Supporting Information for **Direct Photolithographic Pattering of Cuprous Oxide Thin**

Films via Photoelectrodepostion

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Figure S1 - Chronoamperometry measurement of the (photo)electrodeposition of Cu₂O with chopped light at various points during a deposition. The films were grown as described in the main text, under dark conditions or at an intensity of I₀ to a total charge passed of 0.54 C cm⁻². The depositing film maintains this roughly 2:1 light-to-dark current ratio (light on in the yellow periods).



Cu₂O - 1.02μm FTO - 0.7μm **Figure S2** - Cross-sectional SEM micrographs to determine the thickness of 0.54 C cm^{-2} (a) 'dark' Cu₂O thin films electrodeposited (thickness $\approx 1.10 \text{ µm}$) and (b) Cu₂O thin films photoelectrodeposited under I₀ = 1.1×10^{18} photons cm⁻² illumination from a 455 nm LED (thickness $\approx 1.02 \text{ µm}$). Due to the difference in the morphologies of each film (Figure 1), it is not possible to resolve a difference in the growth rate between the two methods.



Figure S3 - Sequence of powder xray diffraction measurements tracking the observable Bragg reflections for Cu₂O thin films as a function of illumination intensity and growth thickness. The orientation of the thin film is consistent for all conditions and thickness, with the Cu_2O (111) (2 θ = 36.6°) and (200) $(2\theta = 42.5^\circ)$ reflections as the most prominent features of the as-grown film. The intensity of each peak scales with the thickness of the deposited film (in proportion to the area-normalized charge passed during the deposition).



Figure S4 - Tauc plot of thin film absorbance from a series of Cu₂O films grown under increasing illumination intensity from a 455nm LED (I₀ = 1.1x10¹⁸ photons cm⁻²). Absorbance (α) was calculated from transmission (%T) and reflectance (%R) spectra and the film thickness (d) from cross-sectional SEM measurements, **[1]** $\alpha(E) = \frac{1}{d} ln(\frac{100\% - \% R}{\% T})$. The linear region of the Tauc plot of ([$\alpha(E)^*E$]² vs. E) for the film grown without illumination was fit to a line (dotted red). The x-intercept of the fit is the direct band gap energy (E_{gap}=2.63 eV) for the as-deposited Cu₂O thin film electrode. The absorbance increases for photon energies below the band gap with increasing illumination during growth.



Figure S5 - Tauc plot of thin film absorbance from a series of Cu₂O films grown under I₀ = 1.1×10^{18} photons cm⁻² from a 455nm LED, then annealed at 280 °C for the specified time. The linear region of the Tauc plot of ([α (E)*E]² vs. E) for the film grown without illumination (dotted black) and to the 225 min annealed sample (dotted orange) was fit to a line to measure the direct band gap of the sample. The annealing process reduced the sub-band gap absorption and reduced the band gap energy (E_{gap}=2.63 eV) in the 225 min annealed film compared to the film grown in the dark without annealing (E_{gap}=2.52 eV).



Figure S6 – The surface reduction of ordinary Cu₂O after the direct use as a photocathode in pH 3 H_2SO_4 . Cu₂O is not a thermodynamically stable phase in aqueous solutions at acidic pH, per the Pourbaix diagram of copper.[2] The highly cathodic photoelectrons act to bias the electrode surface resulting in the unstable thin film to self-reduce to copper metal. This is a different effect than the one observed in the main text, where the deposition occurs at pH 10, stable conditions for Cu₂O. Photoelectrons are generating small nanoparticles of fully reduced copper in the solid Cu₂O phase, but they are distributed throughout the bulk and are stable.

- [1] S. J. Fonash, Solar Cell Device Physics, 2nd ed. (Academic Press, 2010).
- [2] B. Beverskog and I. Puigdomenech, J. Electrochem. Soc., 1997, 144, 3476–3483.