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# Templated Growth of a Homochiral Thin Film Oxide

Alex C. Schilling, Andrew J. Therrien, Ryan T. Hannagan, Matthew D. Marcinkowski, Paul L. Kress, Dipna A. Patel, Tedros A. Balema, Amanda M. Larson, Felicia R. Lucci, Benjamin P. Coughlin, Renqin Zhang, Theodore Thuening, Volkan Çınar, Jean-Sabin McEwen, Andrew J. Gellman, and E. Charles H. Sykes\*



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



with high-resolution scanning tunneling microscopy. We discover that the local underlying metal facet directs the orientation and chirality of the oxide overlayer. Importantly, single homochiral domains of the "29" oxide were found in areas where the Cu step edges that templated growth were  $\leq 20$  nm apart. We use this information to select a Cu(239 241 246) oriented single crystal and demonstrate that a "29" oxide surface can be grown in homochiral domains by templating from the subtle chirality of the underlying metal crystal. This work demonstrates how a small degree of chirality induced by slight misorientation of a metal surface ( $\sim 1$  sites/20 nm<sup>2</sup>) can be amplified by oxidation to yield a homochiral oxide with a regular array of chiral oxide pores ( $\sim 75$  sites/20 nm<sup>2</sup>). This offers a general approach for making chiral oxide surfaces via oxidation of an appropriately "miscut" metal surface.

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

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

This approach has been used to study the transfer of surface chirality to adsorbates, or *vice versa*, as well as using chiral arrays of molecules to impart enantioselectivity to achiral surfaces.<sup>21-30</sup>

While the atomic-scale structure of chiral metal surfaces and their enantiospecific interaction with molecules is fairly well understood, only a handful of chiral oxides are known and their preparation and structural determination is challenging.<sup>15,19,31–35</sup> Work by Switzer *et al.* demonstrated that a

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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.<sup>38</sup> 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 horizontal 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 directions 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.

chiral oxide can be obtained by electrochemically depositing a copper oxide film from solutions containing chiral species such as tartaric acid. The chirality of the deposited film depends on the chirality of the tartrate ions in the deposition solution.<sup>34–36</sup> Other templating work includes pulsed laser deposition experiments performed by Salvador *et al.* in which a chiral Pt

film was grown over a chiral  $SrTiO_3(621)$  surface. The chirality of the substrate surface was imparted to the Pt layer.<sup>37</sup>

Herein we describe a system in which oxidation of a metal surface with a low density of chiral kink sites exhibits direct and robust chirality transfer and amplification during the formation of a homochiral surface oxide film. This effect is demonstrated with the well-defined "29" surface oxide, which is intrinsically chiral.<sup>38–41</sup> High-resolution scanning tunneling microscopy (STM) enables us to correlate the chirality of the "29" surface oxide with its position on a surface structure spread single crystal (S<sup>4</sup>C) and hence its relationship to the underlying Cu(hkl) facet.<sup>42</sup> These S<sup>4</sup>C crystals have spherically shaped surfaces that expose a continuous distribution of step and kink combinations, or microfacets, as described elsewhere.<sup>42</sup> In order to expose these microfacets, single crystals are purchased and then polished to have a shape that mimics the top of a sphere. The preparation of these crystals allows for exposure of all possible face centered cubic crystallographic surface orientations with just a few single-crystal samples. This approach allows us to probe how the subtle chirality of the step edges on a Cu(111)-S<sup>4</sup>C will template the growth of a homochiral "29" surface oxide. We go on to demonstrate that by selecting a subtly "miscut" crystal vicinal to Cu(111), it is possible to grow a single homochiral domain of the "29" oxide.

# **RESULTS AND DISCUSSION**

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

Due to the 3-fold symmetry of the underlying Cu(111) surface, each chirality (+22° and -22°) of the oxide exhibits three rotational domains. Figure 2 shows STM images of all six different orientations of the "29" oxide that can form on a flat Cu(111) surface due to the two enantiomers (denoted +, -) of the "29" oxide aligned with three equivalent directions on the 3-fold symmetric substrate. Each chiral unit cell is rotated 22° from the close-packed directions of Cu(111). The different orientations of the oxide are classified by the angle formed between the oxide and the [101] close-packed direction. We refer to one chirality of the oxide as the +22°, +142°, and +262° oxides, and the opposite chirality as the -22°, -142°,

and  $-262^\circ$  oxides. The structures with positive (counter-clockwise) and negative (clockwise) angles are enantiomers of each other.

Templated Growth of Chiral Oxides on the Curved Cu(111) Single Crystal. In order to determine whether the orientation and chirality of the "29" oxide domains are related to the structure and chirality of the underlying Cu surface, we performed STM measurements to determine how each oxide domain on the S<sup>4</sup>C was related to the local facet orientation of the underlying Cu surface. Because all terraces on the Cu(111)S<sup>4</sup>C surface are flat (111)-oriented planes, and are hence achiral, the step edges, most of which contain chiral kinks, are the only features that can play a role in templating the orientation and chirality of the "29" oxide film. Therefore, we acquired STM images at a number of positions spanning the  $S^4C$  in order to probe the impact of all step and kink combinations (i.e., local orientations of the underlying Cu surface) on the orientation and chirality of the "29" oxide. Figure 3 shows STM images obtained at 12 different points



Figure 3. Local orientation of the copper S<sup>4</sup>C 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 S<sup>4</sup>C. 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 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 S<sup>4</sup>C. The inner circle of Figure 3 lists the type of step edges found on the bare Cu crystal.<sup>42,43</sup> Because the Cu(111) S<sup>4</sup>C surface is polished in a dome shape to expose a continuous distribution of surface orientations, straight, close-packed step edges aligned with the high-symmetry directions of the crystal are either (100) (referred to as A type steps) or (110) oriented steps (B type steps). For steps to run in a low-symmetry direction they must incorporate *R* or *S* kinks and hence expose chiral microfacets.

The combination of step type and kink type alternate around the crystal as seen in Figure 3. The outer circle of Figure 3 shows representative STM images of the "29" oxide taken at multiple locations around the (111) pole ranging from 0.5 to 1.5 mm from the center with terrace widths between 5 and 20 nm. The 3-fold symmetry of the S<sup>4</sup>C leads to three equivalent orientations for each chiral microfacet, for example an A type step that incorporates kinks of a particular chirality, *i.e.*, *R*, is denoted  $A^R$  as seen in Figure 3.

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

Local Step Edge Refaceting during the Formation of the "29" Oxide. In an attempt to further understand the templated growth of the "29" oxide, the local structures of the step edges were studied before and after oxidation, as displayed 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 the 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 S<sup>4</sup>C 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.

substrate that correspond to the schematic below the STM image. The steps in the STM image in Figure 4A run roughly parallel to each other and in the direction dictated by the local surface orientation. The steps themselves, however, meander, which is typical for clean metal surfaces that undergo thermal roughening during the annealing step of their preparation.<sup>44</sup> In contrast, after oxidation, STM imaging reveals that the steps straighten after the "29" oxide formation (Figure 4B). While

we cannot image during oxidation, previous work on the roomtemperature oxidation of Cu(111) surfaces<sup>39,42,45</sup> has shown 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 mechanism of this step refaceting is unclear, but we hypothesize that it could be driven by the "29" Cu oxide if it has larger penalties for variations in the stepped-kinked structure than the Cu metal surface.

Analysis of Step Density on Oxide Templating. While the above conclusions are valid for areas of the S<sup>4</sup>C in which the step density was somewhat high (terraces widths ~10 nm), we systematically studied other areas of the S<sup>4</sup>C in order to investigate the effect of step density on chiral oxide templating. Imaging the very large terraces (>20 nm) at the (111) pole of the S<sup>4</sup>C after oxidation yielded areas that have long-range (>50 nm) order of a single oxide orientation/chirality, as well as areas with several different oxide orientations. Figure 5C shows a large STM image that covers 200 × 200 nm<sup>2</sup>, comprising just one large, flat 160 nm terrace, and no step edges. This area contains two different orientations of the "29" oxide. Farther from the (111) center of the S<sup>4</sup>C, the step density increases, leading to smaller terraces (<10 nm).<sup>42</sup> In most of the STM



Small Terraces Medium Terraces Large Terraces

Figure 5. Effect of local Cu surface facet on the orientation and chirality of the Cu<sub>2</sub>O film. The histogram shows the percent match of the "29" oxide orientation and chirality with local facet as a function of terrace width. The scatter plot above shows the number of times each terrace width was observed. The inset shows a side view photo of the S<sup>4</sup>C. (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.

images taken at similar distances from the center of the crystal to the area in Figure 5B, smaller terraces (<20 nm) of single oxide domains exist. Not all the step edges, however, have the same orientation of the oxide. Figure 5B shows examples in which an oxide domain is surrounded by steps of different orientation, and hence it can only align with one of the steps. By moving farther from the center of the  $S^4C_2$ , the terrace width continues to decrease and regions of oxide and step edges orientated in the same direction become more common. These terraces, shown in Figure 5A, are between 5 and 10 nm wide, and the oxides on adjacent terraces almost always have the same orientation and chirality. The histogram in Figure 5 quantifies the influence of step density on oxide templating; >700 STM images were analyzed, and the oxide orientation with respect to the step edges is plotted as a function of terrace width. Figure 5 shows a strong oxide templating effect for terraces  $\leq$  20 nm. Increasing terrace width above 20 nm leads to more random oxide orientations.

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

Unfortunately, the center of the crystal produced LEED patterns consisting of multiple orientations/chirality of the oxide as seen in Figure 6. This became progressively worse over time, and the results are consistent with an inhomogeneous flux of Ar<sup>+</sup> ions during sputter cleaning treatments that lead to the center of the crystal being sputtered away preferentially, as can be seen visually in the inset of Figure 6. Given that the Cu(239 241 246) single crystal is only a  $0.7^{\circ}$ miscut from the achiral (111) orientation, very little material needs to be removed to destroy the homochirality of the Cu crystal, as is observed in our experiments. For example, in order to transition from the 0.7° miscut crystal surface that exposes just one chirality of kink to a surface that exposes the opposite chirality kink, one must reorient the Cu(239 241 246) surface by  $1.4^{\circ}$ . The width of the misoriented area in the center of the crystal is  $\sim$ 5 mm wide; so to expose an appreciable number of kinks of opposite chirality, geometrically one would have to sputter  $\sim 0.14$  mm into the crystal at this point. Assuming a sputter yield of 3 Cu atoms ejected per Ar<sup>+</sup> under our typical cleaning conditions of 2  $\mu$ A at 1.5 keV, we estimate that it would take ~2000 h of sputtering to create such a defect.<sup>46</sup> This equates to  $\sim$ 2 h per day of cleaning and is in agreement with the total duration of the cleaning 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 surface with nanoscale chiral facets can be used to template the growth of oriented, homochiral oxides at the macroscale.



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.

#### CONCLUSION

We have demonstrated that the orientation and chirality of a single-layer thin film "29" surface oxide can be controlled by the local orientation and structure of the underlying Cu surface before oxidation. The "29" surface oxide exists in two enantiomeric forms, with each chirality having three equivalent orientations due to the 3-fold rotational symmetry of the Cu(111) crystal. Using a S<sup>4</sup>C allowed us to systematically investigate how the local Cu surface orientation influenced the oxide growth. We discovered that the chirality of the underlying Cu surface could be used to template fairly longrange homochiral growth of the oxide film with terraces up to 20 nm wide showing a predominance of just one enantiomer and rotational orientation of the oxide. Our data also revealed that the chiral templating effect can be understood in terms of the direction of the local step edges which align with the orientation of the "29" oxide on the associated terrace.

Given that oxidation starts at step edges on the Cu surface and that they become significantly refaceted during oxidation in a direction that aligns exactly with the oxide orientation, it follows that the oxide forms in the orientation that is closest to the original direction of the step edge.<sup>42</sup> Previous studies have demonstrated the existence of different chiral domains on a "29" oxide surface. However, the driving force behind the formation of these domains was not understood.<sup>39,45</sup> Our systematic study lends insight into this process by emphasizing the direct correlation between local underlying metal surface facet and homochiral oxide domain orientation. We demonstrate that the relatively small number of chiral kink sites on the steps of a Cu(239 241 246) crystal are enough to direct the homochiral growth of the oxide. This chirality transfer between metal surface and thin film oxide may in fact be general and therefore enable a range of oriented homochiral thin film

oxides to be grown in a straightforward manner without the difficulty of cutting and polishing oxide single crystals.

#### **EXPERIMENTAL SECTION**

All of the STM work presented in this study was performed on a  $Cu(111) \pm 11^{\circ} S^{4}C$  crystal prepared at Carnegie Mellon University. The S<sup>4</sup>C was cleaned by consecutive cycles of Ar<sup>+</sup> sputtering (1.5 keV/17  $\mu$ A) and annealing (800 K) in the preparation chamber (base pressure of  $1 \times 10^{-10}$  mbar) of an Omicron Technology variabletemperature ultra-high-vacuum (VT-UHV) STM. The same experiments were performed in an Omicron Technology low-temperature ultra-high-vacuum (LT-UHV) STM. In order to make the surface oxide layer, the surface was exposed to 900 L of O2, through a collimated leak valve, while the crystal was held at 650 K. Once the oxide was formed, the crystal was transferred to the STM chamber (base pressure  $<1 \times 10^{-10}$  mbar) and imaged using a W tip from Omicron Technology. Typical imaging conditions in the presented VT-STM images are a bias of -0.4 V, with respect to the sample, and current of 0.7 nA with all images being recorded at 298 K. LT-STM images were collected at 80 K with typical imaging conditions of -0.5V, with respect to the sample, and 0.5 nA tunneling current. All lowenergy electron diffraction patterns were generated using an OCI Vacuum Microengineering Digital LEED and AES system model LPS300-D with a filament current of 2.64 A, a focus of 88 V, a screen voltage of 5 kV, and a beam energy of 66 eV. The images were captured using a Samsung Galaxy S9 smartphone. The STM images used to generate the chart in Figure 5 were processed with SPIP software and analyzed by measuring the width of every terrace imaged and separating each terrace into one of two categories: (1) the oxide rows are formed in an orientation matching the upper and lower step edges, or (2) the oxide rows are formed in an orientation not matching the step edges. These data are plotted on the chart in Figure 5 as a function of terrace width.

### **AUTHOR INFORMATION**

#### **Corresponding Author**

E. Charles H. Sykes – Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States; orcid.org/0000-0002-0224-2084; Email: charles.sykes@ tufts.edu

#### Authors

- Alex C. Schilling Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Andrew J. Therrien Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Ryan T. Hannagan Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Matthew D. Marcinkowski Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Paul L. Kress Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- **Dipna A. Patel** Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- **Tedros A. Balema** Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Amanda M. Larson Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Felicia R. Lucci Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Benjamin P. Coughlin Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States; orcid.org/0000-0002-9908-7817
- **Renqin Zhang** The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State

University, Pullman, Washington 99164, United States; orcid.org/0000-0002-4489-2050

- **Theodore Thuening** Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Volkan Çınar Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States
- Jean-Sabin McEwen The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Department of Physics and Astronomy, Department of Chemistry, and Department of Biological Systems Engineering, Washington State University, Pullman, Washington 99164, United States; Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, Washington 99352, United States; © orcid.org/0000-0003-0931-4869
- Andrew J. Gellman Department of Chemical Engineering and W.E. Scott Institute for Energy Innovation, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States;
   orcid.org/0000-0001-6618-7427

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.0c00398

## Notes

The authors declare no competing financial interest.

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