

Supporting Information to

On the Structural Evolution of Nanoporous Optically Transparent CuO Photocathodes upon Calcination for Photoelectrochemical Applications

Lukas Korell,¹ Stefan Lauterbach,² Jana Timm,³ Li Wang,⁴ Maximilian Mellin,¹ Anna Kundmann,⁴
Qingyang Wu,¹ Chuanmu Tian,¹ Roland Marschall,³ Jan P. Hofmann,¹ Frank E. Osterloh,⁴ and Marcus
Einert*,¹

¹Surface Science Laboratory, Department of Materials and Earth Sciences, Technical University of
Darmstadt, Otto-Berndt-Straße 3, 64287 Darmstadt, Germany

²Institute for Applied Geosciences, Geomaterial Science, Technical University of Darmstadt,
Schnittspahnstraße 9, 64287 Darmstadt, Germany

³Department of Chemistry, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany

⁴Department of Chemistry, University of California, One Shields Avenue, Davis, CA 95616, USA

corresponding author:

M. Einert – meinert@surface.tu-darmstadt.de

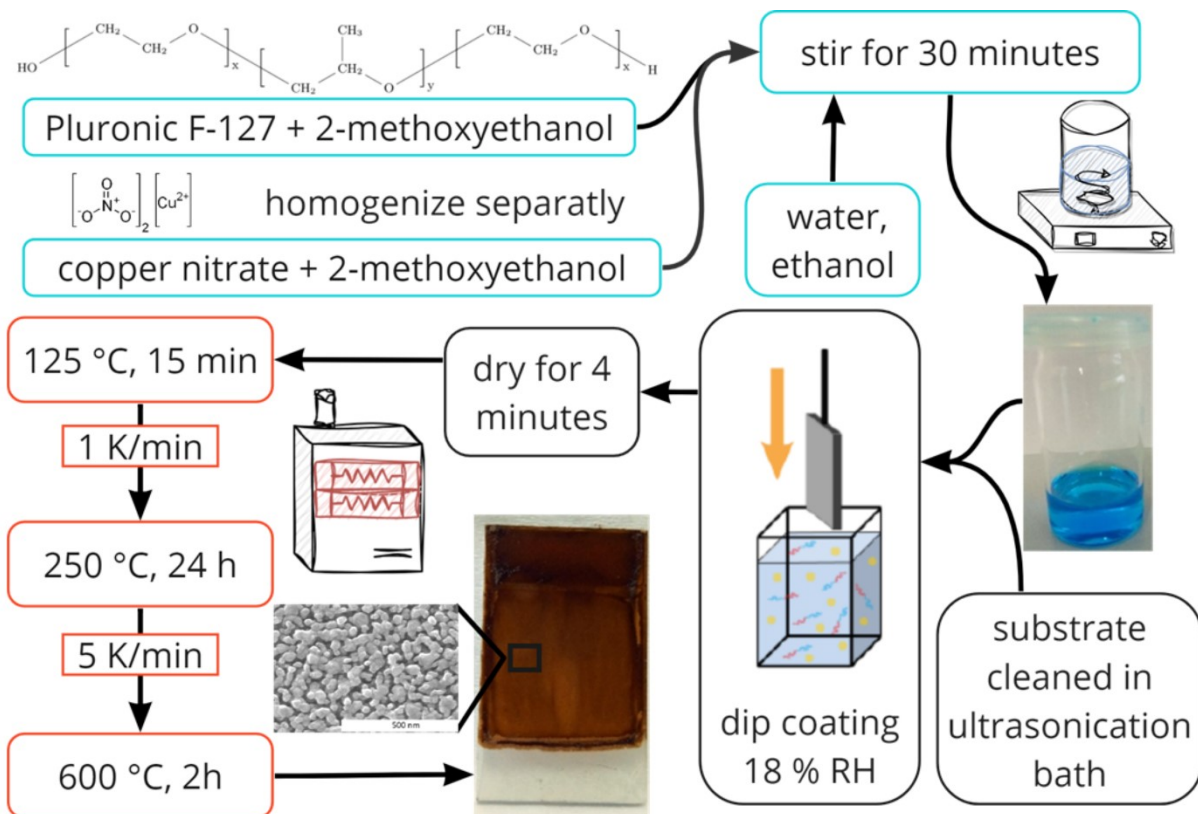


Figure S1. Flow chart representing the novel synthesis route starting from dissolution of the precursors over the dip-coating process to the applied temperature profile for the preparation of nanocrystalline and nanoporous CuO thin films.

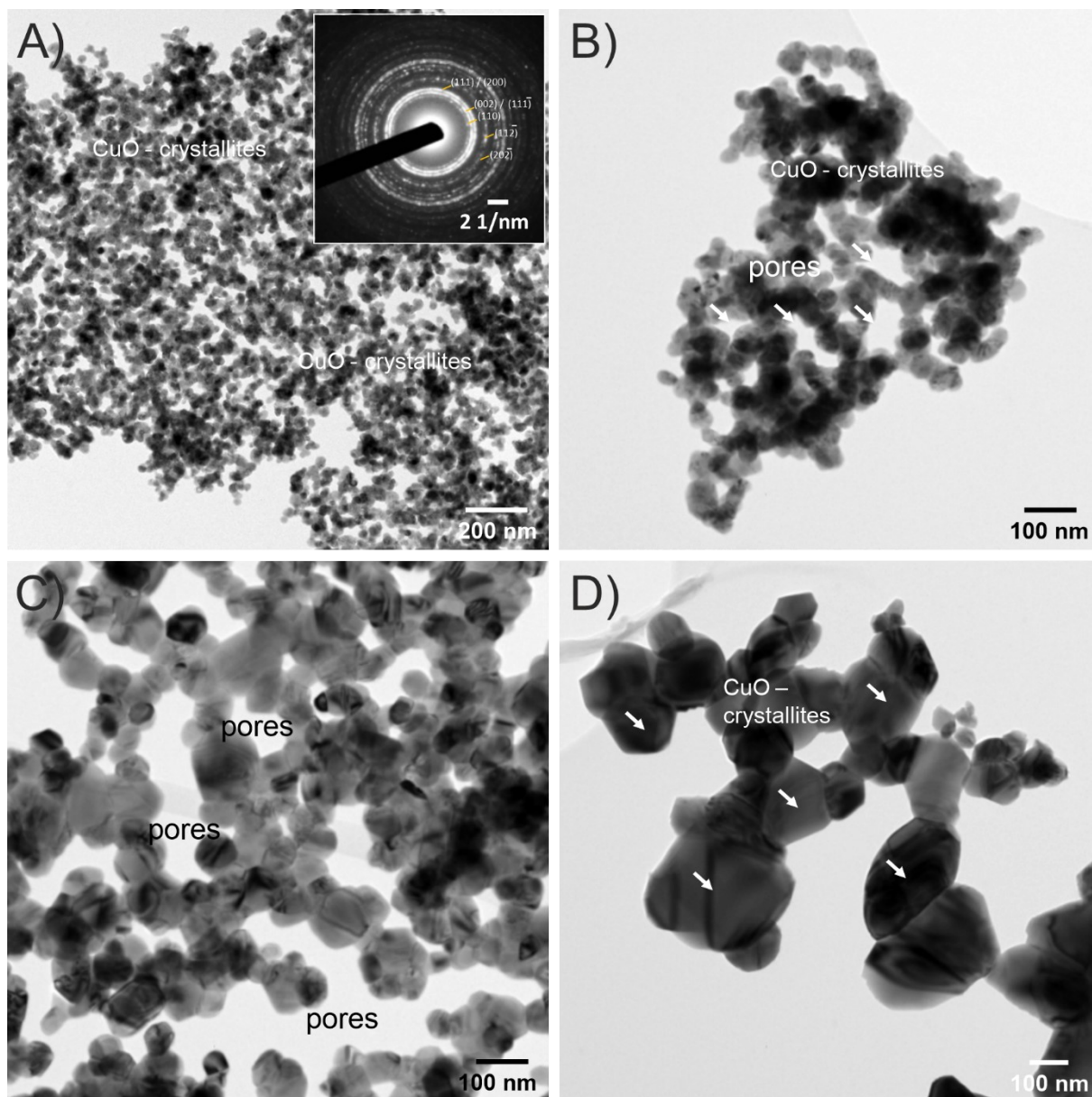


Figure S2. Bright-field TEM images of A) CuO-400, B) CuO-500, C) CuO-600, and D) CuO-750. Arrows indicating CuO crystallites and areas representing the pores. The inset in A) shows a SAED pattern of the area. The pattern is indexed applying the crystallographic data for monoclinic CuO.

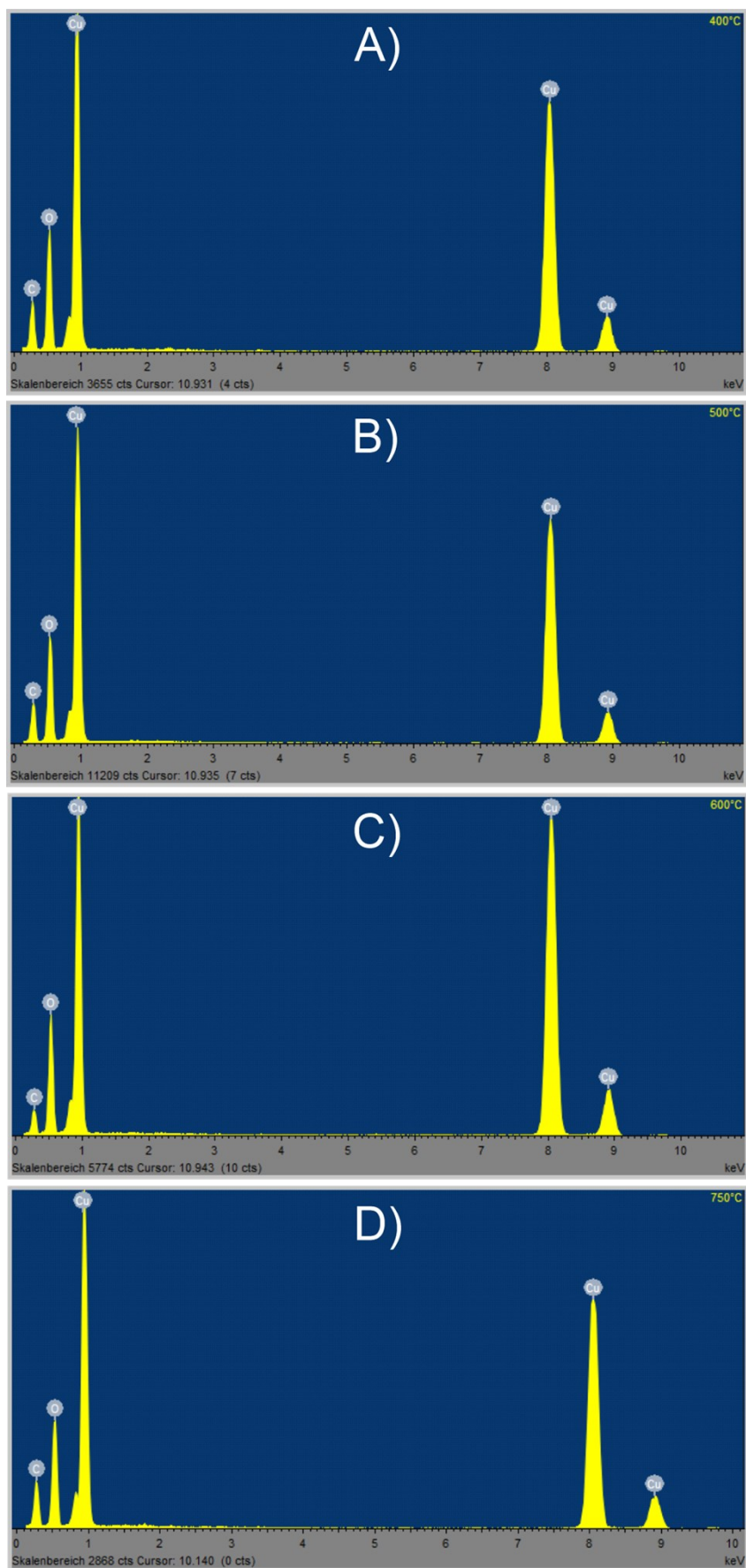


Figure S3. Energy dispersive X-ray spectroscopy (EDS) applied for A) CuO-400, B) CuO-500, C) CuO-600, and D) CuO-750 presenting the detected signals of Cu, O, and C.

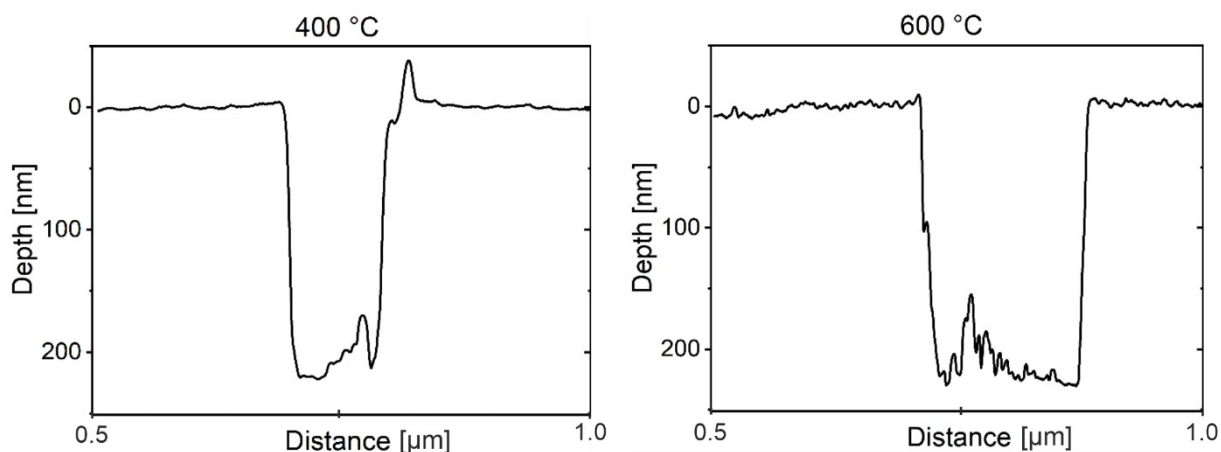


Figure S4. Representative profilometry measurements of mesoporous CuO-400 (left) and CuO-600 (right) thin films.

Table S1: Crystallite sizes and full width at half maximum (FWHM) values of CuO thin films calcinated at four different temperatures and calculated by Williamson-Hall method.

Calcination temperature	400 °C	500 °C	600 °C	750 °C
$\Delta(2\theta)$ (110), (202), and (004)	1.09°, 1.33°, and 1.61°	0.88°, 1.17°, and 1.40°	0.80°, 1.06°, and 1.23°	0.82°, 0.94°, and 1.29°
Crystallite size	8.9 nm	11.9 nm	12.2 nm	13.7 nm

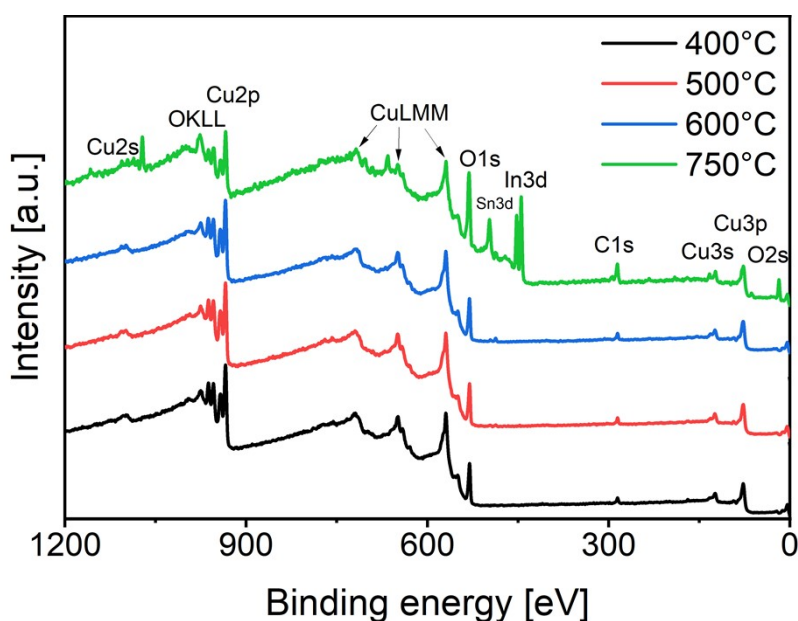


Figure S5. XPS survey spectrum of the mesoporous CuO-400, CuO-500, CuO-600, and CuO-750 thin films. The additional In3d and Sn3d emission lines for CuO-750 originate from the ITO substrate.

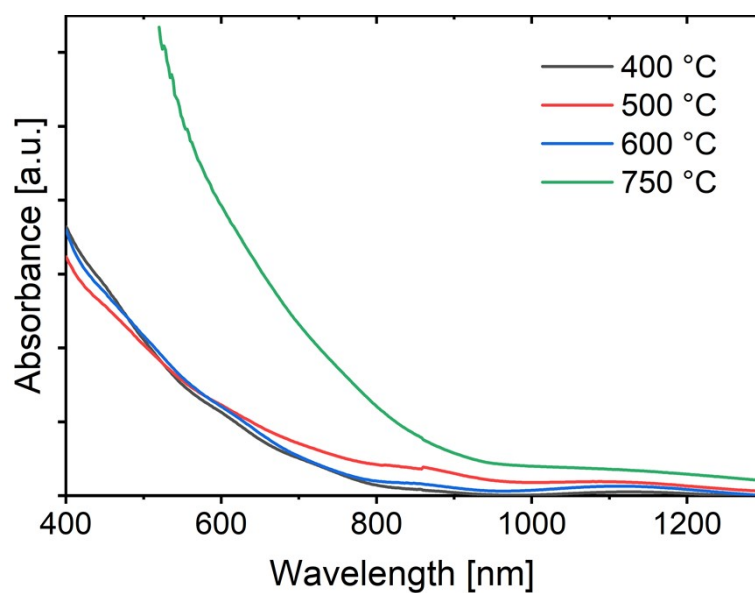


Figure S6. Absorbance spectra of the mesoporous CuO-400, CuO-500, CuO-600, and CuO-750 thin films measured in transmission mode.

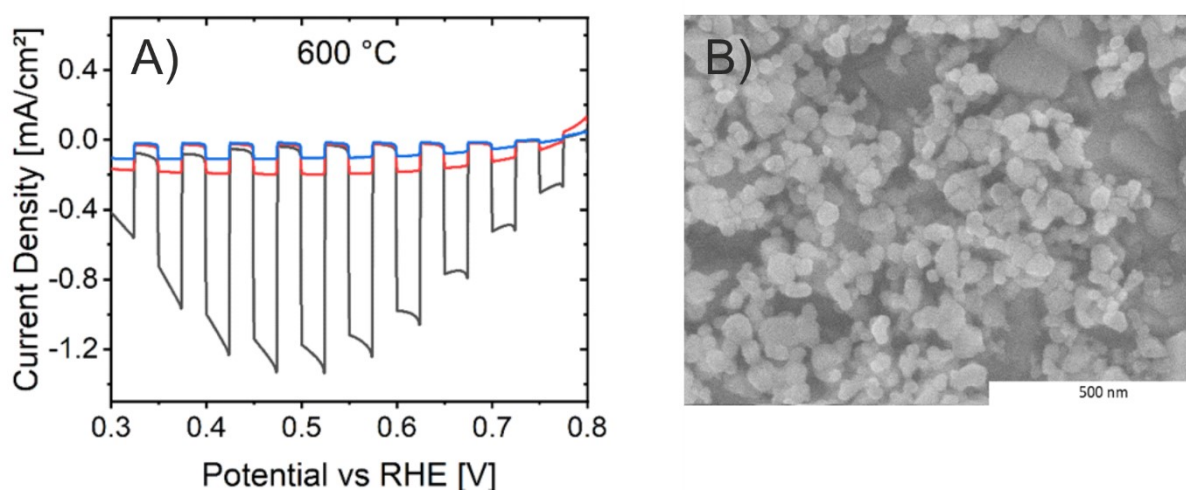


Figure S7. A) Intermittent-light voltammetry for three consecutive measurements at CuO-600 (black 1st, red 2nd, and blue 3rd cycle). B) SEM picture of CuO-600 sample after photoelectrochemical characterization (i.e., subsequential chopped-light voltammetry and Mott-Schottky analysis).

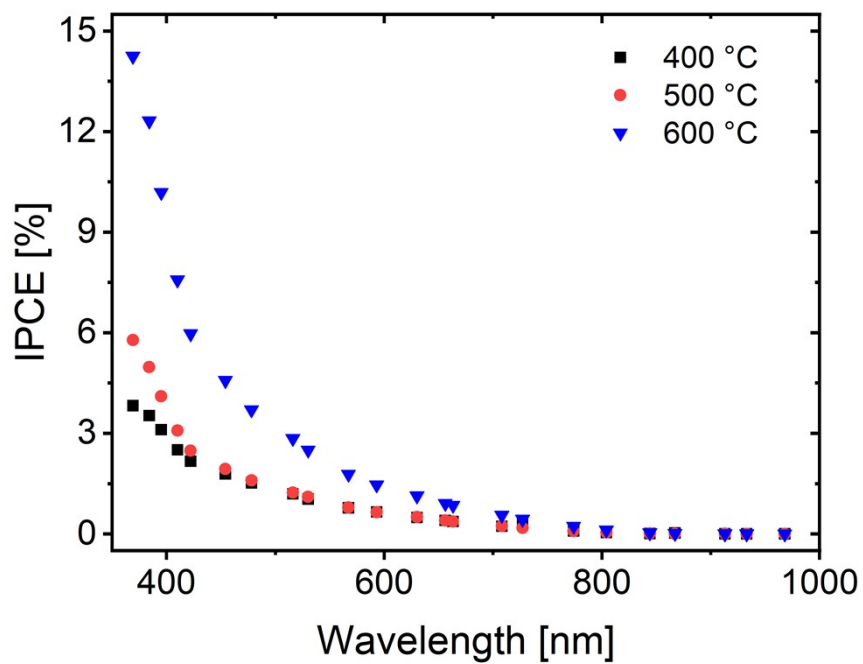


Figure S8. IPCE spectra of CuO-400, CuO-500, and CuO-600 thin films measured at 400 mV vs. RHE in 1.0 M Na₂SO₃ / 0.2 M Na₂SO₄ electrolyte.

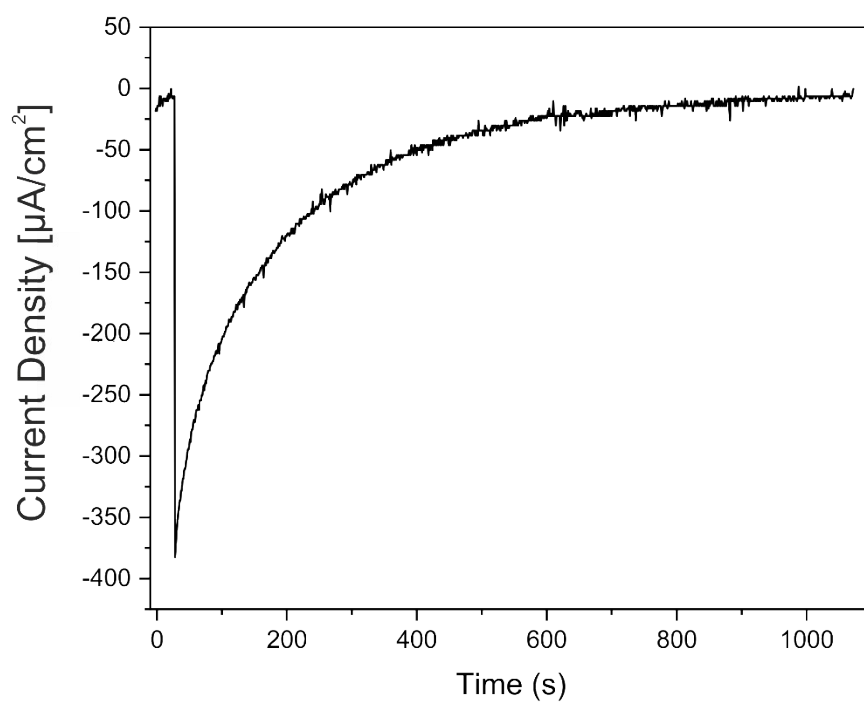


Figure S9. Photocurrent decay curve for CuO thin film in 1.0 M Na₂SO₃ / 0.2 M Na₂SO₄ electrolyte under AM 1.5 irradiation and at 0.3 V vs RHE.

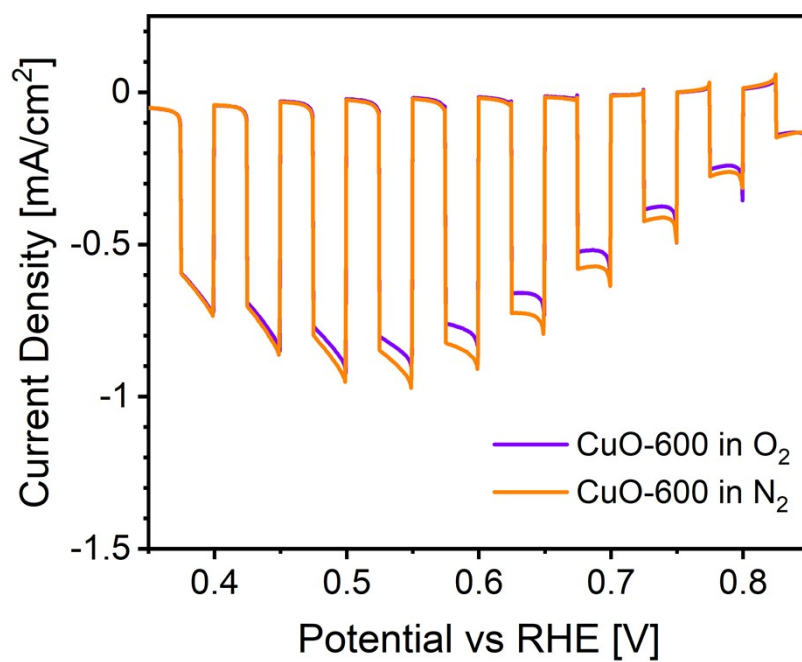


Figure S10. Intermittent-light voltammetry for CuO-600 thin films analyzed in oxygen (violet) and nitrogen (orange) purged aqueous 0.2 M Na₂SO₄ electrolyte (containing a phosphate buffer and 1 M Na₂SO₃).

Table S2: Wavelengths, full width at half maximum (FWHM), and power of the LEDs accessed in the tunable light source.

Wavelength [nm]	FWHM [nm]	P [Wm^{-2}]
1008	44	139
968	35	98
933	46	114
913	37	153
867	32	221
844	25	221
804	23	222
774	22	201
727	20	214
708	21	269
663	17	132
656	56	322
630	14	544
593	12	184
567	63	689
530	22	450
516	22	519
478	15	811
454	13	958
422	10	946
410	15	797
395	10	390
384	8	408
369	8	293

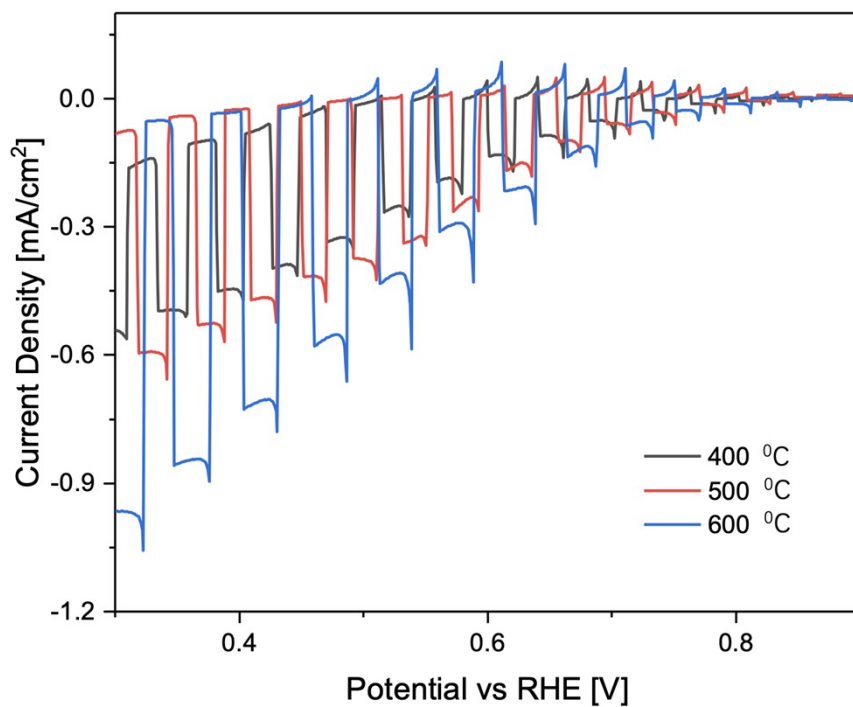


Figure S11. Linear sweep voltammetry (LSV) scans under chopped illumination (AM 1.5) for CuO-400, CuO-500 and CuO-600 photocathodes in 0.01 M MVCl₂/0.05 M sodium phosphate buffer (pH = 7) with continuous N₂ bubbling.

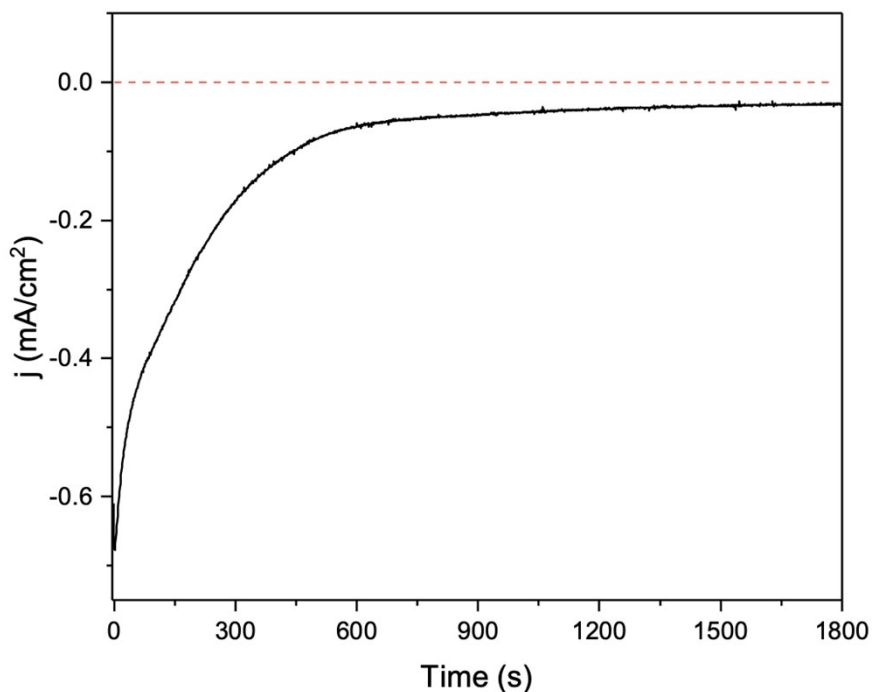


Figure S12. Photocurrent decay curve for CuO-600 thin film under AM 1.5 Illumination at 0.4 V vs. RHE in 0.01 M MVCl₂/ 0.05 M sodium phosphate buffer (pH = 7) with continuous N₂ bubbling.

Table S3. Average film thickness determined by measuring three different spots on the CuO thin films composed of 1, 2, 3, 4, and 5 layers.

Number of layers	1	2	3	4	5
Thickness [nm]	170 ± 20	300 ± 20	380 ± 20	430 ± 20	490 ± 20

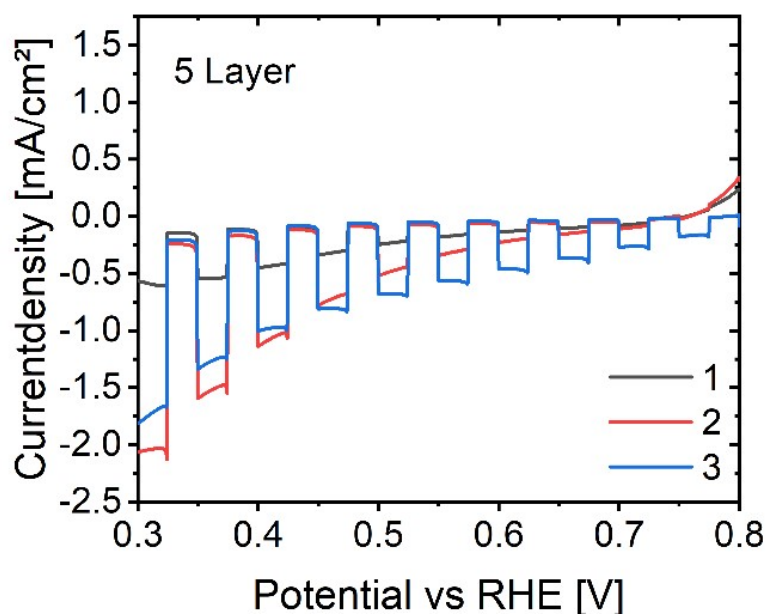


Figure S13. Three consecutive CLV measurements conducted on a five-layered CuO-600 sample.

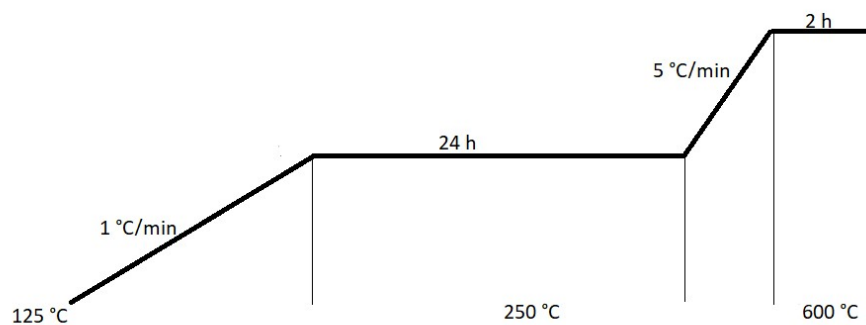


Figure S14. Heating protocol for the preparation of mesoporous CuO thin films calcinated at 600 °C.