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$_3$COO)$_2$·H$_2$O (0.002 mol, purity 99.99%, Aldrich Chem. Co.) and Cr(NO$_3$)$_3$·9H$_2$O (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 °C in air for 1 h with a heating rate of 5 °C/min. Such a deposition procedure was repeated four times. Finally, the samples were post-annealed at 650 °C in an N$_2$ atmosphere for 2 h (with a heating rate of 5 °C/min).

A Bruker D8-Advance X-ray diffractometer operating with Cu-K$\alpha$ radiation ($\lambda$=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° and a sampled step size of 0.013° within 2θ= 10° - 70°. 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·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·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/CuCrO₂ electrode

![UV-vis absorbance spectrum](image)

**Figure S1.** UV-visible absorption spectrum for a CuCrO₂ film supported on conducting glass.

3. Additional SEM image for an FTO/CuCrO₂ electrode

![SEM image with histogram](image)

**Figure S2.** SEM image for a CuCrO₂ thin film with a defective region.
4. Linear scan voltammograms under transient illumination and photocurrent transients under 1 sun in 0.1 M HClO₄.

**Figure S3.** Linear scan voltammograms for a CuCrO₂ electrode in 0.1 M HClO₄ purged with either N₂ or O₂ under 1 sun illumination. Scan rate: 5 mV·s⁻¹.

**Figure S4.** Photocurrent transients under 1 sun illumination for an FTO/CuCrO₂ electrode in contact with a 0.1 M HClO₄ purged with either N₂ or O₂.
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·cm$^{-2}$). Scan rate: 5 mV·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.