

Enantiospecific Electrodeposition of Chiral CuO Films on Single-Crystal Cu(111)

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The enantiomeric form of molecules is critical in biological systems. Synthesis, separation, and detection of enantiomers are necessarily topics of great interest in chemistry. Besides the molecular chirality familiar to chemists, chirality can also be associated with solid surfaces. Electrodeposited monoclinic CuO has recently been shown to deposit enantioselectively from chiral precursors on single-crystal Au(001).¹ The CuO surfaces were enantioselective for the oxidation of tartrate. A great deal of novel work has also been published on chiral surfaces of high index faces of fcc metals.^{2–6} These materials would not ordinarily be expected to exhibit chirality because they do not crystallize in a chiral space group. The classic example of a solid that crystallizes in a chiral space group is quartz. For chirality to be observed in the case of an fcc metal, it is necessary to expose a high index plane such as Pt(643). It has been proposed that the formation of kink sites imparts the chirality to the surface, which has been shown to be enantioselective toward the oxidation of glucose.⁶

Copper substrates are of interest for chiral electrodeposition studies, because other workers have shown that the symmetry of achiral Cu surfaces can be broken by the adsorption of tartaric acid molecules.^{7,8} The assembled tartaric acid molecules expose chiral channels within which the copper atoms are available to react with other molecules. Here, we show that chiral films of CuO can be electrodeposited onto single-crystal Cu(111). The chirality of the electrodeposited CuO is determined by the enantiomer of tartrate ion used in the deposition solution.

The electrodeposition of CuO has been demonstrated previously via the oxidation of complexes of Cu(II) with tartrate ions^{1,9} and amino acids.¹⁰ Figure 1 shows Bragg–Brentano X-ray diffraction patterns of two CuO films electrodeposited at 0.4 V versus SCE for 45 min on a Cu(111) single crystal from a solution of 0.2 M Cu(II), 0.2 M tartrate ion in 3 M NaOH at 30 °C. The anodic charge density was 8 C/cm², and the films were 400 nm thick. Figure 1A shows the pattern for the film deposited from Cu(II) (*S,S*)-tartrate, and Figure 1B shows the pattern for the film deposited from Cu(II) (*R,R*)-tartrate. From the Bragg–Brentano patterns, it appears that there is no difference between the two highly textured films. However, analysis of pole figures obtained from the epitaxial films demonstrates that the films actually have two different orientations, CuO(1 $\bar{1}\bar{1}$) in Figure 1A and CuO($\bar{1}11$) in Figure 1B.

Epitaxial electrodeposition has been demonstrated for a number of oxides on single-crystal metal^{1,11–14} and semiconductor substrates.^{15–17} Because the CuO in the present work was deposited onto single-crystal Cu(111), the absolute configuration of the film can be determined by X-ray pole figure analysis. By choosing a specific *d* spacing to probe while measuring diffracted intensity as a function of tilt and rotation, one obtains a pole figure. Figure 2A shows the CuO(111) pole figure for the CuO film deposited from Cu(II) (*S,S*)-tartrate, while Figure 2B shows the same pole figure for the CuO film deposited from Cu(II) (*R,R*)-tartrate. The two pole

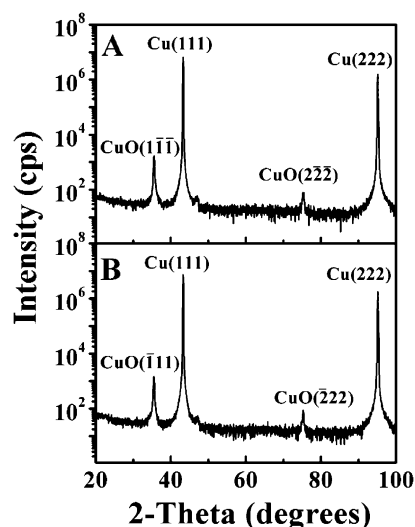


Figure 1. Bragg–Brentano scans of CuO films on Cu(111) single crystals. The film in (A) was electrodeposited from a solution of Cu(II) (*S,S*)-tartrate, while the film in (B) was deposited from a solution of Cu(II) (*R,R*)-tartrate.

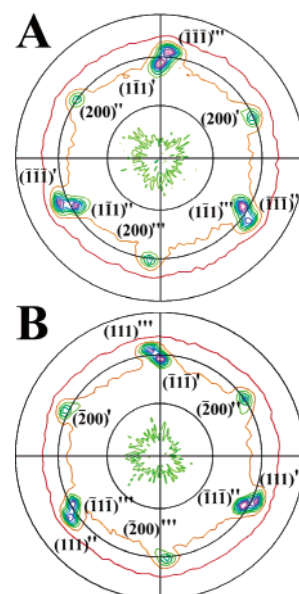


Figure 2. CuO(111) pole figures of a film electrodeposited from solutions of Cu(II) (*S,S*)-tartrate (A) and Cu(II) (*R,R*)-tartrate (B). The (111) and (200) CuO planes have similar *d* spacings and are both observed in the pole figure. The radial grid lines on the pole figures correspond to 30° increments in the tilt angle.

figures are clearly nonsuperimposable mirror images of one another. Further analysis reveals that each pole figure is a result of three crystalline domains rotated 120° from one another. Although the

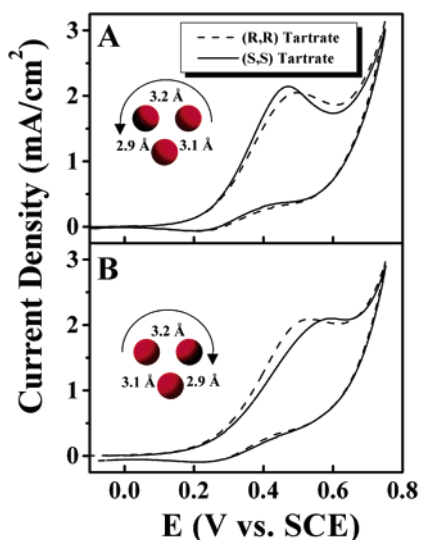


Figure 3. Cyclic voltammograms obtained at a scan rate of 10 mV/s from 5 mM solutions of (*R,R*)- and (*S,S*)-tartrate in 0.1 M NaOH on (A) a CuO($\bar{1}\bar{1}\bar{1}$) working electrode and (B) a CuO(111) working electrode. The CuO($\bar{1}\bar{1}\bar{1}$) surface is seen to be more active toward the oxidation of (*S,S*)-tartrate, while the CuO(111) surface is seen to be more active toward the oxidation of (*R,R*)-tartrate. The inset in (A) shows the arrangement of Cu atoms on the ($\bar{1}\bar{1}\bar{1}$) plane and the counterclockwise rotation observed when assigning priority to increasing distances between the Cu atoms. The inset in (B) shows the same, except on the (111) surface. In this instance, a clockwise rotation is obtained.

spacing for the CuO(111) planes was probed for the pole figures in Figure 2, diffraction from the CuO(200) planes is also observed as the two d spacings are not sufficiently resolved from one another. The film examined in Figure 2A is consistent only with a CuO($\bar{1}\bar{1}\bar{1}$) out-of-plane orientation, while the film in Figure 2B has a CuO(111) out-of-plane orientation. Although not shown due to space limitations, CuO films deposited from Cu(II) complexed with racemic tartrate show equal amounts of the CuO($\bar{1}\bar{1}\bar{1}$) and CuO(111) orientations.

Figure 3A shows cyclic voltammograms obtained on a CuO($\bar{1}\bar{1}\bar{1}$) film in 5 mM solutions of (*S,S*)- and (*R,R*)-tartrate in 0.1 M NaOH, while Figure 3B shows the same for a CuO(111) film on Cu(111). The electrodeposited CuO acts as a catalyst toward the oxidation of tartrate and it exhibits enantioselectivity toward the different chiral forms of the ion. Examination of Figure 3A reveals that the CuO($\bar{1}\bar{1}\bar{1}$) film more readily oxidizes (*S,S*)-tartrate while the CuO(111) film more readily oxidizes the (*R,R*)-tartrate as seen in Figure 3B. Although not shown due to space considerations, CuO films deposited from the racemic Cu(II) tartrate show identical voltammograms in the (*R,R*)- and (*S,S*)-tartrate solutions.

The enantioselective adsorption of tartrate^{7,8} or that of the Cu(II) tartrate complex itself on single-crystal Cu is almost certainly related to the enantioselective electrodeposition observed here. Although the exact mechanism of enantioselectivity observed with cyclic voltammetry is under investigation, one can see how it may arise by examining the arrangement of Cu atoms on the ($\bar{1}\bar{1}\bar{1}$) and (111) CuO planes. The Cu atoms on the CuO($\bar{1}\bar{1}\bar{1}$) plane have a

pseudohexagonal arrangement with three slightly different spacings between the copper atoms. If we arbitrarily assign a rotation based on increasing spacing between the Cu atoms, we obtain a counterclockwise rotation as seen in the inset in Figure 3A. Applying the same set of rules, we get a clockwise rotation for the Cu atoms on the CuO(111) plane as seen in the inset in Figure 3B. The arrangement of Cu atoms on the two planes lacks a center of symmetry, and they are nonsuperimposable mirror images of one another. The tartrate ions may not necessarily be interacting with Cu atoms on the ($\bar{1}\bar{1}\bar{1}$) and (111) planes, but one can reasonably assume that the “true” surface of interaction would contain some manifestation of this two-dimensional chirality.

It should also be possible to electrodeposit other low-symmetry materials, such as monoclinic AgO, on achiral surfaces in the presence of chiral species, inducing the formation of solid chiral surfaces. Extension of this technique to inexpensive textured or polycrystalline substrates is also of great interest. Rolling-assisted biaxially textured substrates (RABiTS)¹⁸ are available at a relatively low cost for a variety of metals, including copper. The single-crystal-like RABiTS tapes may prove useful as a cost-effective substrate for enantiospecific electrodeposition. Electrodeposition also affords the ability to control the morphology and orientation of the films by varying solution conditions,¹⁴ which should prove useful in designing these chiral surfaces. The appropriate choice of catalyst, surface, and target molecule could potentially obviate the need for chiral separation prior to chemical detection in analytical methods.

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