) Complexes of Malic Acid on Cu(111) and Cu(110) 497 Single Crystals. *J. Mater. Chem.* **2011**, *21*, 6209–6216. 498

(34) Bohannan, E. W.; Kothari, H. M.; Nicic, I. M.; Switzer, J. A. 499 Enantiospecific Electrodeposition of Chiral CuO Films on Single- 500 Crystal Cu(111). J. Am. Chem. Soc. **2004**, 126, 488–489. 501

(35) Sarkar, S. K.; Burla, N.; Bohannan, E. W.; Switzer, J. A. 502 Inducing Enantioselectivity in Electrodeposited CuO Films by Chiral 503 Etching. *Electrochim. Acta* **2008**, *53*, 6191–6195. 504

(36) Switzer, J. A.; Kothari, H. M.; Poizot, P.; Nakanishi, S.; 505 Bohannan, E. W. Enantiospecific Electrodeposition of a Chiral 506 Catalyst. *Nature* **2003**, *425*, 490–493. 507

(37) Francis, A. J.; Salvador, P. A. Chirally Oriented Heteroepitaxlal 508 Thin Films Grown by Pulsed Laser Deposition: Pt(621) on 509 SrTiO₃(621). J. Appl. Phys. **2004**, 96, 2482–2493. 510

(38) Therrien, A. J.; Zhang, R.; Lucci, F. R.; Marcinkowski, M. D.; 511 Hensley, A.; McEwen, J. S.; Sykes, E. C. H. Structurally Accurate 512 Model for the "29"-Structure of CuxO/Cu(111): A DFT and STM 513 Study. J. Phys. Chem. C 2016, 120, 10879–10886. 514

(39) Wiame, F.; Maurice, V.; Marcus, P. Initial Stages of Oxidation 515 of Cu(111). Surf. Sci. 2007, 601, 1193–1204. 516

(40) Jensen, F.; Besenbacher, F.; Stensgaard, I.; Laegsgaard, E. 517 Oxidation of Cu(111): Two New Oxygen Induced Reconstructions. 518 *Surf. Sci.* **1991**, 359, L774–L780. 519

(41) Moritani, K.; Okada, M.; Teraoka, Y.; Yoshigoe, A.; Kasai, T. 520 Reconstruction of Cu(111) Induced by a Hyperthermal Oxygen 521 Molecular Beam. J. Phys. Chem. C 2008, 112, 8662–8667. 522

(42) Lawton, T. J.; Pushkarev, V.; Broitman, E.; Reinicker, A.; Sykes, 523 E. C. H.; Gellman, A. J. Initial Oxidation of Cu(hkl) Surfaces Vicinal 524 to Cu(111): A High-Throughput Study of Structure Sensitivity. J. 525 Phys. Chem. C 2012, 116, 16054–16062. 526

(43) De Alwis, A.; Holsclaw, B.; Pushkarev, V. V.; Reinicker, A.; 527 Lawton, T. J.; Blecher, M. E.; Sykes, E. C. H.; Gellman, A. J. Surface 528 Structure Spread Single Crystals (S⁴C): Preparation and Character- 529 ization. *Surf. Sci.* **2013**, 608, 80–87. 530

(44) Jeong, H.-C.; Williams, E. D. Steps on Surfaces: Experiment 531 and Theory. Surf. Sci. Rep. **1999**, 34, 171–294. 532

(45) Matsumoto, T.; Bennett, R. A.; Stone, P.; Yamada, T.; Domen, 533 K.; Bowker, M. Scanning Tunneling Microscopy Studies of Oxygen 534 Adsorption on Cu(111). *Surf. Sci.* **2001**, *471*, 225–245. 535

(46) Matsunami, N.; Yamamura, Y.; Itikawa, Y.; Itoh, N.; Kazumata, 536 Y.; Miyagawa, S.; Morita, K.; Shimizu, R.; Tawara, H. Energy 537 Dependence of the Ion-Induced Sputtering Yields of Monatomic 538 Solids. *At. Data Nucl. Data Tables* **1984**, *31*, 1–80. 539