Supporting online material for

**Spin-Polarized Photoemission from Chiral CuO Catalyst Thin Films**

Paul V. Möllers,*a Jimeng Wei,b Soma Salamon,c Manfred Bartsch,a Heiko Wende,c David H. Waldeck,b Helmut Zacharias**a

a Department of Physics and Center for Soft Nanoscience (SoN) Westfälische Wilhelms-Universität Münster 48149 Münster, Germany *paul.moellers@uni-muenster.de

b Chemistry Department, University of Pittsburgh Pittsburgh, Pennsylvania 15260, United States

c Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE) University of Duisburg-Essen 47057 Duisburg, Germany

This file includes:

- S1: AFM images of the CuO films
- S2: XPS spectra of the CuO films
- S3: ToF-SIMS data on the composition and possible contamination of the CuO samples
- S4: Optical absorption data
- S5: Supplementary data on the relative photoelectron yield from the Au and CuO layers
- S6: An illustration of the spin-canted magnetic order within the oxide layers
Topography images of the untreated samples were acquired using a Bruker Nanoscope Icon AFM operated in tapping mode. Below, representative images are shown for three different CuO film thicknesses. The images show the anticipated nanocrystalline structure of the films. The size of the individual crystallites is on the order of some 10 nm, comparable with the film thickness. The micrometer-scale images show generally homogeneous films with some inhomogeneities such as larger grains and step edges. Oxide films with opposite chirality show no differences in their topography.

The rms roughness values, as stated in the images, predominantly reflect the crystallite structure of the films. The values were determined from the whole images (only the highlighted areas in figures S2 (c) and S3(b)) rather than from the line profiles. The rms roughness increases from about 1.2 nm to 1.4 nm at 5 nm film thickness to 2.2 nm at 10 nm film thickness and up to 9 nm for 50 nm thick films.

Figure S1: Panel (a) shows AFM topography images of a 5 nm thick D-CuO film. Panels (b) and (c) show data from a 10 nm L-CuO film. The rms roughness in panel (b) was calculated omitting the three larger grains present in the image.

Figure S2: Panels (a) to (c) show AFM topography images of a 50 nm thick D-CuO film. For the right image, the roughness was calculated in the highlighted area only.
Figure S3: Panels (a) and (b) show AFM topography images of a 50 nm thick D-CuO film. For the right image, the roughness was calculated in the highlighted area only.

S2 XPS

XPS measurements were carried out on a Kratos Axis Ultra system using monochromatized Al Kα radiation at hν = 1486.6 eV. The binding energy scale was calibrated to the Fermi edge and the C 1s peak at 284.8 eV. Figure S4 shows representative spectra for two different film thicknesses.

The spectra exhibit all expected gold and copper oxide features; no contamination is evident. Mass spectra (see below) indicate that the carbon peak arises purely from atmospheric contaminants and is not related to residual tartaric acid.

Figure S4: XPS survey spectra acquired on an Au substrate and samples with different CuO layer thickness.

S3 ToF-SIMS

Time-of-flight secondary ion mass spectra were acquired to assess possible contamination with ferromagnetic elements (Cr, Mn, Fe, Co, Ni) and residuals from the chiral tartaric acid precursor, i.e., tartaric acid (C4H6O6, mass 150) or copper tartrate (C4H4CuO6, mass 211.6). Representative data are shown in figure S5 as depth profiles of the
selected masses. The profiles are acquired by sputtering an area of 500*500 µm² over which the data is averaged. On the horizontal axis, the sputter time is stated, which is approximately proportional to the probing depth.

![Figure S5: ToF-SIMS depth profiles of selected masses are shown. These include Cu and Si as the signals expected from the CuO layer and the fused silica substrate and possible ferromagnetic contaminants. No cobalt could be detected.](image)

After about 380 s sputtering, a silicon signal becomes evident, indicating that the fused silica substrate underneath the CuO layer is now gradually being exposed. Due to the large area that is eroded throughout the data acquisition and due to the slightly different sputtering yields of the different secondary species, the transition between the copper and silicon signals is significantly broadened. After approximately 420 s sputtering time, slight traces of Mg, Fe, and Ni become visible. These contaminations have a relative intensity of about 10⁻³ to 10⁻² and originate from the fused silica substrate rather than the CuO layer. These contaminations are evident in all investigated samples and most likely come from the receptacle in which the silica was fused. As shown in figure 7 (a), these contaminations do not yield a measurable contribution to the magnetization curves.

### S4 Optical absorption data

Figure S6 (a) shows representative spectra of the absorbance \( A = -\log_{10}(T) \). All spectra are corrected for a baseline measured on the gold-coated quartz substrate. The lower Fresnel reflection losses of coated gold samples and the quenching of the plasmonic absorption at the gold surface leads to a nominally negative differential absorbance of the very thin films. The optical absorption in CuO increases roughly monotonously and exponentially in the UV region.

The inset of panel (a) shows a plot of the absorbance \( A \) as a function of the nominal film thickness \( d \) at \( \lambda = 213 \) nm for all the investigated samples. The linear relation confirms that the film thicknesses behave as expected. Figures S6 (b) and (c) show Tauc plots which indicate the position of the main absorption edges. The direct (figure S6 (b)) and indirect (figure S6 (c)) band gaps are identified at \( \Delta E_{\text{dir}} = 3.08 \) eV and \( \Delta E_{\text{ind}} = 1.20 \) eV, respectively. For the determination of the indirect band gap (figure S6 (c)), a 200 nm CuO layer was employed to increase the absolute absorption and to avoid interference effects caused by the thin film structure of the samples in the relevant wavelength range. A thickness dependence of the band gaps was not observed in the present study.

![Figure S6: CuO film absorbance (a) and Tauc plots derived from absorption spectra of (b) 30 nm and (c) 200 nm CuO thin films are shown. All spectra are baseline corrected by a measurement on a 20 nm Au film on fused silica. See text for discussion.](image)
**S5 UPS with 213 nm excitation**

Besides the helium UPS spectra, UPS data were acquired using the laser wavelength of $\lambda = 213$ nm that was also employed for the spin polarization measurements. These spectra show over which electron energies the spin polarization is averaged.

To estimate the relative amount of photoelectrons originating from the 10 nm thick oxide layer and the gold layer underneath, respectively, the gold reference spectrum was scaled to match the higher-energy part of the respective CuO photoelectron spectra, as shown in figure S7 (a) and (b) for front and back side illumination, respectively.

The photoelectron yield was quantified by integrating each spectrum; the area under each curve is stated in arbitrary units in the figures. The area labelled “A” corresponds to the total area underneath the CuO/Au spectrum; the area underneath the scaled Au reference sample spectrum is labelled “B”. The difference $A - B$ reflects the total electron signal from the oxide layer.

The area ratios are $(A-B)/B = 4.17$ and $(A-B)/B = 0.25$. These numbers indicate that the signal from the oxide layer is approximately four times higher than the signal from the gold layer for front side illumination. For back side illumination, the ratio is roughly reversed, i.e., only one quarter of the photoelectrons is emitted from the oxide layer.

![Figure S7: (a) Photoelectron spectra obtained from the 10 nm thin CuO film (grey) and from the bare gold surface (blue curve), as shown in figure 6 (b) in the main publication. The gold spectrum is scaled to match the higher-energy parts of the CuO spectra. The numbers indicate the rounded area underneath each curve, providing a measure for the photoelectron yield. (b) Corresponding data for back side illumination.](image-url)
S6 Illustration of the spin-canted magnetic order

The CuO films deposited using L- and D-tartaric acid precursors have textures in which chiral \{1\overline{1}1\} and \{\overline{1}11\} planes, respectively, are preferentially oriented along the sample surface. This was shown for chiral CuO layers deposited on Au(001)\textsuperscript{1,2} and Cu(111)\textsuperscript{3} substrates. These planes are shown in figure S8 (a).

The copper atoms in CuO form one-dimensional antiferromagnetic (AF) chains along the [10\overline{1}] direction,\textsuperscript{4} drawn as a bright red line in figure S8 (a). Since the Miller indices (hkl) of all chiral planes satisfy \( k \neq 0 \), the AF chains cannot be oriented exactly perpendicular to any chiral plane.

![Diagram showing the spin-canted magnetic order](image)

Figure S8: (a) Shown are the chiral \{1\overline{1}1\} (red) and \{\overline{1}11\} (blue) planes and the directions of the respective surface normal vectors. The direction [10\overline{1}] of the one-dimensional AF ordering is indicated by a red line. (b) Spin canting gives rise to a magnetic moment \( \mu \) that is oriented perpendicularly to the direction of the ordering of the magnetic moments of the Cu atoms (black arrows). The sample surface normal \( n \) is oriented roughly along the green line. Note that CuO has a monoclinic structure, which is negligible in the present context. (c) Scheme of two crystallites within a textured film that have different azimuthal but identical out-of-plane orientations. The faces of the crystallites, shown in gray, have no physical meaning.

A canted AF order\textsuperscript{5} gives rise to a non-vanishing magnetic moment \( \mu \) perpendicular to the AF direction, as illustrated in figure S8 (b). Since the AF direction cannot be exactly perpendicular to any chiral plane, \( \mu \) has a component perpendicular to the preferentially exposed chiral planes and thus a component along the surface normal of the sample.\textsuperscript{6} The plane in which the magnetic moment induced by the spin canting is oriented (i.e., the rotation angle shown in dark red) is not known. However, its orientation is always the same within the crystal lattice. Due to the film texture, the out-of-plane orientation of all CuO crystallites is the same.

Therefore, the out-of-plane components of the spin canting-induced magnetic moment do not cancel out even if the in-plane (azimuthal, green) angle of the crystallites is random, see figure S8 (c).

---

\textsuperscript{1}Switzer, J.A.; Kothari, H.M.; Poizot, P.; Nakanishi, S.; Bohannan, E.W. Enantiospecific electrodeposition of a chiral catalyst, Nature \textbf{2003}, \textit{425}, 490–493
\textsuperscript{2}Kothari, H.M.; Kulp, E.A.; Boosnalee, S.; Nikiforov, M.P.; Bohannan, E.W.; Poizot, P.; Nakanishi, S.; Switzer, J.A. Enantiospecific Electro-deposition of Chiral CuO Films from Copper(II) Complexes of Tartaric and Amino Acids on Single-Crystal Au(001), Chem. Mater. \textbf{2004}, \textit{16}, 4232–4244
\textsuperscript{3}Bohannan, E.W.; Kothari, H.M.; Nicic, I.M.; Switzer, J.A. Enantiospecific Electrodeposition of Chiral CuO Films on Single-Crystal Cu(111), J. Am. Chem. Soc. \textbf{2004}, \textit{126}, 488–489
\textsuperscript{4}Filippetti, A.; Fiorentini, V. Magnetic Ordering in CuO from First Principles: A Cuprate Antiferromagnet with Fully Three-Dimensional Exchange Interactions, Phys. Rev. Lett. \textbf{2005}, \textit{95}, 086405
\textsuperscript{5}Dmitrienko, V.E.; Ovchinnikova, E.N.; Collins, S.P.; Nisbet, G.; Beutler, G.; Kvashnin, Y.O.; Mazurenko, V.V.; Lichtenstein, A.I.; Katsnelson, M.I. Measuring the Dzyaloshinskii–Moriya interaction in a weak ferromagnet, Nat. Phys. \textbf{2014}, \textit{10}, 202–206
\textsuperscript{6}This holds true for all chiral planes except two which could, in principle, correspond to the plane defined by the AF direction and \( \mu \) (viewed from both sides).