Chiral Electrodeposition

by Jay A. Switzer

Chirality is ubiquitous in Nature. One enantiomer of a molecule is often physiologically active, while the other enantiomer may be either inactive or toxic. For example, S-ibuprofen is up to 100 times more active than R-ibuprofen. R-thalidomide is a sedative, but S-thalidomide causes birth defects. Worldwide sales of single-enantiomer drugs reached $159 billion in 2003.¹ The industrial synthesis of chiral compounds presently utilizes solution-phase, homogeneous catalysts and enzymes. Chiral surfaces offer the possibility of developing heterogeneous enantiospecific catalysts that can more readily be separated from the products and reused. In addition, such surfaces may serve as electrochemical sensors for chiral molecules, perhaps even implantable chiral sensors that could be used to monitor drug levels in the body. Another application would be post-chromatographic chiral electrochemical detectors, which would obviate the need for chiral separation of analyte molecules before chemical detection.

Chiral surfaces have been produced previously by adsorbing chiral molecules on achiral substrates,²⁻⁸ or by slicing single crystals so that they exhibit high-index faces with chiral kink sites.⁹⁻¹⁷ These high index single crystals have been shown to act as enantioselective heterogeneous catalysts.¹⁵ Recently, we showed that chiral films of metal oxides such as CuO can be electrodeposited on achiral surfaces, using chiral molecules such as tartaric or amino acids to direct the chirality.¹⁸⁻²⁰ In this respect, electrodeposition resembles biomineralization in that organic molecules adsorbed on surfaces may have profound effects on the morphology of the inorganic deposits.¹⁷, ²¹⁻²⁵ The reduction of symmetry of surfaces by the adsorption of chiral molecules is known in biomineralization to produce chiral crystal habits on minerals such as calcite and gypsum which have achiral space groups. Enantioselective adsorption on the surfaces of minerals such as calcite has also been invoked to explain the genesis of biogenic homochirality.²⁶

Our approach to the development of new chiral heterogeneous catalysts and sensors is to electrodeposited low symmetry metal oxide films with chiral orientations on achiral substrates. We have deposited chiral orientations of CuO on single-crystal Au and Cu using both tartaric acid and the amino acids alanine and valine to control the handedness of the electrodeposited films.¹⁸⁻²⁰ The use of chiral solution agents to control the chirality of electrodeposited films provides a degree of freedom that is not available to ultrahigh-vacuum vapor deposition methods. Previously, we showed that CuO can be electrodeposited by oxidizing Cu(II) complexes of tartaric acid,²⁷ and Nakaoka and Ogura have shown that the material can be produced by oxidizing Cu(II) complexes of amino acids.²⁸ An outline of the enantiospecific electrodeposition scheme for CuO on Au(001) is shown in Fig. 1. Chiral CuO with either a (111) or (111) orientation is electrodeposited on Au(001). The films grown from L-tartaric acid [(R,R)-(−)-tartaric acid] have a CuO (111) orientation, while films grown from D-tartaric acid [(S,S)-(−)-tartaric acid] have a CuO (111) orientation. The smaller dark red spheres at the bottom of Fig. 1 represent Cu atoms. There are two non-equivalent O atoms which are blue. The filled, blue O atoms are closest to the Cu plane, and sit in threefold hollow sites. The open, blue O atoms are nearly atop the Cu atoms. The two orientations of CuO are clearly nonsuperimposable mirror images.

FIG. 1. Outline of the chiral electrodeposition scheme. Chiral CuO with either a (111) or (111) orientation is electrodeposited onto achiral substrates such as Au(001). The (111) orientation is produced by oxidation of Cu(II) L-tartrate, and the (111) orientation is produced by oxidation of Cu(II) D-tartrate. The two orientations of CuO lack mirror symmetry, and are clearly nonsuperimposable mirror images.
FIG. 2. Polyhedral models of the chiral (111) and (−111) orientations of CuO. The Cu atoms are shown in red, while the O atoms are shown in blue. The planes in light and dark blue show the Cu coordination with the nearest O atoms along the [110] and [−110] directions.

CuO can be deposited with chiral orientations even though the bulk crystal structure of CuO is centrosymmetric, but orientations such as (643) and (6−43) are nonsuperimposable mirror images.9–17 With lower symmetry materials such as CuO, it is not necessary to have large values for the Miller indices to observe chirality. Chiral crystal surfaces lack mirror or glide plane symmetry.29 CuO has a monoclinic structure (space group C2/c), with a = 0.4685 nm, b = 0.3430 nm, c = 0.5139 nm, and β = 99.08°. The unique twofold axis for CuO is the b axis, and the mirror plane is perpendicular to the b axis. Achiral orientations, therefore, correspond to those planes parallel with the b axis (planes of the [010] zone). Achiral planes are those with k = 0, such as (100), (101), (709), (001), and, in the general case, (h0l). Remaining planes with k ≠ 0, such as (010), (111), and (011) are all chiral. For an orientation which satisfies the conditions for chirality, the planes (hkl) and (−h−k−l) form an enantiomorphic pair.

The absolute configuration of chiral films can be determined by X-ray pole figure analysis. Pole figures can be used to probe planes that are not parallel with the geometric plane of the sample. The sample is moved through a series of tilt angles, χ, and at each tilt angle the sample is rotated through azimuthal angles, ϕ, of 0 to 360°. Peaks occur in the pole figure when the Bragg condition is satisfied. The pole figure determines both the out-of-plane and in-plane orientations of the film, in addition to the orientation of the film relative to the substrate. Figure 3 shows (111) pole figures for 300 nm thick CuO films deposited on a Au(001) single crystal from solutions of (a) L-tartaric acid, (b) D-tartaric acid, and (c) DL-tartaric acid. The radial direction is the tilt of the sample with grid lines spaced 30° apart. The films grown from L-tartaric acid have a CuO(111) orientation, while films grown from D-tartaric acid have a CuO(−111) orientation. The film deposited from DL-tartaric acid has nearly equal amounts of the two chiral orientations.

The enantiomeric excess of one orientation over the other may also be determined by X-ray diffraction (XRD)
using azimuthal scans. Figure 4 shows azimuthal scans extracted from the (111) pole figures in Fig. 3 at $\chi = 63^\circ$ with the azimuthal angle, $\phi$, varying from 60 to 120°. The peaks in blue and red correspond to the (1\bar{1}1) and (\bar{1}11) orientations, respectively. The film produced from L-tartaric acid has the (111) orientation in 95% enantiomeric excess, while the film produced from D-tartaric acid has the (111) orientation in 93% enantiomeric excess. The film deposited from DL-tartaric acid has equal amounts of both orientations and has essentially zero enantiomeric excess.

Other chiral agents besides tartaric acid can be used as templates for chiral electrodeposition. We have used amino acids such as valine and alanine to deposit chiral CuO films on single-crystal Au and Cu. Figure 5 shows (111) pole figures for CuO deposited on Cu(110) from D-alanine and L-alanine. CuO films deposited from D-alanine (Fig. 5a) grow with the (\bar{1}10) orientation, while films deposited from L-alanine (Fig. 5b) grow with the (110) orientation. These orientations both lack mirror symmetry and are nonsuperimposable mirror images of each other. CuO films grown from either DL-alanine or the achiral amino acid glycine consist of a racemic mixture of the (110) and (1\bar{1}0) orientations.

The X-ray pole figures show that the bulk films grown in tartaric or amino acids are enantiomers, but they do not provide information on the chirality of the surface. Electrochemical oxidation studies were done to probe the surface chirality. CuO has been shown by other workers to be a potent electrocatalyst for the oxidation of carbonates, amino acids, simple alcohols, aliphatic diols, and alkyl polyethoxy alcohol detergents.30 Cyclic voltammograms (CVs) showing the oxidation of tartaric acid on CuO deposited from L-, D-, and DL-tartaric acid onto Au(001) are shown in Fig. 6. The chiral recognition studies were run in a solution containing 5 mM tartaric acid in 0.1 M NaOH. The CVs were obtained in unstirred solutions by scanning from the rest potential to +0.75 V vs. SCE on the CuO electrodes at a scan rate of 10 mV/s. Before switching solutions the electrode was cleaned by scanning in 0.1 M NaOH. Oxidation of the solvent occurs at about 0.6 V vs. SCE on the CuO electrodes (dotted curves in Fig. 6). The CVs show that films grown in L-tartaric acid (Fig. 6a) selectively oxidize L-tartaric acid, while films grown in D-tartaric acid (Fig. 6b) selectively oxidize D-tartaric acid. A film grown in DL-tartaric acid (Fig. 6c) shows no selectivity. Chiral recognition of tartaric acid is also observed for films deposited from amino acids. In this case, films deposited from D-amino acids are selective for the oxidation of L-tartaric acid, and films deposited from L-amino acids are selec-
tive for the oxidation of D-tartaric acid. Chiral recognition studies of other molecules on the chiral CuO surfaces are currently underway in our group.

We have shown that chiral films of CuO can be deposited on achiral Au and Cu substrates. Typical of research, there are now more unanswered questions than solutions. How general is chiral electrodeposition? Because the only requirement for materials to be chiral is that the surface does not contain mirror or glide planes, there is a huge number of materials that may be used to produce chiral surfaces. How does chiral electrodeposition work? Much more research must be done to understand the mechanism of chiral electrodeposition. Obviously, the chiral solution agents are directing the growth, but the templating or imprinting mechanisms are unclear. Also, what molecules beside tartaric acid can be differentiated on these surfaces? Will these surfaces be used to produce practical chiral catalysts, sensors, or detectors? We invite the scientific community to help answer these questions.

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References


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Historical Perspectives on the Evolution of Electrochemical Tools

At the 201st ECS meeting in Philadelphia in May 2002, the Physical Electrochemistry Division organized a symposium, entitled “Progress in Methods Used to Solve Electrochemical Problems: Historical Perspectives.” Using an unorthodox approach in preparing a publication based on this symposium, the organizers taped the lectures of the five invited senior leaders in the field (B. E. CONWAY, A. T. HUBBARD, W. R. HEINEMAN, D. M. KOLB AND R. W. MURRAY), who were the keynote speakers, and later transcribed their talks into articles suitable for a symposium volume. This volume is now available.

In addition to the five long chapters, the volume also includes sixteen vignettes from other key researchers and members of the Physical Electrochemistry Division. (F. C. ANSON, A. J. BARD, J. O’M. BOCKRIS, W. R. FAWCETT, S. W. FELDBERG, A. HELLER, P. T. KISSINGER, Z. NAGY, K. NIKI, M. G. HILL, H. B. GRAY, K. B. OLDHAM, G. N. PAPATHODOPOULOS, P. N. ROSS JR., W. VIELSTICH, M. J. WEAVER, AND P. ZUMAN) J. LEDDY, the lead editor, prepared an introductory chapter to the volume, providing the scientific lineage of the many contributors and including other items of great interest.

This symposium volume will be of historical and scientific interest to all members of ECS, serving both as a fascinating summary of personal experiences and historical breakthrough research in physical electrochemistry, as well as a powerful teaching aid for undergraduate and graduate courses in electrochemistry.


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JAY A. SWITZER is the Donald L. Castleman Distinguished Professor of Chemistry at the University of Missouri-Rolla. He is also a Senior Investigator in the Materials Research Center at UMR. He received his BS in chemistry from the University of Cincinnati in 1973, and his PhD in inorganic chemistry from Wayne State University in 1979. His PhD work with Professor John F. Endicott was on the kinetics and mechanisms of electron transfer reactions. After receiving his PhD, he joined Union Oil Company of California (UNOCAL) as a Senior Research Chemist. His research at UNOCAL was on photoelectrochemistry and the electrochemical processing of photovoltaic cells. In 1986 Dr. Switzer joined the Materials Science and Engineering Department of the University of Pittsburgh as an Associate Professor. In 1990, he moved to UMR as a Professor of Chemistry. He has spent most of his career working on the electrodeposition of nanostructured metal oxide semiconductors, magnetic materials, and catalysts. The goal is not to imitate vapor deposition, but to exploit the wet aspects of electrodeposition to produce architectures which may not be accessible to UHV methods.

Dr. Switzer serves on the editorial board of Chemistry of Materials and is a Principal Editor of the Journal of Materials Research. He has been a member of ECS since 1980, and has organized several ECS symposia on electrodeposition. Professor Switzer received the ECS Electrodeposition Award in 2003, and he will serve as the chair of the Gordon Research Conference on Electrodeposition in 2006.

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