## Supporting Information

# Stabilized Solar Hydrogen Production with CuO/CdS Heterojunction Thin Film Photocathodes

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#### **Additional Information for Experimental Section**

*Photoelectrochemical Measurements*: The photocurrent values from all the photoelectrochemical measurements performed in this study were multiplied by a factor of 0.862 to take into account unintended reflections of light inside the first generation of our white teflon photoelectrochemical cell, which gave ~16% higher photon flux at the plane of the photoelectrode than intended. We uncovered this fact during measurement of the IPCE, which was not integrating correctly. Under 1–1.16 sun illumination, we expect a linear response in the photocurrent to illumination intensity, enabling the use of the linear scaling factor 0.862.

*Electrochemical Impedance Spectroscopy (EIS)*: The measurements were carried out in the same PEC cell as for the JV measurements. The geometric surface area ( $0.28 \text{ cm}^2$ ) was multiplied by a factor of 2 to give an estimate of the real surface area, due to the roughness of the CuO sample (see Figure 1b of the main text). To circumvent frequency dispersion in the Mott-Schottky plots, we determined the frequency-independent space charge capacitance at each bias potential by a complete impedence analysis. The Nyquist plots of the ALD TiO<sub>2</sub> showed only



one semicircle and were therefore fitted with a simple RC element (with the capacitance in parallel to the resistance shown below).  $R_{ct}$  represents the charge transfer resistance and  $C_{sc}$  the space charge capacity. In all fitting procedures, the capacity is modeled by a constant phase element (CPE). The series resistance from cables, contacts and the electrolyte solution,  $R_{series}$ , is represented by a resistance in series to the RC element.

In the case of the CuO, the Nyquist plot showed a more complex shape. Normally two semicircles could be observed in the Nyquist plot. To deduce if one of the semicircles is related to the resistivity of the sample itself three different thicknesses of the CuO were investigated by EIS. The resistance of the high frequency arc increased roughly from 19 to 119 to 225 Ohm (at 700mV vs RHE) with the thickness of the CuO. This clearly shows that the high frequency arc is related to the resistivity of the CuO itself and that the low frequency arc must relate to the charge transfer resistance and the space charge capacity. After the fitting procedures, the CPE values were converted into capacitance ( $C = \frac{(R*Q)^{(\frac{1}{R})}}{R}$ ), with R as the resistance in parallel to the desired capacitance and Q as the charge from the CPE and n as the exponent of the CPE.

To account for the roughness of the CuO surface we have multiplied the projected area by 2. The doping we have determined with this modified electrode area is  $3.2 \times 10^{21}$  cm<sup>-3</sup>. This value of doping is high. To get an estimate what that implies in terms of CuO composition, we have determined the atomic percentage of vacancies that could form such a highly doped semiconductor (omitting occupation of interstitial sites by atoms).

The states in the valence band can be calculated by:

$$N_V = 2(\frac{2\pi m^* kT}{h^2})^{3/2}$$

with m<sup>\*</sup> for the effective mass of the holes, k as the Boltzmann constant, T as temperature in Kelvin and h as the Planck constant. For CuO, N<sub>V</sub> at room temperature with an effective hole mass of  $7.9m_0$  (T. Seri et al, Extraction of important electrical parameters of CuO. Physica B: Condensed matter. 406, 575-578 (2011)) is ~6×10<sup>20</sup> cm<sup>-3</sup>.

Assuming the amount of all atoms to be in the range of  $1 \times 10^{23}$  cm<sup>-3</sup> and the states in the valence band to be  $6 \times 10^{20}$  cm<sup>-3</sup>, about  $2.6 \times 10^{21}$  cm<sup>-3</sup> states must originate from copper vacancies whose states are located in the forbidden gap. EDX measurements showed up to 10% copper deficiency, although this is only an approximation. As  $-5 \times 10^{22}$  of all atoms per cm<sup>-3</sup> in CuO are copper, about 5% copper vacancies would lead to the observed high doping.



Figure S1. XRD patterns at  $2\theta$  of  $35^{\circ}$  to  $40^{\circ}$  for an electroplated Cu film as well as the one-step and two-step annealed films.



Figure S2. Top-view SEM image of electroplated Cu that was annealed at 600  $^{\circ}$ C for 1h under Ar atmosphere at base pressure of 10<sup>-2</sup> mbar, showing larger grains than the as deposited film.



Figure S3. Example of an inhomogenous CuO film that was sometimes obtained from the onestep annealing method. Top-view SEM images of different parts of the film are also shown. The roughness of the parts with gray appearance are also apparent in the top-view SEM on the right.



Figure S4. Tauc plot to estimate the band gap of CuO, constructed from diffuse-reflectance data and using the formula for a direct, allowed transition.



Figure S5. (a) XRD pattern of CuO film after photoelectrochemical measurement at a fixed bias of 0.4  $V_{RHE}$  for 30 min., (b) possible chemical reactions within the gap of CuO.



Figure S6. Current density-potential curves of CuO/CdS/Pt measured in 1 M phosphate buffer (pH 7) under chopped illumination from simulated 1 sun illumination, indicating corrosion.



Figure S7. Reproducibility of the CuO/CdS/TiO<sub>2</sub>/Pt photocathode measured in 1 M phosphate buffer (pH 7) under chopped illumination from simulated 1 sun illumination.





Figure S8. (a) Top-view SEM images of CuO/CdS and CuO/CdS/TiO<sub>2</sub>. (b) Current densitypotential curve of FTO/CdS film with and without ALD-TiO<sub>2</sub> measured using 0.1 M Na<sub>2</sub>SO<sub>3</sub> (pH 9.5) as hole scavenger, demonstrating that the ALD-TiO<sub>2</sub> effectively blocks the charge transfer from CdS, thus confirmed the conformality of the deposition.



Figure S9. Current density-potential curves of CuO/ZnO/TiO<sub>2</sub>/Pt measured in 1 M phosphate buffer (pH 7) under chopped illumination from AM 1.5 solar simulator.



Figure S10. Mott-Schottky plots of a CuO film measured in 0.1 M KOH and ALD-TiO<sub>2</sub> on FTO measured in 1 M  $H_2SO_4$  (in the dark).



Figure S11. Faradaic efficiency of the CuO/CdS/TiO<sub>2</sub>/Pt photocathode measured at 0  $V_{RHE}$ . Due to a slow equilibration between hydrogen generated in the aqeuous phase and hydrogen in the head space, an induction period of *ca*. 35 min was observed, afterwhich the slopes overlay, as shown in the main text (Figure 5b).



Figure S12. Typical current density-potential curves of CuO/CdS/TiO<sub>2</sub>/Pt when sweeped for the first and second time consecutively in the negative direction. The decrease of the photocurrent in the potential range more positive than *ca*. 0.45 V after the first sweep indicates that the photocurrent in this region was due to the photoreduction of remaining Pt(II) into Pt(0). The initial oxidative dark current in the second sweep is due to oxidation of H<sub>2</sub> formed during the first sweep.



Figure S13. Extended current density-time profile of photocathode CuO/CdS/TiO<sub>2</sub>/Pt measured at 0  $V_{RHE}$  in 1M phosphate buffer (pH 7).



Figure S14. Current density-time profile of CuO/CdS/TiO<sub>2</sub> (without Pt) measured at 0  $V_{RHE}$  in 1M phosphate buffer (pH 7).



Figure S15. Current density-voltage profile of bare CuO in 1M phosphate buffer (pH 7), indicating an onset of corrosion photocurrents in the same range as the measured flatband, as determined by Mott-Schottky.

Table S1. Reports on CuO-based photocathodes.\*

Photoelectrode	Fabrication method	Solution	Photocurrent	Dark current	Photostability (remaining current)	Faradaic efficiency	Ref.
CuO	Sputtering	0.1 M Na <sub>2</sub> SO <sub>4</sub> (pH 5.84)	2.5 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca.</i> 0.25 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca</i> . 70% (after 20 min @ 0.125 V <sub>RHE</sub> )	-	(1)
CuO	Sputtering	0.1 M Na <sub>2</sub> SO <sub>4</sub> (pH 5.84)	1.68 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca.</i> 0.25 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca.</i> 70% (after 15 min @ 0 V <sub>RHE</sub> )	-	(2)
CuO	Spray-annealing	1 M KOH (pH 14)	3.1 mA/cm <sup>2</sup> @ 0.42 V <sub>RHE</sub>	ca. 0.1 - 0.25 mA/cm <sup>2</sup> @ 0.42 V <sub>RHE</sub>	-	-	(3)
CuO	Electrodeposition -microwave heating (nanostructured)	0.5 M Na <sub>2</sub> SO <sub>4</sub> (pH 6)	4.4 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca.</i> 0.5 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca</i> . 70% (after 20 min@0.2 V <sub>RHE</sub> )	82% @ 0.1 V <sub>RHE</sub> )	(4)
CuO/ZnO	CuO: thermal oxidation (nanowire) ZnO: hydrothermal	0.25 M Na <sub>2</sub> SO <sub>4</sub> (pH 7.25)	1.5 to 1.75 mA/cm <sup>2</sup> (with reflector) $@ 0.17 V_{RHE}$	<i>ca.</i> 0.25 to 0.5 mA/cm <sup>2</sup> @ 0.17 $V_{RHE}$	<i>ca</i> . 50% (after 3 min @0.07 V <sub>RHE</sub> )	-	(5)

CuO	Spin coating- annealing	1 M KOH (pH 14)	1.2 mA/cm <sup>2</sup> @ 0.47 V <sub>RHE</sub>	<i>ca.</i> 0.3 mA/cm <sup>2</sup> @ 0.32 $V_{RHE}$	-	-	(6)
CuO/ZnO/TiO <sub>2</sub>	CuO: electrodeposition (nano) ZnO: ALD , TiO <sub>2</sub> : ALD	1 M KOH (pH 14)	4.1 mA/cm <sup>2</sup> @ 0.42 V <sub>RHE</sub>	1.25 mA/cm <sup>2</sup> @ 0.42 V <sub>RHE</sub>	-	-	(7)
CuO	Spin coating- annealing	0.1 M Na <sub>2</sub> SO <sub>4</sub> (pH 5.84)	0.5 mA/cm <sup>2</sup> @ 0.05 V <sub>RHE</sub>	0.05 mA/cm <sup>2</sup> @ 0.05 V <sub>RHE</sub>	<i>ca.</i> 90% (after 5 min @ 0.05 V <sub>RHE</sub> )	-	(8)
CuO/CuBiO <sub>4</sub> /Pt	CuO: drop casting CuBiO <sub>4</sub> : drop casting Pt: photodeposition	0.3 M K <sub>2</sub> SO <sub>4</sub> , 0.1 M phosphate (pH 6.8)	<i>ca.</i> 0.8 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	ca. 0.3 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca.</i> 60% (after 20 min @ 0.2 V <sub>RHE</sub> )	-	(9)
Porous ATO /CuO	hydrothermal (nanosheets)	0.5 M Na <sub>2</sub> SO <sub>4</sub> (pH 6.5)	<i>ca</i> . 4.6 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca.</i> 1 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca</i> . 60-70% (after 20 min @ 0.35 V <sub>RHE</sub> )	-	(10)

CuO/ZnO	CuO: electrodeposition (nanorod) ZnO: hydrothermal (nanorod)	0.1 M KOH	0.9 mA/cm <sup>2</sup> @ <i>ca</i> . 0.464 V <sub>RHE</sub>	<i>ca</i> . 0.1 mA/cm <sup>2</sup> @ 0.464 V <sub>RHE</sub>	<i>ca.</i> 90% (after - 20 min @ 0.464 V <sub>RHE</sub>	(1	11)
CuO/ZnO	CuO: hydrothermal (nanocone) ZnO: ALD	0.25 M Na <sub>2</sub> SO <sub>4</sub> (pH 6.8)	<i>ca.</i> 4.6 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca.</i> 0.35 mA/cm <sup>2</sup> @ 0 V <sub>RHE</sub>	<i>ca</i> . 70% (after - 6 min 40 s @ 0.2 V <sub>RHE</sub>	(1	12)
CuO (Li-doped)	Flame spray- pyrolysis	1 M KOH (pH 14)	1.52 mA/cm <sup>2</sup> @ 0.473 V <sub>RHE</sub>	<i>ca</i> . 0.25 mA/cm <sup>2</sup> @ 0.323 V <sub>RHE</sub>		(1	13)
CuO/Pd	CuO: spin- coating Pd: photodeposition	0.2 M H <sub>2</sub> BO <sub>3</sub> - /H <sub>3</sub> BO <sub>3</sub> buffer (pH 9.2)	<i>ca.</i> 0.8 mA/cm <sup>2</sup> @ 0.44 V <sub>RHE</sub>	<i>ca.</i> 0.2 mA/cm <sup>2</sup> @ 0.44 V <sub>RHE</sub>	<i>ca.</i> 50% (after - 10h @ 0.44 V <sub>RHE</sub>	(1	14)

\* If the value is not specifically written, we estimated the value based on the data/graph shown in the reports.

Table S2. Reports on CuO solar cells.

Structure	Fabrication method	J <sub>SC</sub> /mA cm <sup>-2</sup>	V <sub>OC</sub> / V	FF	Efficiency / %	Ref.
CuO/n-Si	CuO: sputtering Si: single crystal	6.27	0.33	0.2	0.41	(15)
CuO/n-Si	CuO: sputtering Si: single crystal	6.4	0.49	0.32	1.0	(16)
CuO/ZnO	CuO: sputtering ZnO: sputtering	0.85	0.35	0.27	0.08	(17)
CuO/ZnO	CuO: electrodeposition ZnO: electrodeposition	1.6	0.00028	0.25	0.0001	(18)
CuO/ZnO	CuO: electrodeposition ZnO: electrodeposition	0.0024	0.017	0.25	0.00001	(19)
CuO/ZnO	CuO: sputtering ZnO: sputtering	-	-	-	0.0003	(20)
CuO/TiO <sub>2</sub>	CuO: sputtering TiO <sub>2</sub> : spray pyrolysis	<0.1	<0.15	-	-	(21)

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