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## **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  $O_2$  and  $H_2O_2$ . We show that chiral CuO is selective for  $O_2$ ;  $H_2O_2$  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,<sup>1</sup> a variety of experimental methods have been used to demonstrate that the electron transmission through chiral molecules and chiral molecular films is spindependent.<sup>2</sup> 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.<sup>3,4</sup> 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 electrodes<sup>5</sup> to organic spintronic devices,<sup>6</sup> 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,<sup>7</sup> proteins,<sup>8</sup> oligopeptides, <sup>9</sup>and helicene<sup>10</sup> on Au, as well as on other substrates like A1,<sup>8</sup> Si,<sup>11</sup> Cu, and Ag.<sup>10</sup>

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 O<sub>2</sub> 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,<sup>12</sup> and extensive research effort has focused on finding a suitable catalyst that reduces this overpotential.<sup>13,14,15</sup> Theoretical work suggests that the overpotential arises from electron spin restrictions in forming the ground state triplet oxygen molecule.<sup>16,17</sup> While magnetic electrodes have been shown to address this challenge, they have not proven economically or technologically viable.<sup>18,19</sup> 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;<sup>20-22</sup> albeit with a low overall current density (microamps/cm<sup>2</sup>).

#### September 23

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,<sup>23,24,25</sup> 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<sub>2</sub>O<sub>2</sub>) byproduct.

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 Mottpolarimetry 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.,<sup>26</sup> is used to create a chiral CuO film on polycrystalline gold and on TiO<sub>2</sub>/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<sup>2+</sup>/L-tartaric acid solution have a (111) orientation, and those electrodeposited from Cu<sup>2+</sup>/D-tartaric acid solution have a preferred (111) orientation.

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<sub>2</sub>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<sup>2+</sup> 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).<sup>28</sup> 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<sup>29,30,31</sup> with some quantum confinement shift.<sup>32</sup>

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.<sup>77</sup> 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  $\sim 1 \text{ eV}$  were extracted parallel to the surface normal of the CuO sample, bent around electrostatically by 90°, 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°, 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



**Figure 2.** The plot shows the spin polarization *P* of photoelectrons from the Au/CuO films as a function of the CuO film thickness *d* and its chirality. The red diamonds are the L-CuO formed from L-tartrate: $Cu^{2+}$  solutions and the blue diamonds are the D-CuO formed from the D-tartrate: $Cu^{2+}$  solutions.

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/cm<sup>2</sup>) 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, <sup>33</sup> and/or highly active Au oxides on the surface.<sup>34</sup> Panel 3B shows current-voltage



**Figure 3.** Panel A shows linear sweep voltammograms for 10 nm thick L-CuO (red), 10 nm thick D-CuO (blue) film electrodes, and bare Au (black) electrodes. The inset provides a zoomed-in view of the data and reveals a current pre-peak which has been associated with a small percentage of highly active catalytic sites (see text). The potential is reported versus NHE and the current density is given in mA/cm<sup>2</sup>. Panel B shows 500 nm thick films for which the onset potential shifts to larger values; the glycine-CuO films (shown in light green) are achiral and display less electrocatalytic activity than the chiral CuO films.

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<sup>35,36</sup> 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<sup>37, 38,39,40</sup> 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  $\mu$ m thickness were electrodeposited on TiO<sub>2</sub> (~1  $\mu$ m) 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 Na<sub>2</sub>SO<sub>4</sub>, 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.

300

Wavelength (nm)



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/cm<sup>2</sup> whereas that of the achiral anode was  $0.35 \text{ mA/cm}^2$ , over the course of the data collection. Although the current differs by a factor of two, the H<sub>2</sub> yield data show that the chiral anode (blue points, 187 nL/s) produces eight times more H<sub>2</sub> 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.<sup>41</sup> 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 Na<sub>2</sub>SO<sub>4</sub>, 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  $H_2O_2$  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.

<u>Comparing Chirality effect for CuO anode and CuO cathode</u>: Figure 5 summarizes the currentvoltage behavior of an electrochemical cell, in which both the anode and the cathode comprise CuO electrodes, both in the dark and under illumination. Figure 5<u>A</u> shows the electrical set-up used to apply a negative voltage on the cathode, relative to the anode. Figure <u>5b-5B</u> 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 <u>5B</u>, however the chiral and achiral electrodes have similar current-voltage responses. Because H<sub>2</sub> (a singlet) is generated on the cathode, preservation of the spin orientation of H radicals should inhibit product for mation. 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** 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): **B** when the bias is applied to cathode and **Dd**) when the bias is applied to anode. Electrochemical measurements were performed using 0.1 M Na<sub>2</sub>SO<sub>4</sub> 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.<sup>42</sup>

Figure <u>5e-5C</u> and <u>5d-5D</u> 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.<sup>37,38,40,43</sup> The OER is strongly dependent on the solution pH and hydrogen peroxide is a significant side-product in this reaction. The generation of H<sub>2</sub>O<sub>2</sub>, along with the O<sub>2</sub>, 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> ground electronic state; but if the OH radicals have their spins antiparallel they can combine to form either H<sub>2</sub>O<sub>2</sub> or the O<sub>2</sub> 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.<sup>44</sup>



**Figure 6.** 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<sub>2</sub>O<sub>2</sub> formation if the OH radical spins are aligned.

September 23

The selectivity for oxygen production is like that found in earlier work with chiral molecules,<sup>20-22</sup> 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<sup>2</sup> versus  $\mu$ A/cm<sup>2</sup>).

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<sub>2</sub> 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<sub>2</sub> over that of H<sub>2</sub>O<sub>2</sub>. 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.<sup>13</sup>

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#### References

- 1 Ray, K., Ananthavel, S. P., Waldeck, D. H. and Naaman, R. Asymmetry in the Transmission of Polarized Electrons through Organized Organic Films of Chiral Molecules, Science 283, 814-816 (1999).
- 2 Naaman, R. and Waldeck, D. H. Spintronics and Chirality: Spin Selectivity in Electron Transport through Chiral Molecules Ann Rev Phys Chem. 66, 263-281 (2015).
- 3 Naaman, R., and Waldeck, D. H. *Chiral-Induced Spin Selectivity Effect* J. Phys. Chem. Lett **3**, 2178-2187 (2012).
- 4 Medina, E., González-Arraga, L. A., Finkelstein-Shapiro, D. Berche, B., and Mujica, V. Continuum model for chiral induced spin selectivity in helical molecules J. Chem. Phys. 142, 194308 (2015).
- 5 Michaeli, K., Kantor-Uriel, N., Naaman, R., and Waldeck, D. H. *The electron's spin and molecular chirality- How are they related and how do they affect life processes?*, Chem. Soc. Rev. **45**, 6478 6487 (2016).

- 6 Michaeli, K., Varade, V., Naaman, R., and Waldeck, D. H. A New Approach towards Spintronics- Spintronics with no Magnets J. Phys.: Condens. Matter 29, 103002 (2016).
- 7 Göhler, B., Hamelbeck, V., Markus, T.Z., Kettner, M., Hanne, G.F., Vager, Z., Naaman, R., and Zacharias, H. *Spin selectivity in electron transmission through self- assembled monolayers of double-stranded DNA*, Science **331**, 894 (2011).
- 8 Mishra, D., Markus, T.Z., Naaman, R., Kettner, M., Göhler, B., Zacharias, H., Friedman, N., Sheves, M., and Fontanesi, C. Spin-dependent electron transmission through bacteriorhodopsin embedded in purple membrane, Proc. Nat. Acad. Sci. 110, 14872 (2013).
- 9 Kettner, M., Göhler, B., Zacharias, H., Mishra, D., Kiran, V., Naaman, R., Fontanesi, C., Waldeck, D. H., Sęk, S., Pawłowski, J. and Juhaniewicz, J. *Spin filtering in electron transport through chiral oligopeptides*, J. Phys. Chem. C **119**, 14542 (2015).
- 10 Kettner, M., Maslyuk, V.V., Nürenberg, D., Seibel, J., Gutierrez, R., Cuniberti, G., Ernst, K.-H., and Zacharias, H. *Chirality-dependent electron spin filtering by molecular monolayers of helicenes*, J. Phys. Chem. Lett. 9, 2025 (2018).
- 11 Kettner, M., Bhowmick, D. K., Bartsch, M., Göhler, B., and Zacharias, H. A silicon-based room temperature spin source without magnetic layers, Adv. Mater. Interfaces **3**, 1600595 (2016).
- 12a) Tahir, M., Pan, L., Idrees, F., Zhang, X., Wang, L., Zou, J.-J., and Wang, Z. L. *Electrocatalytic oxygen evolution reaction for energy conversion and storage: A comprehensive review.* Nano Energy **37**, 136-157 (2017); b) Xia, Z. H. *Guiding principles.* Nat Energy **1**, 1-2 (2016).
- 13 Siahrostami, S., Li, G.L., Viswanathan, V. and Norskov, J. K. One- or Two-Electron Water Oxidation, Hydroxyl Radical, or H<sub>2</sub>O<sub>2</sub> Evolution. J Phys Chem Lett 8, 1157-1160 (2017).
- 14 a) Hisatomi, T., Kubota, J., and Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. Chem Soc Rev 43, 7520-7535 (2014);
  b) Roger, I., Shipman, M. A., and Symes, M. D. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. Nat Rev Chem 1 (2017) 1-13; c) Anantharaj, S., Ede, S.R., Sakthikumar, K., Karthick, K., Mishra, S., and Kundu, S. Recent Trends and Perspectives in Electrochemical Water Splitting with an Emphasis on Sulfide, Selenide, and Phosphide Catalysts of Fe, Co, and Ni: A Review. ACS Catal 6, 8069-8097 (2016).
- 15 a) Martin, D. J., Reardon, P. J. T., Moniz, S. J. A., and Tang, J. W. Visible Light-Driven Pure Water Splitting by a Nature-Inspired Organic Semiconductor-Based System. J Am Chem Soc 136, 12568-12571 (2014); b) Zhang, Z.Z., Long, J., Yang, L., Chen, W., Dai, W., Fua, X., and Wang, X. Organic semiconductor for artificial photosynthesis: water splitting into hydrogen by a bioinspired C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> polymer under visible light irradiation. Chem Sci 2, 1826-1830 (2011); c) A. C. Arango, L. R. Johnson, V. N. Bliznyuk, Z. Schlesinger, S. A. Carter, and H. - H. Hörhold Efficient titanium oxide/conjugated polymer photovoltaics for solar energy conversion. Adv Matererials 12, 1689-1692 (2000).
- 16 Chretien, S., and Metiu, H., *O*<sub>2</sub> evolution on a clean partially reduced rutile TiO2(110) surface and on the same surface precovered with Au<sub>1</sub> and Au<sub>2</sub>: The importance of spin conservation. J Chem Phys **129** (2008) 074705-1 074705-16.
- 17 Gracia, J. Spin dependent interactions catalyse the oxygen electrochemistry, Phys. Chem. Chem. Phys. **19**, 20451-20456 (2017).
- 18 Torun, E., Fang, C. M., de Wijs, G. A., and de Groot, R. A. *Role of Magnetism in Catalysis: RuO*<sub>2</sub> (*110*) *Surface*. J Phys Chem C **117**, 6353-6357 (2013).
- 19 Yang, W., Yu, Y., Starr, M.B., Yin, X., Li, Z., Kvit, A., Wang, S., Zhao, P., and Wang, X. Ferroelectric Polarization-Enhanced Photoelectrochemical Water Splitting in TiO<sub>2</sub>–BaTiO<sub>3</sub> Core–Shell Nanowire Photoanodes, Nano Letters, 15, 7574–7580 (2015).

- 20 Mtangi, W., Tassinari, F., Vankayala, K., Jentzsch, A. V., Adelizzi, B., Palmans, A. R. A., Fontanesi, C., Meijer, E. W., and Naaman, R. *Control of Electrons' Spin Eliminates Hydrogen Peroxide Formation During Water Splitting*. J. Am. Chem. Soc. **139**, 2794-2798 (2017).
- 21 Mtangi, W., Kiran, V., Fontanesi, C., and Naaman, R. *Role of the Electron Spin Polarization in Water Splitting*.J Phys Chem Letters **6**, 4916-4922 (2015).
- 22 Tassinari, F., Banerjee-Ghosh, K., Parenti, F., Kiran, V., Mucci, A., and Naaman, R. Enhanced Hydrogen Production with Chiral Conductive Polymer Based Electrodes. J Phys Chem C 121, 15777-15783 (2017).
- 23 Deng, Y. L., Handoko, A. D., Du, Y. H., Xi, S. B., and Yeo, B. S. In Situ Raman Spectroscopy of Copper and Copper Oxide Surfaces during Electrochemical Oxygen Evolution Reaction: Identification of Cu-III Oxides as Catalytically Active Species ACS Catalysis 6, 2473-2481 (2016).
- 24 Shi, Y. Y., Gimbert-Suriñach, C., Han, T., Berardi, S., Lanza, M., and Llobet, A. *CuO-Functionalized Silicon Photoanodes for Photoelectrochemical Water Splitting Devices*. ACS Appl Mater Inter **8**, 696-702 (2016).
- 25 DeBrito JF, Tavella F, Genovese C, Ampelli C, Zanoni MVB, Centi G, Perathoner S *Role of CuO in the modification of the photocatalytic water splitting behavior of TiO2 nanotube thin films*. Appl Catal B-Environ **224**, 136-145 (2018).
- 26 Kothari, H. M., Kulp, E. A., Boonsalee, S., Nikiforov, M.P., Bohannan, E., Poizot, P., Nakanishi, S., and Switzer, J. A. *Enantiospecific Electrodeposition of Chiral CuO Films from Copper(II) Complexes of Tartaric and Amino Acids on Single-Crystal Au(001)*. Chem. Mater. **16**, 4232-4244 (2004).
- 27 Widmer, R., Haug, F.-J., Ruffieux, P., Groening, O., Bielmann, M., Groening, P., and Fasel, R. *Surface Chirality of CuO Thin Films* J. Am. Chem. Soc. 128, 14103-14108 (2006).
- 28 Pankove, J. I. Optical Processes in Semiconductors (Dover, 1971, NY)
- 29 Dhineshbabu, N.R., Rajendran, V., Nithyavathy, N., and Vetumperumal, R., *Study of structural and optical properties of cupric oxide nanoparticles* Applied Nanoscience **6**, 933-939 (2006).
- 30 a) Wang, D.; Song, C.; Lv, X.; Wang, Y., Design of preparation parameters for commendable photocatalytic properties in CuO nanostructures Applied Physics A 122 1020 (2016); b) Erdoğan,
  İ. Y.; Güllü, Ö., Optical and structural properties of CuO nanofilm: Its diode application J. of Alloys and Compounds 492, 378-383 (2010); c) Liu, Q.; Liu, H.; Liang, Y.; Xu, Z.; Yin, G., Large-scale synthesis of single-crystalline CuO nanoplatelets by a hydrothermal process Materials Research Bulletin 41, 697-702 (2006); d) Han, X.; Liao, F.; Zhang, Y.; Xu, C.; Chen, H., Dendrite-like cupric oxide microstructures prepared via a facile SDBS-assisted hydrothermal route Journal of Materials Science: Materials in Electronics 29, 3178-3181 (2018).
- 31 a) Jiang, T.; Wang, Y.; Meng, D.; Wu, X.; Wang, J.; Chen, J., Controllable fabrication of CuO nanostructure by hydrothermal method and its properties Applied Surface Science 311, 602-608 (2014); b) Zhang, X.; Zhang, D.; Ni, X.; Zheng, H., Optical and electrochemical properties of nanosized CuO via thermal decomposition of copper oxalate Solid-State Electronics 52 245-248 (2008); c) Jan, M.; F., W. H.; Wolfram, J.; Andreas, K., Influence of grain boundaries and interfaces on the electronic structure of polycrystalline CuO thin films 213, 1615-1624 (2016); d) Gaur, U. K.; Kumar, A.; Varma, G. D., The synthesis of self-assembled polycrystalline 1-D CuO nanostructures in aqueous medium and a study of their multifunctional features CrystEngComm 16, 3005-3014 (2014); e) Das, S.; Alford, T. L., Structural and optical properties of Ag-doped copper oxide thin films on polyethylene napthalate substrate prepared by low temperature microwave annealing Journal of Applied Physics 113, 244905 (2013); e) Izaki, M., Nagai, M., Maeda, K., Mohamad, F. B., Motomura, K., Sasano, J., Shinagawa, T., and Watase, S. Electrodeposition of 1.4-eV-Bandgap p-Copper (II) Oxide Film With Excellent Photoactivity J. Electrochemical Society 158, D578-D584 (2011); f) Koffyberg, F. P. and Benko,

F. A. A photoelectrochemical determination of the position of the conduction and valence band edges of *p* - type CuO J. Appl. Phys. **53**, 1173-1177 (1982).

- 32 a) Maji, S. K., Mukherjee, N., Mondal, A., Adhikary, B., and Karmakar, B. Chemical synthesis of mesoporous CuO from a single precursor: Structural, optical and electrical propertiesJournal of Solid State Chemistry 183, 1900-1904 (2010); b) Pappas, S. D., Poulopoulos, P., Kapaklis, V., Grammatikopoulos, S., Trachylis, D., Velgakis, M.J., Meletis, E.I., and Politis, C. Growth and Experimental Evidence of Quantum Confinement Effects in Cu<sub>2</sub>O and CuO Thin Films J. of Nano Research 15, 69-74 (2011); c) Borgohain, K. and Mahamuni, S. Formation of Single-phase CuO Quantum Particles J. Materials Research 17,1220-1223 (2002).
- 33 Klaus, S., Trotochaud, L., Cheng, M.-J., Head-Gordon, M., and Bell, A. T. *Experimental and Computational evidence of Highly Active Fe Impurity Sites on the Surface of Oxidized Au for the Electrocatalytic Oixdation of Water in Basic Media* Chem Electro Chem **3** 66-73 (2016).
- 34 Doyle, R. L., and Lyons, M. E. G. *The mechanism of oxygen evolution at superactivated gold electrodes in aqueous alkaline solution* J. Solid Sate Electrochem **18**, 3271-3286 (2014).
- 35 Shinagawa, T., Garcia-Esparza, A. T., and Takanabe, K. Insight on Tafel slopes from a microkinetics analysis of aqueous electrocatalysis for energy conversion Scientific Reports 5 13801 (2015).
- 36 Y.-H. Fang and Z. P. Liiu *Tafel Kinetics of Electrocatalytic Reactions: From Experiment to First Principles* ACS Catalysis 4, 464-4376 (2014).
- 37 H. Chen, Y. Gao, Z. Lu, and L. Sun Copper Oxide Film In-situ Electrodeposited from Cu(II) Complex as Highly Efficient Catalyst for Water Oxidation Electrochimica Acta 230, 501-507 (2017).
- 38 Liu, X., Cui, S., Sun, Z., Ren, Y., Zhang, X., and Du, P. Self-Supported Copper Oxide Electrocatalyst for Water Oxidation at Low Overpotential and Confirmation of Its Robustness by Cu K-Edge X-ray Absorption Spectroscopy J. Phys. Chem. C 120, 831-840 (2016).
- 39 Liu, X., Jia, H., Sun, Z., Chen, H., Xu, P., and Du, P. *Nanostructured Copper oxide electrodeposited from copper(II) complexes as an active catalyst for electrocatalytic oxygen evolution reaction* Electrochemistry Communications **46**, 1-4 (2014).
- 40 Yu, F., Li, F., Zhang, B., Li, H., and Sun, L. *Efficient Electrocatalytic Water Oxidation by a Copper Oxide Thin Film in Borate Buffer* ACS Catalysis **5**, 627-630 (2015).
- 41 a) Li, Z., Kong, C., and Lu, G. Visible Photocatalytic Water Splitting and Photocatalytic Two-Electron Oxygen Formation over Cu- and Fe-Doped γ-C<sub>3</sub>N<sub>4</sub>, J. Phys. Chem. C. 120, 56 – 63 (2016); b) Gu, B., Kiwi, J., and Gratzel, M. Photochemical Water Cleavage in Suspensions of Pt-Loaded Titania Particles with 0.7% Overall Light to Chemical Conversion Efficiency Nouv. J. Chimie. 9, 539-543 (1985).
- 42 Zhangab, Z., Wang, P. Highly stable copper oxide composite as an effective photocathode for water splitting via a facile electrochemical synthesis strategy J. Materials Chemistry 22, 2456 (2012).
- 43 Liu, X., Zheng, H., Sun, Z., Han, A., and Du, P. *Earth-Abundant Copper-Based Bifunctional Electrocatalyst for Both Catalytic Hydrogen Production and Water Oxidation* ACS Catal. 5, 1530–1538 (2015).
- 44 Bockris, J. O'M. *Kinetics of Activation Controlled Consecutive Electrochemical Reactions:* Anodic Evolution of Oxygen J. Chem. Phys. 24, 817, 1956.

