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ELECTRONIC SUPPLEMENTARY INFORMATION

Sol-gel copper chromium delafossite thin films as stable oxide photocathodes for water splitting

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1. **Experimental details**

$CuCrO_2$ thin films were prepared on commercial fluorine-doped tin oxide (FTO) glass substrates by a sol-gel method. According to the literature [32], $Cu(CH_3COO)_2 \cdot H_2O$ (0.002 mol, purity 99.99%+, Aldrich Chem. Co.) and $Cr(NO_3)_3 \cdot 9H_2O$ (0.002 mol, purity 99%, Aldrich Chem. Co.) were dissolved in 8 mL of ethanol, and triethanolamine (0.004 mol, purity 98%, Aldrich Chem. Co.) was added to the solution. This precursor solution was stable indefinitely. It was spin-coated on FTO at 1500 rpm for 15 s. The resulting samples were annealed at 400 ^oC in air for 1 h with a heating rate of 5 ºC/min. Such a deposition procedure was repeated four times. Finally, the samples were post-annealed at 650 ºC in an N_2 atmosphere for 2 h (with a heating rate of 5 ºC/min).

A Bruker D8-Advance X-ray diffractometer operating with Cu-Kα radiation (λ=0.154nm) at 40 kV and 40 mA was used to determine the X-ray diffraction pattern. The grazing incidence operating mode was used with an incidence angle of 0.25^o and a sampled step size of 0.013^o within $2\theta = 10^o - 70^o$. The surface morphology of the films was analyzed using a JEOL JEM-1400 field emission scanning electron microscope (FE-SEM). Photoelectrochemical measurements were performed at room temperature using a three-electrode cell with a fused silica window and a computer-controlled Autolab PGSTAT30 potentiostat. In all the cases, an Ag/AgCl/KCl(sat) electrode and a Pt wire were employed as a reference and as a counter electrode, respectively. Potentials are referred either to the Ag/AgCl/KCl(sat) electrode or to the RHE. Three different working electrolytes were used: 0.1 M $HClO_4$ solution, 0.1 M acetate/acetic acid buffer solution (pH=4.6) and 0.1 M NaOH, all of them prepared with ultrapure water and purged with either N_2 or O_2 before the measurements. Cyclic voltammograms were obtained in the dark at a scan rate of 20 $mV \cdot s^{-1}$. An ozone-free 300 W Xe arc lamp (Thermo Oriel) was employed for electrode illumination (equipped with a water filter). The electrode was illuminated from the electrolyte side (EE illumination). The light intensity was measured by coupling an optical power meter (Thorlabs model PM100D) with a thermopile. The typical value of the light intensity on the sample was 0.65 $W \cdot cm^{-2}$. Illumination was also performed with a solar simulator (Abett, 550 W) at 1 sun (AM 1.5).

2. **UV-vis absorbance spectrum for an FTO/$CuCrO_2$ electrode**

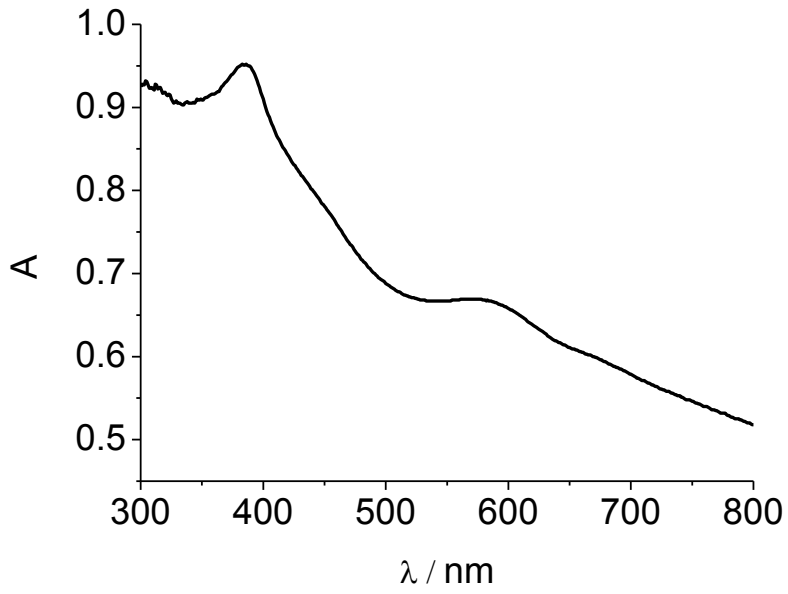

Figure S1. UV-visible absorption spectrum for a $CuCrO_2$ film supported on conducting glass.

3. Additional SEM image for an FTO/$CuCrO_2$ electrode

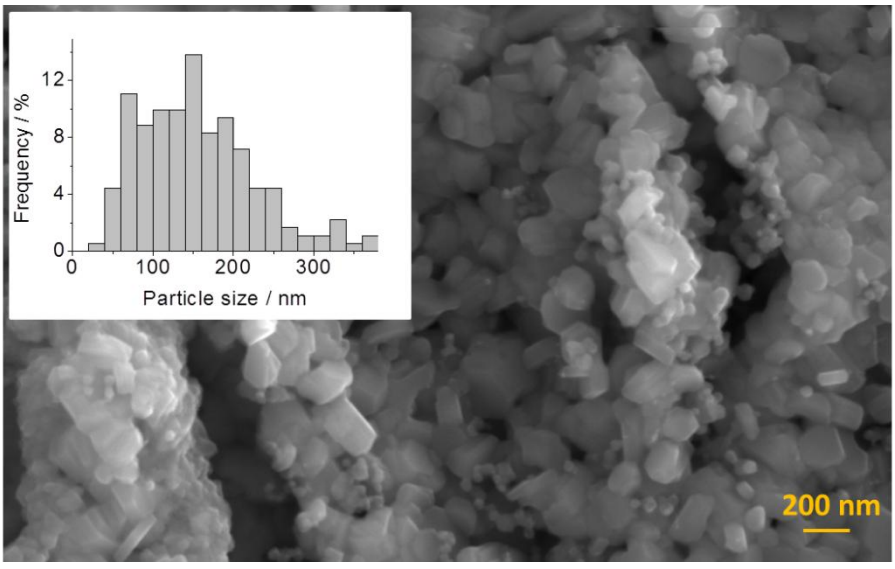

Figure S2. SEM image for a $CuCrO_2$ thin film with a defective region.

4. Linear scan voltammograms under transient illumination and photocurrent transients under 1 sun in 0.1 M $HClO_4$.

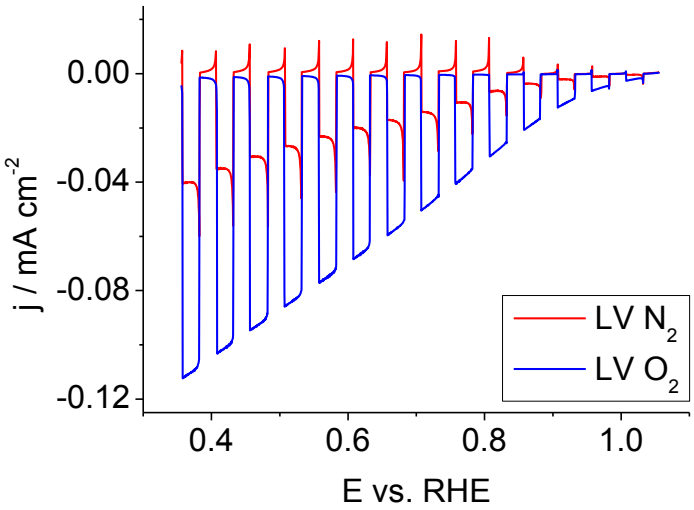

Figure S3. Linear scan voltammograms for a $CuCrO_2$ electrode in 0.1 M $HClO_4$ purged with either N_2 or O_2 under 1 sun illumination. Scan rate: 5 $mV{\cdot}s^{-1}$.

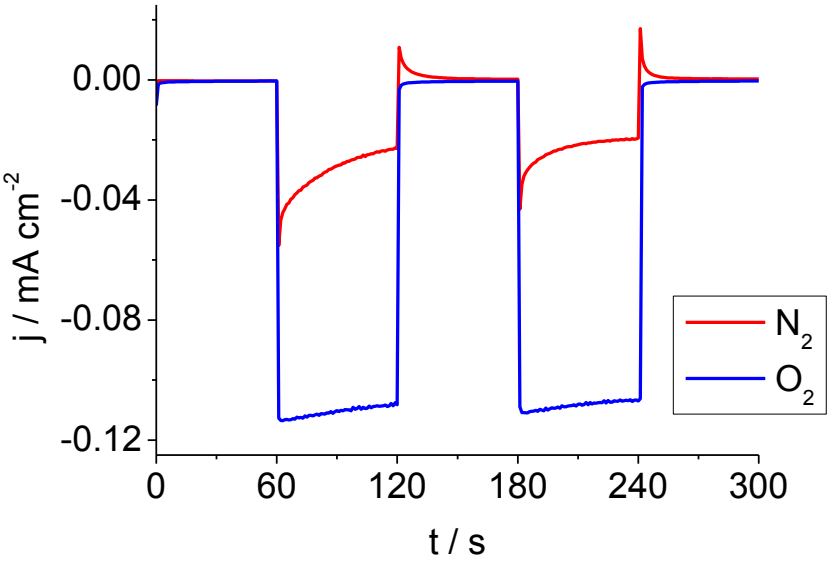

Figure S4. Photocurrent transients under 1 sun illumination for an FTO/$CuCrO_2$ electrode in contact with a 0.1 M $HClO_4$ purged with either N_2 or O_2.

5. **Linear scan voltammograms under transient illumination in 0.1 M NaOH**

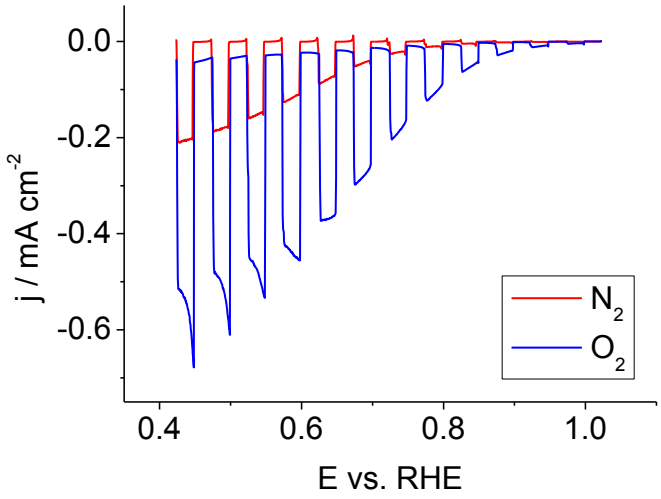

Figure S5. Linear scan voltammograms for a $CuCrO_2$ electrode in 0.1 M NaOH purged with either N_2 or O_2 under transient illumination from an ozone-free Xe arc lamp (0.65 $W \cdot cm^{-2}$). Scan rate: 5 $mV \cdot s^{-1}$.

6. Long-term chronoamperometric experiments under transient illumination in 0.1 M $HClO_4$ and 0.1 M NaOH.

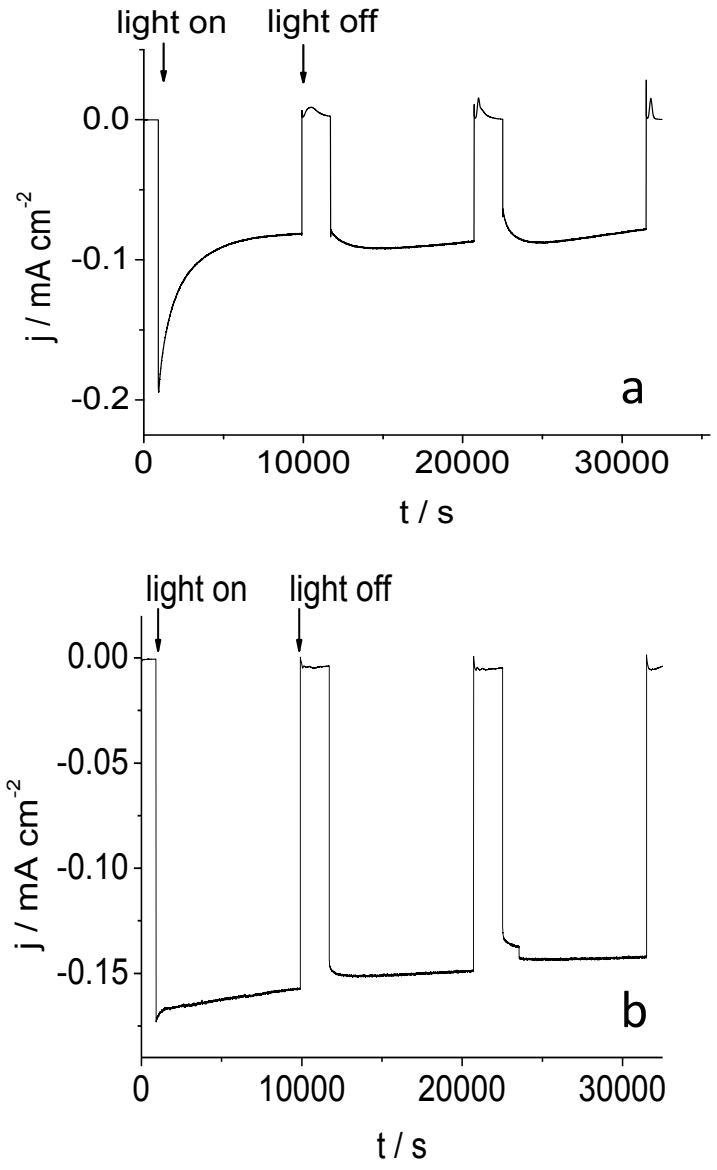

Figure S6. Long-term chronoamperometric experiments under transient illumination for FTO/$CuCrO_2$ electrodes in contact with either (a) N_2-purged 0.1 M $HClO_4$ or (b) N_2-purged 0.1 M NaOH solutions.