Communication

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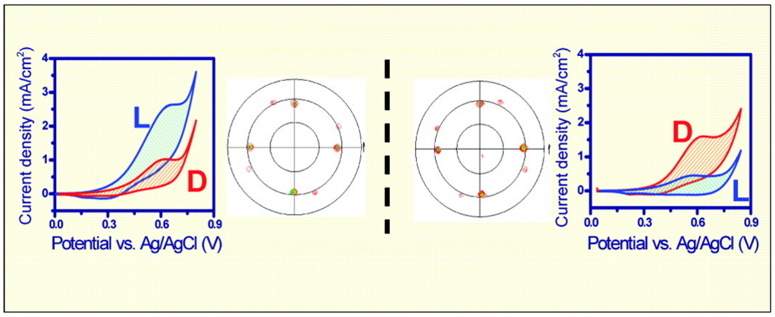

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Enhancing Enantioselectivity of Electrodeposited CuO Films by Chiral Etching

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There is great interest in producing chiral surfaces for the enantiospecific synthesis, separation, and sensing of chiral molecules. One approach to producing chiral surfaces of inorganic materials is to produce high index surfaces (such as (643) and ($\bar{6}\bar{4}\bar{3}$)) on single crystals of highly symmetrical materials such as fcc metals.[1] The surface chirality of these high index surfaces is attributed to kink sites. Our approach to producing chiral surfaces is to electrodeposit low-symmetry materials such as monoclinic CuO onto high-symmetry surfaces such as Au or Cu in the presence of chiral molecules such as tartaric acid or amino acids that template the growth of chiral orientations.[2] In our earlier work we showed by X-ray diffraction that the electrodeposited CuO had chiral *orientations*, and by chiral selectivity experiments that the films also exposed chiral *surfaces*. Widmer et al. verified by X-ray photoelectron diffraction that the electrodeposited CuO films had chiral orientations.[3] In this Communication we show that the enantioselectivity of electrochemical sensors based on electrodeposited CuO films with chiral orientations can be greatly enhanced by etching the films in tartaric acid. We attribute the enhancement to an increase in area of chiral surfaces.

A chiral surface lacks mirror or glide-plane symmetry.[4] Chiral surfaces of CuO can be produced even though the material crystallizes in an achiral space group. CuO has a monoclinic structure (space group $C2/c$) with $a = 0.4685$, $b = 0.3430$, and $c = 0.5139$ nm and $\beta = 99.08°$. The unique twofold axis for CuO is the b axis, and the mirror plane is perpendicular to the b axis. Achiral orientations correspond to those planes parallel with the b axis (planes of the (010) zone). Achiral planes are those with $k = 0$, that is (h0l). Remaining planes with $k \neq 0$ are all chiral. For an orientation which satisfies the conditions for chirality, the planes (hkl) and ($\overline{\mathrm{hkl}}$) form an enantiomorphic pair.

Films of CuO were electrochemically deposited onto single-crystal Au(001) substrates from a bath containing 0.2 M $CuSO_4$, 0.2 M tartaric acid, and 3 M NaOH. The films were deposited at a constant anodic current density of 1 mA/cm^2 for 30 min at 30 °C. The chiral nature of the films is obvious from the CuO(111) X-ray pole figures that are shown in Figure 1. The film deposited from L(+)-tartrate in Figure 1a has a ($1\bar{1}\bar{1}$) orientation, while the film shown in Figure 1b that was deposited from D(−)-tartrate has a ($\bar{1}11$) orientation. The pole figures are clearly non-superimposable mirror images of one another, and the two orientations are enantiomers. We emphasize here that the X-ray pole figure determines the crystallographic orientation of the films, but it does not determine which surfaces are exposed. For example, the film deposited from L(+)-tartrate is oriented with the ($1\bar{1}\bar{1}$) planes parallel with the electrode surface, but the surface can be faceted with planes other than ($1\bar{1}\bar{1}$) exposed.

The electrodeposited films were also etched for 10 min in a 10 mM solution of tartaric acid (pH = 2.7) to enhance their enantioselectivity. Because CuO is amphoteric, it can be etched in either acidic or strongly alkaline solution. The solubility reaches a minimum at about pH 9. The dissolution was followed in-situ using an electrochemical quartz crystal microbalance (EQCM).[5] The 300 nm thick CuO film completely dissolves after etching for approximately 30 min. The EQCM results in Figure 2 show that a film deposited from L(+)-tartrate dissolves faster in L(+)-tartaric acid than it does in D(−)-tartaric acid. Likewise, a film deposited from D(−)-tartrate dissolves faster in D(−)-tartaric acid than it does in L(+)-tartaric acid. X-ray pole figures of the films were unchanged after etching for 10 min, showing that the orientation of the film does not change.

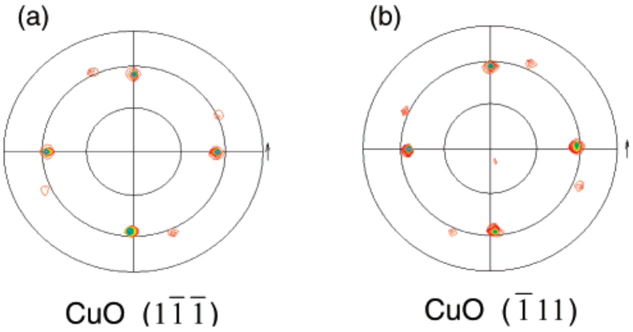

Figure 1. CuO(111) X-ray pole figures of CuO films that were electrodeposited onto single-crystal Au(001) from solutions of (a) L(+)-tartrate and (b) D(−)-tartrate. The radial grid lines correspond to 30° increments of the tilt angle.

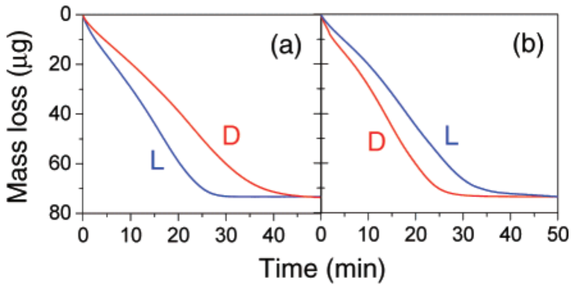

Figure 2. EQCM measurements of the mass loss of CuO films deposited from (a) L(+)-tartrate and (b) D(−)-tartrate during etching with L(+)-tartaric acid (blue curve) and D(−)-tartaric acid (red curve) at pH 2.7.

The surface chirality of the as-deposited and etched CuO films was studied electrochemically by cyclic voltammetry (CV) using 5 mM L- or D-tartrate ion in 0.1 M NaOH as the chiral redox agent. Figure 3a and 3b show the CVs of CuO films that were deposited from L(+)-tartrate. The as-deposited film (Figure 3a) shows a slight enantioselectivity for the oxidation of L(+)-tartrate, which is manifested in a slight shift in potential of the CVs. After etching for 10 min in L(+)-tartaric acid (Figure 3b), the film shows a greatly enhanced enantioselectivity for the oxidation of L(+)-tartrate. After etching, the oxidation limiting current is larger for the enantiomer

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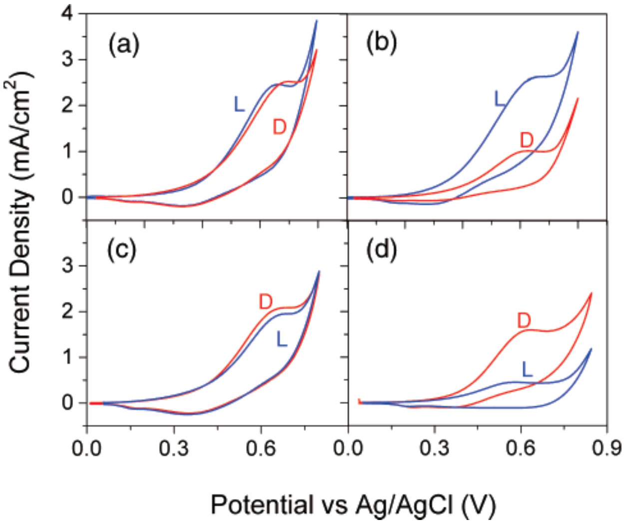


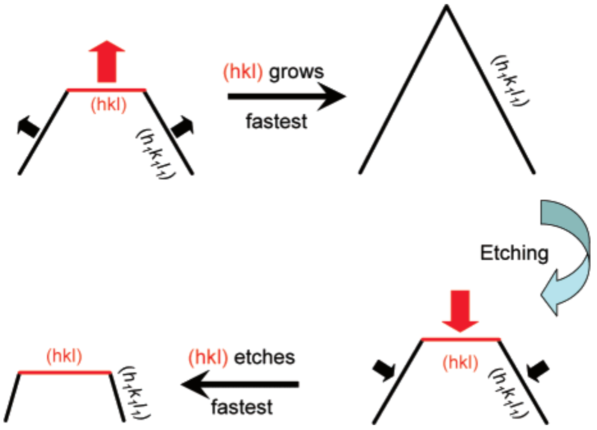
Figure 3. Cyclic voltammetric (CV) measurements to show the effect of etching on chiral recognition of tartrate ion on electrodeposited CuO. CVs in L(+)-tartrate are blue and D(-) tartrate are red: (a) as-deposited CuO from L(+)-tartrate, (b) same film after etching in L(+)-tartaric acid, (c) as-deposited CuO film from D(−)-tartrate, (d) same film after etching in D-(−)-tartaric acid. The CVs were scanned at 10 mV/s in unstirred 5 mM solutions of tartrate in 1.0 M NaOH.

that is used to etch the film. The limiting current density is 2.7 mA/cm^2 for the oxidation of L(+)-tartrate and 1.0 mA/cm^2 for the oxidation of D(−)-tartrate. Figure 3c and 3d show the CVs for tartrate oxidation on a film that was as-deposited from D(−)-tartrate (Figure 3c) and a film that was subsequently etched in 10 mM D(−)-tartaric acid (Figure 3d). Again, there is a slight enantioselectivity for D(−)-tartrate for the as-deposited film and an enhanced enantioselectivity for D(−)-tartrate after etching in D(−)-tartaric acid. The limiting current density on the etched film in Figure 3d is 1.6 mA/cm^2 for the oxidation of D(−)-tartrate and 0.4 mA/cm^2 for the oxidation of L(+)-tartrate. In both cases, etching with a given enantiomer of tartaric acid appears to inhibit the oxidation of the opposite enantiomer of tartrate ion.

The mechanism of enantioselective enhancement by chiral etching is not clear. One explanation would be that the chiral response is due to an adsorbed monolayer or multilayer of tartrate or Cu(II)-tartrate that remains on the surface after etching. Our experiments, however, suggest that this is not the mechanism for chiral enhancement. The chiral response persists for the etched electrodes after the CuO is electrochemically cleaned by cycling the potential into the oxygen evolution regime. The chiral response is not enhanced if the CuO electrode is soaked for 10 min in a tartrate solution at pH 9. At this pH, the etching of the film is minimized. Finally, if a film that was deposited from L(+)-tartrate is etched in D(−)-tartaric acid, the electrode does not become selective for D(−)-tartrate.

The model we use to explain the enhancement of enantioselectivity by etching is shown in Scheme 1. In this model, we assume that the (*hkl*) planes are the most active and therefore grow and etch the fastest. If we start with a faceted CuO film that has a (*hkl*) orientation with both (*hkl*) and ($h_1k_1l_1$) planes exposed and then deposit additional material, the fastest growing (*hkl*) plane will grow out of existence, leaving only the ($h_1k_1l_1$) planes exposed.[6] The microstructure shown at the top right of the figure still has a (*hkl*) orientation (if determined by X-ray diffraction), but there are no (*hkl*) planes exposed. If the film is then anisotropically etched with the (*hkl*) planes etching fastest, the final microstructure will be dominated by (*hkl*) planes. If the (*hkl*) surface is the most enantioselective, etching of the film will enhance the enantioselectivity by exposing a larger (*hkl*) surface area.

Scheme 1. Proposed Scheme for the Increase in the Surface Area of (*hkl*) Planes by Chiral Etching



The ability to enhance enantioselectivity in electrodeposited chiral films could lead to the development of chiral surfaces that can be used for the synthesis, separation, and sensing of important chiral molecules, such as single-enantiomer pharmaceuticals. In addition, it may be possible to *induce* chirality in powders of low-symmetry inorganic materials such as CuO, calcite, and gypsum to produce chromatographic supports for chiral separations.

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