# **Electronic Supporting Information**

# How photocorrosion can trick you: A detailed study on low-bandgap Li doped CuO photocathodes for solar hydrogen production

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## **Experimental details**

## Preparation of Li<sub>x</sub>Cu<sub>1-x</sub>O films

 $Li_xCu_{1-x}O$  thin film photocathodes were prepared by spin coating (1000 rpm, 30 s, 100 µL) a precursor solution containing 1 M Cu(NO<sub>3</sub>)<sub>2</sub> · 3 H<sub>2</sub>O and 1 M LiNO<sub>3</sub> in ethanol. Undoped CuO films were prepared with the same method, but in absence of LiNO<sub>3</sub>. Fluorine-doped tin oxide (FTO) coated glass (TEC 15 Glass, Dyesol) with a size of 1.5 cm x 2.0 cm was used as a substrate. The samples were subsequently calcined in air at 400 °C for 2 h (1.3 °C/min) and slowly cooled down to room temperature.

### Atomic Layer Deposition of Niobium doped Titanium oxide films

Atomic layer deposition of niobium doped titanium oxide thin films was carried out in a Picosun R-200 reactor at a temperature of 200 °C and a base pressure of 2 hPa. Nitrogen (Air Liquide, 99.999 %) was used as the purge and carrier gas. The carrier gas line flow during pulses was 40 sccm. Titanium isopropoxide (TIPO, Aldrich, 99.999 %) was supplied from a stainless steel vessel at 85 °C, niobium ethoxide (NEO, Strem, 99.9+ %) was evaporated from a glass vessel at 160 °C. Ultrapure water (MilliQ, 18.2 M $\Omega$  cm) was used as oxygen source and held in a stainless steel cylinder at room temperature. Each ALD cycle for TiO<sub>2</sub> includes two TIPO pulses (1.6 s pulse, 4.5 s static exposure, 6 s purge) and one water pulse (2 s pulse, 4.5 s static exposure, 7.5 s purge). The resulting growth rate was 0.038 nm cycle<sup>-1</sup> with a non-uniformity of 4 % across a 20 cm wafer. The ALD cycle for niobium oxide consisted of four NEO pulses (1.6 s pulse, 6.5 s static exposure,

6 s purge) and one water pulse as in the  $TiO_2$  process. The resulting growth rate was 0.068 nm cycle<sup>-1</sup> with a non-uniformity of 4 % across a 20 cm wafer. Mixed oxide layers were grown by alternating 6  $TiO_2$  cycles with 1 NbO<sub>x</sub> cycle resulting in an amorphous  $Ti_{0.80}Nb_{0.20}O_x$  dense film.

#### Pt deposition

For the deposition of Pt co-catalyst nanoparticles, an NTO-protected  $Li_xCu_{1-x}O$  film, a platinum mesh counter electrode and a Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (sat.) reference electrode were connected to a  $\mu$ -Autolab III potentiostat and immersed in a methanolic 1 mM H<sub>2</sub>PtCl<sub>6</sub> solution. Afterwards, a static potential of -0.557 V vs. Hg/Hg<sub>2</sub>SO<sub>4</sub> was applied for 10 minutes without illumination.

#### Crystallographic Characterization

Powder X-ray diffraction (XRD) patterns were acquired on a STOE powder diffractometer (Cu-K<sub> $\alpha$ </sub>,  $\lambda = 1.5406$  Å) equipped with a position-sensitive Mythen-1K detector in transmission geometry. Lanthanum hexaboride (NIST LaB6 SRM 660b; space group: Pm<sup>3</sup>m; a = 4.15689(8) Å) was used as an internal standard for calibration of diffraction line positions. The XRD pattern of the sample and ~5% of lanthanum hexaboride were collected over a 20 range of 10 to 81° with a step size of 0.015°. Li<sub>x</sub>Cu<sub>1-x</sub>O unit cell parameters were obtained using the results from the Rietveld refinements<sup>[1]</sup> of a powder diffraction pattern. The observed parameters are structurally closely related to those of tenorite (CuO, space group: C2/c; a = 4.6853(3) Å; b = 3.4257(1) Å; c = 5.1303(3) Å;  $\beta = 99.549(4)^{\circ}$ ; JCPDS-ICDD PDF card No. 45-937). XRD patterns of the thin film electrodes were acquired on a Bruker D8 Discover with Ni-filtered Cu K $\alpha$  radiation and a LynxEye position-sensitive detector.

#### **Electron microscopy**

Scanning electron microscopy (SEM) measurements were performed on an FEI Helios NanoLab G3 UC scanning electron microscope using a 1 - 30 kV field emission gun and an Oxford instruments energy dispersive X-ray (EDX) spectroscopy detector.

A probe-corrected FEI Titan Themis transmission electron microscope (TEM) with a field emission gun (X-FEG) operated at 300 kV was applied to determine morphology, crystallography and elemental distribution. High-resolution TEM (HRTEM) and bright field (BF) images were received with a Ceta 16M camera while scanning TEM (STEM) measurements were performed with an annular dark field (ADF) detector. The thin film material was carefully scraped from the substrate with a razor blade and the powder was dispersed in ethanol. This liquid was deposited dropwise on a holey carbon grid to prepare the sample.

In addition, focused ion beam (FIB)-machined lamellae of film cross-sections were prepared in a FEI Helios 600i Dual Beam workstation. To locally probe the oxidation state of Cu, electron energy loss spectroscopy (EELS) in a transmission electron microscope (TEM) was used. Ion beam assisted Pt deposition with dimensions of  $10 \times 2 \times 2 \ \mu\text{m}^3$  (length × width × height) was applied for sample surface protection during Ga<sup>+</sup> ion milling. 2  $\ \mu\text{m}$  thick TEM lamellae were cut out of the films, transferred to a Mo TEM grid and initially thinned down to a thickness of around 0.7  $\ \mu\text{m}$  using an acceleration voltage of 30 kV and beam currents of 430 pA and 230 pA. Final lamellae thinning was performed at 5 kV and 120 pA and subsequent polishing to minimize beam damage was carried out at 2 kV and 72 pA until a thickness of below 100 nm was reached.

Electron energy loss spectroscopy (EELS) data were acquired in scanning transmission mode at 300 kV using a probe-corrected FEI Titan Themis equipped with a monochromator and an Gatan Enfinium ER spectrometer. An energy resolution of 0.2 eV was realized during the experiment, using a dispersion of 0.1 channels/pixel and a spectrometer entrance aperature of 5 mm. Subpixel scanning was used to reduce the electron beam damage during the spectrum acquisition on the sample yielding pixel sizes between 2 and 5 nm.

#### <sup>7</sup>Li NMR

Solid-State MAS NMR: Experiments were performed at 11.74 T on a Bruker DSX 500 spectrometer equipped with a commercial 4 mm triple-resonance MAS probe at <sup>7</sup>Li frequencies of 194.399 MHz. All experiments were performed in  $ZrO_2$  rotors at room temperature. The one-dimensional <sup>7</sup>Li NMR spectrum was acquired with a 90° pulse length of 2.0  $\mu$ s, a recycle delay of 64 s and at a sample spinning frequency of 8 kHz.

#### Hall measurements

Hall measurements were performed using the *van der Pauw* technique in a four-point setup. For the characterization, pellets were pressed (80 kg/cm<sup>2</sup>) from powders (thickness 0.31 mm) and sintered at 400 °C for 24 h (2 °C/min) prior to the measurement.

#### **Optical Characterization**

UV-Vis spectra were obtained on a Perkin Elmer Lambda 1050 UV/Visible/NIR spectrophotometer with an integrating sphere. The absorbance of the films was calculated from both the

transmittance and reflectance of the films correcting for the absorbance of the FTO substrate by applying an expression derived by Klahr *et al.*<sup>[2]</sup> to the UV-Vis data.

#### Photoelectrochemical Characterization

Current-voltage (CV) and chrono-amperometry (CA) measurements were performed in a three electrode setup. A custom built closed one-compartment cell allowed a photoelectrochemical characterization in the absence of air. Therefore, argon or nitrogen purging of the aqueous 0.1 M Na<sub>2</sub>SO<sub>4</sub> or 1mM iodide/triioide ( $I^{-}/I_{3}^{-}$ ) propylene carbonate electrolyte was started 30 minutes before the experiment and was continued during the measurement. The thin film photocathodes were masked with Teflon adhesive tape leaving free an area of 0.196 cm<sup>2</sup> for illumination. Argent conductive varnish was used to improve the electrical contact to the potentiostat. The photoelectrode, a Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (sat.) or RHE reference electrode and a platinum mesh counter electrode were connected to a  $\mu$ -Autolab III potentiostat. Measurements were either performed in the dark or under simulated sunlight illumination. For the latter, the thin film electrodes were illuminated through the substrate side by an AM1.5G solar simulator (Solar Light Model 16S) at 100 mW cm<sup>-2</sup>. CV measurements were performed either in the dark or under illumination by starting at 0.85 V vs. RHE, scanning at a sweep rate of 20 mV/s from positive to negative potentials down to 0.0 V vs. RHE and back to 0.9 V vs. RHE. In total, two cycles were performed for each measurement. Linear sweep voltammograms were performed at a scan rate of 2 mV/s, starting at 0.7 V vs. RHE and scanning down to -0.1 V vs. RHE. The light source was chopped manually. In the case of CA measurements, a steady potential was applied for a defined time and the resulting current was recorded in a time interval of 1 s. Electrochemical impedance spectroscopy was performed in nitrogen purged aqueous  $0.1 \text{ M Na}_2\text{SO}_4$  electrolyte at 0.3 V vs. RHE under AM1.5 substrate illumination with 10 mV amplitude over a frequency range between 1000000 and 100 Hz (logarithmic step size).

#### Hydrogen detection

In order to verify that the observed photocurrent results from the reduction of water, a micro sensor (*Unisense A/S H<sub>2</sub>-NPLR*) with a hydrogen selective silicone membrane was combined with a three electrode PEC setup. The micro sensor was calibrated in a two-point measurement using the corresponding program (*Unisense A/S SensorTrace 1.4*). The data point for c = 0 mM was acquired in Nitrogen-purged electrolyte (aqueous 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at pH 7), while the

second measuring point of c = 40.7 mM was recorded in the same electrolyte purged with forming gas (5 vol% H<sub>2</sub> in Ar, *AirLiquide ARCAL15*) for 20 minutes, taking in account the saturation concentration of pure H<sub>2</sub> gas in water of 813  $\mu$ M atm<sup>-1.[3]</sup> To minimize the electrolyte volume and therefore maximize the detectable hydrogen concentration, a 2 mL poly(methyl methacrylate) (PMMA) cuvette was used as PEC cell. The working electrode was glued on a drilled-in hole ( $^{\emptyset}$  7 mm) and connected to the potentiostat together with a Platinum wire counter electrode and a Hg/Hg<sub>2</sub>SO4/K<sub>2</sub>SO<sub>4</sub> (sat.) reference electrode and filled with 1.7 mL electrolyte. The hydrogen micro sensor was placed in the cuvette, which was subsequently sealed using modelling clay. The hydrogen concentration was recorded with an interval time of 10 seconds. As the polarization of the micro sensor is very sensitive and critical for a correct measurement, magnetic stirring was not possible in order to avoid any interfering signals.

#### **Computational details**

Density-functional theory (DFT) calculations were performed using the VASP<sup>[4]</sup> code with projector-augmented wave (PAW) pseudopotentials<sup>[5]</sup>. The generalized-gradient approximation (GGA)<sup>[6]</sup> was used for the exchange-correlation functional, including an on-site Hubbard *U* term. The rotationally invariant approach of Dudarev et al.<sup>[7]</sup> was adopted for the GGA+U calculations. A Hubbard-U value for Cu of 8.0 eV gives an indirect gap of 1.46 eV for CuO, in close agreement with the 1.39 eV determined from the Tauc plot. This is consistent wih previous LDA+U results.<sup>[8]</sup> We note that previous experimental values range between 1.35-1.7eV.<sup>8-11</sup> To model different doping concentrations two different cell sizes with 8 and 64 atoms were adopted, corresponding to the bulk CuO and a 2x2x2 supercell, respectively. A plane-wave cut-off of 500 eV and a Monkhorst-Pack k-point mesh of 8×8×8 and 4×4×4 were used for the two unit cells, respectively. The Li solution energy (SE) indicates the preferred lattice positions of Li incorporation in the CuO structure and is defined as follows:

$$SE_{Li} = E_{Li_x Cu_1 - x^0} - E_{Cu0} - NE_{Li} + ME_{0/Cu}$$
 Eq. 1

 $E_{Li_x}Cuo$  and  $E_{Cuo}$  represent the total energy of the doped and undoped structure, respectively.  $E_{Li}$  and  $E_{O/Cu}$  is the energy of the elemental ground state of lithium, oxygen and copper. *N* is the number of lithium atoms substituted by *M* oxygen or copper. To calculate the solution energy a Cu or O was substituted by a Li atom and the structure fully relaxed.

# Additional figures



**ESI Fig. 1.** XRD pattern of the film obtained directly after calcination. The film is a mixture of Li doped CuO,  $Li_2CO_3$  and  $LiNO_3$ . To obtain the single Li doped CuO phase the film is immersed in water for 2 hours to remove  $Li_2CO_3$  and  $LiNO_3$ .



**ESI Fig. 2.** Rietveld refinement of undoped CuO with observed data (·) and calculated pattern (red line), blue vertical bars mark the positions of the diffraction lines of CuO (tenorite).



**ESI Fig. 3**. a) Band gap and b) lattice constants of CuO as a function of Hubbard U. Experimental band gaps range between 1.35-1.7 eV, highlighted in green.<sup>[9]</sup> The band gap of 1.39 eV determined from the Tauc plot in this work is marked by a dashed line in a). The experimental lattice parameters denoted by dashed lines in b) are from Åsbrink *et al.*.<sup>[10]</sup>



**ESI Fig. 4.** Linear sweep voltammetry measurements of bare copper oxide photocathodes in the dark (dashed lines) and under AM1.5 illumination (solid lines). Li<sub>x</sub>Cu<sub>1-x</sub>O films (red) exhibit significantly higher photocurrents compared to undoped CuO films.



**ESI Fig. 5.** Cyclic voltammetry measurements of a bare  $Li_xCu_{1-x}O$  electrode in successive order from a – f. The potential range was extended stepwise to lower potentials, and consequently the photocorrosion gets more and more pronounced.



**ESI Fig. 6.** To generate the EELS map tracking the oxidation state of Copper, the spectra were first aligned. After subtraction of the background via a power-law fit the intensity ratio of the  $Cu-L_3$  edge of CuO (red) and  $Cu_2O$  (blue) were integrated in defined energy windows. The distribution of the two oxidation states is estimated by this intensity ratio.



**ESI Fig. 7.** Chronoamperometric data of unprotected  $Li_xCu_{1-x}O$  photocathodes at various potentials from 0.0 to 0.6 V vs. RHE in the dark (black) and under AM1.5 illumination (red). Afterwards, the respective samples were characterized by XPS (see Figure 3c,d). The spikes in (c) were caused by an increased flow of nitrogen purging.



**ESI Fig. 8.** An as-synthesized sample, which was never used in an electrochemical measurement, was used to investigate the effect of the FIB sample preparation. While the sample preparation causes a slight reduction of some regions of the  $Li_xCu_{1-x}O$  surface, no cubic  $Cu_2O$  crystals are formed by this procedure. Therefore, the FIB preparation method is supposed to have no effect on the photocorrosion study of  $Li_xCu_{1-x}O$  photocathodes.



**ESI Fig. 9.**  $CuO/Cu_2O$  ratio maps based on EELS data of samples used for PEC water splitting at different potentials. (a) 0.1 V for 15 min, (b) 0.2 V for 15 min and (c) 0.3 V for 15 min. \*Artifact of the spectrum alignment, should be  $Cu_2O$ .



**ESI Fig. 10.** TEM cross section images of  $Li_xCu_{1-x}O$  films after an electrochemistry experiment performed for 15 min at 0.3 V vs. RHE under illumination (a, c) with corresponding EELS maps (b, d, pixel size 4 nm<sup>2</sup>).



**ESI Fig. 11.** a) Potentiostatic measurement of a bare, undoped CuO electrode at 0.2 V vs. RHE under AM 1.5 illumination. b) XRD pattern of the CuO film after the 15-minute stability test shown in (a), indicating the formation of Cu<sub>2</sub>O (blue). c) High resolution TEM image showing one square crystal grown on the surface of the CuO structure. The FFTs of the marked regions were indexed for CuO (d) and Cu<sub>2</sub>O (e). f, g) Further TEM images of Cu<sub>2</sub>O grown on different spots of the CuO surface. h) Electron diffraction pattern of the cubic crystal depicted in (g) with the reflections indexed for Cu<sub>2</sub>O.



**ESI Fig. 12.** XRD pattern of  $Ti_{0.8}Nb_{0.2}O_x$  ALD films as deposited (black). These layers are amorphous, in contrast to pure  $TiO_2$  layers (black). After calcination in 5%H<sub>2</sub>/N<sub>2</sub> atmosphere at 600°C (blue), crystalline  $Ti_{0.8}Nb_{0.2}O_x$  ALD layers are obtained.



**ESI Fig. 13.** XPS characterization of  $Li_xCu_{1-x}O$  photocathodes after electrochemical stability tests at the respective potentials vs. RHE for 15 minutes each in the dark (left side, a and c) and under AM1.5G illumination (right side, b and d). The upper two diagrams show the deconvolution of the Cu  $2p_{3/2}$  peaks

into a Cu(I)-component at 932.4 eV and a Cu(II)-component at ca. 933.6 eV. At the lowest potential (0.0 V vs. RHE) a third feature appears at higher binding energies, which might be caused by differential charging of the samples as a result of proceeding corrosion. The corresponding Cu L<sub>3</sub>VV Auger signals are displayed in the graphs (c) and (d) below with the positions of the Cu(I) and Cu(II) peaks indicated by the dashed lines.



**ESI Fig. 14.** Cyclic voltammograms of  $Li_xCu_{1-x}O$  photocathodes covered with Nb:TiO<sub>2</sub> (NTO) or TiO<sub>2</sub> (TO). A protection layer of 2.5 nm NTO showed the highest activity of all tested NTO layer thicknesses (a) and also an improvement compared to undoped TiO<sub>2</sub> (b).



**ESI Fig. 15.** Energy dispersive X-ray (EDX) mappings of a  $Li_xCu_{1-x}O/NTO/Pt$  TEM cross section. The  $Li_xCu_{1-x}O$  structure (a, b) is homogenously covered with Nb:TiO<sub>2</sub> (NTO, c, d) and Pt (e).



**ESI Fig. 16.** a) TEM cross section of a  $Li_xCu_{1-x}O/NTO/Pt$  device held for 15 min at 0.2 V vs. RHE under AM1.5 illumination. The marked area (white, b) was used for EDX mapping of Cu (c), O (d) and Ti (e). The corresponding EELS map (f) shows no sign of photocorrosion.



**ESI Fig. 17.** SEM top view images of a  $Li_xCu_{1-x}O/NTO/Pt$  photocathode after 90 minutes at 0.3 V vs. RHE and AM1.5G substrate illumination. The 20 nm sized Pt particles are not adhering on the surface anymore, which is believed to cause the observed loss in activity.



**ESI Fig. 18.** XRD patterns of unprotected  $Li_xCu_{1-x}O$  films before (black) and after (red) the hydrogen evolution test at 0.3 V vs. RHE (**Fehler! Verweisquelle konnte nicht gefunden werden.**a). After 30 minutes of illumination and progressing photocorrosion, the cuprite phase of Cu<sub>2</sub>O emerges (blue). Reflections of the FTO substrate are marked with (\*).



**ESI Fig. 19.** TEM image of unprotected  $Li_xCu_{1-x}O$  after 60 sec at 0.2 V vs. RHE under AM1.5 illumination. Cubic crystals on the surface indicate that photocorrosion starts directly with the photoelectrochemical stability test.



**ESI Fig. 20.** Nyquist plots of a single  $Li_xCu_{1-x}O$  electrode. The photocathode was held at 0.3 V vs. RHE under AM1.5 illumination for a 60 minutes stability test, intermitted by impedance measurements at the same photoelectrochemical conditions. With advancing photocorrosion, the charge transport resistance on the photocathode – electrolyte interface increases.

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