Controlling Chemical Selectivity in Electrocatalysis with Chiral CuO Coated Electrodes

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Abstract

This work demonstrates the chiral induced spin selectivity effect for inorganic copper oxide films and exploits it to enhance the chemical selectivity in electrocatalytic water splitting. Chiral CuO films are electrodeposited on a polycrystalline Au substrate, and their spin filtering effect on electrons is demonstrated using Mott-polarimetry analysis of photoelectrons. CuO is known to act as an electrocatalyst for the oxygen evolution reaction; however it, like other metal oxide electrocatalysts, is not selective and generates both O₂ and H₂O₂. We show that chiral CuO is selective for O₂; H₂O₂ generation is strongly suppressed on chiral CuO but is present with achiral CuO. The selectivity is rationalized in terms of the electron spin filtering properties of the chiral CuO and the spin constraints for the generation of triplet oxygen. These findings represent an important step toward the development of all inorganic chiral materials for electron spin filtering and the creation of efficient, spin-selective (photo)electrocatalysts for water-splitting.
Introduction

Since its initial report in 1999,1 a variety of experimental methods have been used to demonstrate that the electron transmission through chiral molecules and chiral molecular films is spin-dependent.2 The chiral-induced spin selectivity (CISS) effect results from the motion of the electron probability density in the chiral electrostatic field of the molecules, which gives rise to an effective magnetic field, in the rest frame of the electron, that acts on the electron’s magnetic moment.3,4 Experimental studies have shown that the effect manifests in a variety of processes, ranging from electron transfer in redox proteins and multi-electron redox processes with chiral electrodes5 to organic spintronic devices,6 but all of these studies involve organic molecules in the electron transmission process. Applications in electronics and in electrocatalysis would benefit from robust inorganic nanomaterials that act as a spin filter.

The present work describes the creation of ultrathin, inorganic, chiral CuO films which act as spin filters and demonstrates their use for controlling the product formation in electrocatalytic water-splitting. CuO films were grown by electrodeposition onto electrodes from an electrolyte solution containing chiral Cu(II) complexes, and the film’s chiral nature was confirmed by circular dichroism spectroscopy. Spin-dependent photoemission spectroscopy was used to measure the spin filtering of electrons by the ultrathin (5 nm to 50 nm) CuO films on Au electrodes. This method was used in earlier work to demonstrate the spin filtering properties of chiral molecular layers of ds-DNA oligomers,7 proteins,8 oligopeptides,9 and helicene10 on Au, as well as on other substrates like Al,8 Si,11 Cu, and Ag.10

Photoelectrochemical water splitting has received much attention as a possible path for the production of hydrogen from water, however the efficiency of the oxygen evolution reaction (OER) on the anode remains a roadblock to widespread applications. In OER, the production of O2 molecules requires transfer of four electrons and the kinetically favorable OER process is believed to occur through a multi-step reaction with single-electron transfers at each step. It has been found that the electrochemical OER process requires a significant overpotential, of about 0.4 V,12 and extensive research effort has focused on finding a suitable catalyst that reduces this overpotential.13,14,15 Theoretical work suggests that the overpotential arises from electron spin restrictions in forming the ground state triplet oxygen molecule.16,17 While magnetic electrodes have been shown to address this challenge, they have not proven economically or technologically viable.18,19 In recent experimental work with chiral, organic molecule-coated anodes, it has been shown that the overpotential is reduced and the formation of hydrogen peroxide as a by-product is suppressed;20-22 albeit with a low overall current density (microamps/cm²).
Because of the CISS effect, a chiral electrocatalyst should polarize the electron spin distribution on the catalytic surface and favor the production of the spin allowed triplet oxygen channel over that of singlet oxygen and hydrogen peroxide. CuO is a small bandgap (1.3 to 1.7 eV) material that is known to display (photo)electrocatalytic properties for the water splitting reaction,\textsuperscript{23,24,25} and we postulate that chiral CuO should be a more efficient electrocatalyst than achiral CuO. When the anode is coated with a chiral CuO layer, the electron transfer from the hydroxide species to the anode is spin-specific, leaving the unpaired electrons on the hydroxyl radicals aligned in a spin parallel fashion. Because the ground state oxygen molecule is a triplet, the reaction of two hydroxyl radicals of parallel spins is spin-allowed. In contrast, the formation of hydrogen peroxide, which is a singlet species, is spin-forbidden. For the case of an achiral anode, no correlation between the spins of the two hydroxyl radicals is expected and the interaction between the two hydroxyls may occur on a singlet surface, which correlates with the production of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) by-product.

In the present study, we report on the role played by chirality for inorganic CuO anodes in electrochemical water splitting. We find that the CuO chirality reduces the overpotential and suppresses the production of the hydrogen peroxide by-product, while maintaining currents that are orders of magnitude higher than that obtained when the electrode is coated with organic chiral molecules. The manuscript is divided into three major parts. First we describe the creation of CuO films, their characterization, and their circular dichroism properties. Second we describe the Mott-polarimetry photoemission measurements for electrodeposited chiral CuO films. Third, we describe our measurements of the oxygen evolution reaction (OER) for different chiral CuO anodes.

**Growth and Characterization of CuO films**

Metal oxide films, which are typically considered to be achiral, can display chirality if the film deposition process or the substrate has a chiral bias. In this work, the electrodeposition method, pioneered by Switzer et al.,\textsuperscript{26} is used to create a chiral CuO film on polycrystalline gold and on TiO\textsubscript{2}/FTO thin film electrodes. In this method, the CuO film is electrodeposited from an electrolyte solution that contains chiral complexes of Cu-tartrate, and the CuO film growth occurs through irreversible electro-oxidation of the tartrate ligand, leaving a pure CuO layer on the substrate. Even though the bulk structure of CuO is achiral, the CuO films electrodeposited by way of Cu(II)-tartrate complexes display a preferred chiral crystallographic orientation; e.g., films deposited on Au(001) from Cu\textsuperscript{2+}/L-tartaric acid solution have a (11\overline{1}) orientation, and those electrodeposited from Cu\textsuperscript{2+}/D-tartaric acid solution have a preferred (\overline{1}11) orientation.\textsuperscript{26,27}
CuO films were grown from a basic (3M NaOH) solution of 0.2 M Cu-tartrate, and subsequently were baked to remove any moisture and to oxidize any Cu$_2$O. The film thickness was determined by optical absorbance and atomic force microscopy measurements, and X-ray photoelectron spectra were obtained to confirm that the films were >99% pure CuO (see supporting information for further details). The film chirality was confirmed by circular dichroism (CD) spectroscopy. Figure 1A shows an optical absorbance spectrum for a 50 nm thick CuO film grown from a L-tartrate:Cu$^{2+}$ solution on a 20 nm Au substrate. The direct and indirect band gap of the CuO film were extracted from Tauc plots of the absorbance spectrum and are found to be 2.84 eV and 1.25 eV respectively (See supporting Figure S3). The indirect gap is consistent with literature reports; and the higher energy, direct band gap is consistent with literature reports for a polycrystalline bulk CuO bandgap with some quantum confinement shift.

The circular dichroism (CD) spectra of two 50 nm CuO films, electrodeposited from L-tartrate: Cu$^{2+}$ (L-CuO) and from D-tartrate: Cu$^{2+}$ (D-CuO) onto Au films, are shown in Figure 1B. The peak at 400 nm in the CD spectrum is close to the energy of the direct band gap. The CD spectra display an approximate mirror symmetry for the CuO films, which are grown from aqueous solutions of different Cu-tartrate chirality, and indicate that the chirality of the two CuO films are opposite. Note that the measurement is for two separately prepared films for which small differences in thickness and/or morphology can cause deviations from perfect mirror symmetry. Meso-tartrate:Cu$^{2+}$ complexes do not possess a net average chirality because the meso-tartrate has two opposite chiral centers; in this case an achiral film is electrodeposited on the substrate (the purple curve in 1B).

Figure 1. Panel A shows a UV-visible spectrum of a 50 nm thick L-CuO film with the UV-visible spectrum of a 20 nm Au substrate subtracted. Panel B shows circular dichroism (CD) spectra of 50 nm L-CuO film (red), D-CuO films (blue), and a meso-CuO film (purple). Note the approximate mirror symmetry of the L-CuO and D-CuO films, and the zero CD for the achiral meso-CuO.
**Photoemission studies**

The spin polarization of the photoemitted electrons was measured as a function of the CuO film thickness and the CuO chirality. The photoemission spectrometer (see Figure S7 in SI) and the Mott polarimetry method have been described previously.\(^2\) Photoelectrons were ejected from the Au/CuO films by excitation with a 213 nm (hv = 5.83 eV) laser pulse (circa 200 ps pulse duration, 20 kHz repetition rate) that impinged normal upon the CuO/vacuum interface. Photoelectrons with a kinetic energy of up to \(~ 1\) eV were extracted parallel to the surface normal of the CuO sample, bent around electrostatically by \(90^\circ\), and accelerated with 50 kV towards the target in a Mott scattering apparatus. Two detectors at \(\pm 120^\circ\) scattering angle from the incident electron beam direction register the scattering intensity. The asymmetry in the detectors’ count rates provides the average spin orientation of the electrons; see supplementary section S3. In this way the longitudinal spin polarization of the electrons ejected from the sample is determined. A polycrystalline Au sample, which was mounted right beneath the CuO sample on the sample manipulator, was used as a reference. When excited by linearly polarized light, the intensities from this reference measured by the Mott detectors are taken to determine the instrumental asymmetries and thus calibrate zero spin polarization. A quarter wave plate was used to generate either clockwise (cw), counter clockwise (ccw), or linearly polarized light. For each experimental run, this quarter wave plate was rotated once about \(360^\circ\), then the reference sample was moved into the measurement position to determine the spin zero.

For each experimental run about \(10^6\) laser pulses were applied which resulted in one spin polarization determination. All measurement results are plotted as a histogram; see the Supplemental Information, Fig S8. A Gaussian fit to the histogram distribution yields the average spin polarization with its FWHM denoted as the error. It should be noted that before and after the measurements of one sample, the spin polarization from a clean Au(111) sample was measured, yielding spin polarizations of about \(+25\%\) and \(-25\%\) for ccw and cw polarized light, respectively. Only when the same spin polarization was measured for the Au(111) with circular polarized excitation, both before and after the CuO measurement, were the results for the CuO sample taken as valid.

Figure 2 shows a plot of the spin polarization measured as a function of the chiral CuO film thickness in different trials and with different samples for each nominal thickness. The spin polarization, which is defined as \(P = (I_+ - I_-)/(I_+ + I_-) \times 100\%\), is found to change sign as the chirality of the CuO film is changed; \(I_+(I_-)\) is the average intensity of electrons measured that correspond to...
spin up (down). The polarization has a negative value for the L-CuO film and, on average, has a positive value for the D-CuO. The spin polarization obtained from the L-CuO films has a significantly higher absolute value than that obtained with the D-CuO films. For films with thicknesses below 20 nm, the spin polarization increases with the film thickness; and for films thicker than 20 nm, the spin polarization remains relatively constant with increase of the film thickness up to about 50 nm.

**Electrolysis Studies**

*Current-Voltage Behavior:* Linear sweep voltammetry was used to examine the oxygen evolution reaction (OER) for 10 nm thick and 500 nm thick CuO electrodes on Au at pH 9.5. The current-voltage curves in Figure 3A display a clear enhancement of the OER rate when a 10 nm CuO film is present (onset potentials between 1.20 and 1.28 V versus NHE), as compared to the case of bare Au (onset potential of 1.4 to 1.5 V versus NHE) which is the black trace. The CuO onset potential range represents a 350 mV to 450 mV overpotential for the pH 9.5 solutions used here. The inset of Figure 3A shows an expanded current scale (0 to 1 mA/cm²) and reveals small pre-peaks that are observed before the full onset of OER by the electrode. Following previous literature, these peaks are tentatively assigned to the presence of highly active impurities ions from the electrolyte, e.g., Fe ions, and/or highly active Au oxides on the surface. Panel 3B shows current-voltage
curves for 500 nm CuO films, in which the chiral electrodes (red and blue) have a higher current density than the achiral CuO film (black curve).

Plots of the overpotential versus the logarithm of the current (Tafel plots) provide information about the electrochemical exchange current and the reaction mechanism. For 400 mV to 600 mV overpotentials the slope is 70 to 80 mV/decade; these values are similar to those reported for achiral CuO electrocatalysis. Tafel plots and more discussion for the data in Figure 3 are shown in the Supplemental Information (Figures S12 and S13). The remainder of the work focusses on thicker CuO films.

Chiral CuO layers of ~3 µm thickness were electrodeposited on TiO₂ (~1 µm) coated FTO glass, using L-tartaric acid as the chiral bias and meso-tartaric acid as the achiral control; see section S2 of the Supporting Information for more details. Figure 4A shows plots of the current density vs. applied voltage that were obtained using the electrochemically deposited chiral and achiral CuO coated anodes in 0.1 M Na₂SO₄, pH=6.5 solution in the dark. The onset potentials were found to be higher for the achiral CuO (1.43 V vs. NHE) than for the chiral CuO (1.38 V vs. NHE), which represents an overpotential shift of 50 mV; see Figure S11 in SI for details.
Hydrogen evolution and Peroxide suppression: The rate of hydrogen production for the chiral and achiral electrocatalysts was measured at a constant voltage of 1.4 V vs. NHE (Figure 4B). The steady-state current of the chiral anode was 0.62 mA/cm² whereas that of the achiral anode was 0.35 mA/cm², over the course of the data collection. Although the current differs by a factor of two, the H₂ yield data show that the chiral anode (blue points, 187 nL/s) produces eight times more H₂ than the achiral anode (red points, 23.5 nL/s), indicating that the chiral electrode is much more efficient than the achiral electrode.

To detect the production of hydrogen peroxide we employed o-tolidine as an indicator. Figure 4c shows the UV-Visible absorption spectra obtained after titration with o-tolidine when the solution used as the electrolyte in the electrolysis cell was 0.1 M Na₂SO₄, pH=6.5. The titrations were performed after keeping the chiral and achiral CuO anode of the electrochemical cell at a constant voltage of 1.7 V vs. NHE for 40 minutes in the dark. The cell with an achiral CuO anode shows an absorbance peak at 436 nm which indicates the production of H₂O₂ during water oxidation.
For the chiral CuO anodes, the peroxide signal is thirteen times weaker, for the same reaction time and conditions. Together these data explain how the current densities (Fig 4a) can differ by only a factor of about two but the hydrogen yields (Fig 4b) can differ by eight times; a significant amount of the current in the achiral electrodes generates hydrogen peroxide.

**Comparing Chirality effect for CuO anode and CuO cathode: Figure 5** summarizes the current-voltage behavior of an electrochemical cell, in which both the anode and the cathode comprise CuO electrodes, both in the dark and under illumination. Figure 5A shows the electrical set-up used to apply a negative voltage on the cathode, relative to the anode. Figure 5B shows the current density vs. applied voltage that was measured in this arrangement for both chiral (blue curves) and achiral (red curves) CuO-coated cathodes. A pronounced photocurrent is evident for the data in Figure 5B, however the chiral and achiral electrodes have similar current-voltage responses. Because H₂ (a singlet) is generated on the cathode, preservation of the spin orientation of H radicals should inhibit product formation. The achiral cathodes, which generate a statistical mixture of spin orientations, do have somewhat larger negative currents than the chiral electrodes, but the effect is

![Figure 5](image)

**Figure 5** Schematic of the electrochemical set up used when electrochemically deposited CuO used as both cathode and anode when cathode was illuminated. The results with the cell containing chiral CuO are presented in blue while those with achiral CuO is red. The current density vs applied potential plots with respect to Normal Hydrogen Electrode (NHE): **Bb** when the bias is applied to cathode and **Db** when the bias is applied to anode. Electrochemical measurements were performed using 0.1 M Na₂SO₄ solution with pH 6.5. The scan is performed up to 1.5 V vs. Ag/AgCl (3M NaCl) with scan rate 20 mV/s in dark. E(NHE) = E (vs. Ag/AgCl) + E°(Ag/AgCl); where E°(Ag/AgCl, 3M NaCl)=0.195 V.
small. The significant photocurrent is consistent with a forward bias band structure postulated for metal-copper oxide interfaces.\textsuperscript{42}

Figure 5c and 5d show the case in which the anode potential is ramped positive with respect to the reference electrode. In this case, the cell with the chiral CuO produces a higher current density than the cell with achiral electrodes, and there is an observable but small photocurrent under illumination. The chirality effect is consistent with the production of spin polarized OH radicals which facilitate the production of triplet oxygen, over singlet oxygen and hydrogen peroxide. The onset potentials for oxygen production are calculated (see SI for details) to be 1.38 V and 1.35 V for chiral CuO in dark and light, and 1.43 V and 1.39 V for the achiral CuO in the dark and in the light, respectively. The chiral CuO-coated anode displays a higher current density and a somewhat lower threshold potential for water splitting, as compared to the achiral electrode.

Others have examined the oxygen evolution reaction (OER) on achiral CuO electrodes, and recent studies find overpotentials in the 300 to 400 mV range, for pH =9.\textsuperscript{37,38,40,43} The OER is strongly dependent on the solution pH and hydrogen peroxide is a significant side-product in this reaction. The generation of H\textsubscript{2}O\textsubscript{2}, along with the O\textsubscript{2}, was demonstrated in this study by the use of an achiral electrode, see Fig 4c. In contrast, anodes comprising chiral CuO-films inhibit the formation of H\textsubscript{2}O\textsubscript{2} and maintain low overpotentials. Figure 6 shows an energy scheme that rationalizes how the selectivity occurs, for a mechanism assuming the combination of OH radicals. When the surface OH radicals are spin parallel, they can combine and produce a triplet state product, the O\textsubscript{2} ground electronic state; but if the OH radicals have their spins antiparallel they can combine to form either H\textsubscript{2}O\textsubscript{2} or the O\textsubscript{2} first excited state, which is a singlet. Because of the CISS effect, the charge transfer at the CuO surface generates a spin polarization (preference for aligned spins) and this enhances the production of the triplet product, as compared to the possible singlet products. While the rationale is given here for a mechanism involving the recombination of OH radicals, the rationale should apply to other mechanisms, such as the oxide path and the metal peroxide path.\textsuperscript{44}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{The energy diagram illustrates the possible reaction products from the combination of hydroxyl groups on the CuO surface. The spin restriction on the recombination leads to selectivity against H\textsubscript{2}O\textsubscript{2} formation if the OH radical spins are aligned.}
\end{figure}
The selectivity for oxygen production is like that found in earlier work with chiral molecules, but this study uses an all inorganic system (CuO) and generates a current density more than $10^3$ times higher than that observed with organic molecule coated electrodes (mA/cm$^2$ versus $\mu$A/cm$^2$).

This work demonstrates that chiral CuO films act as electron spin filters and can be used as selective electrocatalysts in the oxygen evolution reaction. Chiral CuO films were electrodeposited on an Au substrate and their spin filtering properties were demonstrated by Mott polarimetry measurements for a range of CuO thicknesses. Chiral CuO films were grown on both Au and FTO/TiO$_2$ electrodes and they were used in electrolysis studies of water. Because of the electron spin dependence for the oxygen evolution reaction and the generation of spin-polarized reaction intermediates, the chiral CuO anodes enables selective production of O$_2$ over that of H$_2$O$_2$. While CuO is used in this study, it should not be considered unique, other chiral metal oxides should display analogous properties. This work demonstrates that chiral electrocatalysts offer a new approach to realizing selectivity in electrochemical transformations, and it should be synergistic with other electrocatalysis strategies.

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CHIRAL

\[ 2H^+ + 2e^- \rightarrow H_2 \]
\[ 2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \]

CATHODE

ENERGY

ANODE

ACHIRAL

\[ 2H^+ + 2e^- \rightarrow H_2 \]
\[ 2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \]

CATHODE

ANODE