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## **Supplementary information**

## Achieving visible light-driven hydrogen evolution at positive bias with a hybrid copper-iron oxide | TiO<sub>2</sub>-cobaloxime photocathode

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## Characterization of CuFe<sub>x</sub>O<sub>y</sub> layers: Equations

The **band-gap energy (Eg)** of the thin films deposited on FTO was calculated from the UV-visible absorbance spectrum (bare FTO spectrum was subtracted) using the relation :

$$\alpha h v \approx A (h v - Eg)^{2}$$

where hv is the photon energy and  $\alpha$  is absorption coefficient given by

 $\alpha = 1/t \ln ((1-R)^2/T)$  or  $\alpha = 2.303*A/t$ 

where t is the sample thickness, R is the reflectance, T is the transmission and A the absorbance<sup>1,2</sup>.

Through a Tauc plot, by plotting  $(\alpha h v)^{1/r}$  versus (h v), we extrapolated the Eg value from the intersection of straight lines drawn from the slope of the curve as shown in **figure 4A**.

The value of r is dependent on the electronic transition type: r=1/2 for direct allowed transition, r=2 for indirect allowed transition, r=3 for direct forbidden transition and r=3/2 indirect forbidden transition.

The **flat band potential** ( $\mathbf{E}_{FB}$ ) was calculated assuming ideal semiconductor behavior and the following relationship,

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r e N_A A^2} \cdot \left( \varphi_A - E_{FB} - \frac{kT}{e} \right)$$

where C is the differential capacitance of the space charge (F/cm<sup>2</sup>),  $\varepsilon_r$  is the relative permittivity or dielectric constant,  $\varepsilon_0$  is the permittivity of free space,  $N_A$  in the acceptor density (m<sup>-3</sup>),  $\phi_A$  is the applied potential and  $E_{FB}$  the flat band potential, the value of the flat band potential is given by the intercepton the potential axis.<sup>3</sup>



**Figure S1**. Determination of the thickness of the  $CuFe_xO_y$  layer structured with F-108 polymer. A  $CuFe_xO_y$  sample was prepared with F-108 polymer added in the sol-gel used for all 5 spin-coating/ annealing cycles; A) Thickness measurements by laser scanning microscope. The thickness of the sample was  $683 \pm 44$  nm; B) Cross section SEM image of the same sample showing homogeneity within the whole film. The thickness of each layer of  $CuFe_xO_y$  structured with F-108 was estimated to  $137 \pm 9$  nm by dividing by 5 the total thickness measured by laser scanning microscopy.



Figure S2. EDX map for CuFe<sub>x</sub>O<sub>yFLAT</sub> sample.



**Figure S3**. RAMAN spectra. The samples 1A, 1B and 1C ( $CuFe_xO_{yFLAT}$ ) are composed of a mixture of hematite, spinel  $CuFe_2O_4$  and delafossite  $CuFeO_2$ . The samples 2A and 2B ( $CuFe_xO_{ySTRUCT}$ ) are composed only of spinel  $CuFe_2O_4$ .



Figure S4. XPS spectra Cu 2p and Fe 2p of (a)CuFe<sub>x</sub>O<sub>ystruct</sub>, (b) CuFe<sub>x</sub>O<sub>ystruct</sub> – CoHEC, (c)CuFe<sub>x</sub>O<sub>ystruct</sub> after CA and (d) CuFe<sub>x</sub>O<sub>ystruct</sub> – CoHEC after CA.



**Figure S5**. Flat band potential determination of  $CuFe_xO_{yFLAT}$  by EIS in 0.2 M phosphate pH 6.7 10 kHz.



**Figure S6.** Open Circuit potential (OCP) CuFe<sub>x</sub>O<sub>yFLAT</sub> layers in 0.2 M phosphate pH 6.7. Arrows indicates when light was on and off (0-4 min dark, 4-10 min light, 10-14 min dark). Under nitrogen.



**Figure S7**. UV-Vis spectrum of  $CuFe_xO_{ySTRUCT}$  (a')  $CuFe_xO_{ySTRUCT}$ -CoHEC (a),  $CuFe_xO_y|TiO_2$  (b') and  $CuFe_xO_y|TiO_2$  -CoHEC (b). In black line is the represented the UV-Vis spectrum of 0.1 mM CoHEC in EtOH.

CuFe <sub>x</sub> O <sub>y</sub>	CuFe <sub>x</sub> O <sub>ySTRUCT</sub> -CoHEC	CuFe <sub>x</sub> O <sub>ySTRUCT</sub> -CoHEC After CA
Co 228.616 Cond 1 x	Co 228.616 Cond 1 x	Co 228.616 Cond 1 x

**Figure S8**. ICP measurements. Band of Cobalt in CuFe<sub>x</sub>O<sub>ySTRUCT</sub> -CoHEC, not present neither after 20 min chronoamperometry at 0.4 V vs RHE nor in CuFe<sub>x</sub>O<sub>ySTRUCT</sub> samples.



**Figure S9**. A) XPS analysis. Co and N bands are shown for  $CuFe_xO_{ySTRUCT}$ -CoHEC,  $CuFe_xO_y|TiO_2 - CoHEC$  and  $CuFe_xO_y$ -CoHEC after 20 min chronoamperometry at 0.4 V vs RHE. The deconvolution of Co 2p3/2 peaks takes into account various transitions and shake-up features previously described;<sup>4</sup> B) XPS survey of  $CuFe_xO_y|TiO_2 - CoHEC$ .



**Figure S10**. LSV of FTO electrode immersed in 0.2 M PB pH 7 in absence (dashed line, a) and presence (straight line, b) of 0.7 mM CoHEC in solution. Insert) molecular structure of CoHEC. Red vertical dashed line indicates the onset potential of the currents. Scan rate 10 mV/s. Measurements under nitrogen.



**Figure S11**. LSV of  $CuFe_xO_{ySTRUCT}$  -CoHEC at 10mV/s in 0.2 M phosphate pH 6.7. 1 sun irradiation (400-780 nm) under nitrogen.



Figure S12. EDX map for CuFe<sub>x</sub>O<sub>yFLAT</sub> sample after CA treatment at 0.4V vs RHE.



**Figure S13**. SEM images of  $CuFe_xO_{yFLAT}$  (a) before and (b) after chronoamperometries at 0.4 V vs RHE during 2 h in 0.2 M phosphate pH 6.7 under light irradiation.

![](_page_10_Figure_0.jpeg)

**Figure S14**. XRD of  $CuFe_xO_{ySTRUCT}$  electrode before (red) and after (green) 20 min chronoamperometry at +0.4 V vs RHE. XRD pattern of FTO in dark blue. All peaks are referenced to delafossite CuFeO<sub>2</sub> ref 04-015-2087 (brown) and spinel CuFe<sub>2</sub>O<sub>4</sub> ref 01-074-8585 (black). Question marks indicates the new peaks appeared in CuFe<sub>x</sub>O<sub>ySTRUCT</sub> after treatment, which are still unknown.

![](_page_10_Figure_2.jpeg)

Figure S15. Ellipsometry measurement to calculate the thickness of the TiO<sub>2</sub> layer deposited by 355 cycles ALD on Si. Three measurements were done in different locations:  $8.33 \pm 0.068$  nm,  $8.36 \pm 0.067$  nm and  $8.32 \pm 0.068$  nm.

![](_page_11_Figure_0.jpeg)

**Figure S16**. XRD of  $CuFe_xO_y|TiO_2$  electrode before (black) and after (pink) 20 min chronoamperometry at +0.4 V vs RHE. XRD pattern of FTO in dark blue and for TiO<sub>2</sub> anatase ref 04-022-3338<sup>5</sup> in red. All peaks are referenced to spinel CuFe<sub>2</sub>O<sub>4</sub> ref 01-074-8585 (black).

![](_page_12_Figure_0.jpeg)

Figure S17. EDX map for CuFe<sub>x</sub>O<sub>y</sub>|TiO<sub>2</sub>.

![](_page_13_Figure_0.jpeg)

**Figure S18**. LSV of  $CuFe_xO_y|TiO_2$  electrode immersed in 0.2 M PB pH 7 and irradiated with chopped light (1sun, 400-780nm). Red vertical dashed line indicates the onset potential of the photocurrents. Scan rate 10 mV/s. Measurements under nitrogen.

![](_page_13_Figure_2.jpeg)

**Figure S19**. Tauc plot for indirect bandgap of  $CuFe_xO_y|TiO_2$  (blue, a) and  $CuFe_xO_y|TiO_2$  -CoHEC (black, b).

![](_page_14_Figure_0.jpeg)

**Figure S20.** Chronoamperometry at 0.3 V vs RHE on  $CuFe_xO_{ySTRUCT}$  (red, a) and  $CuFe_xO_{ySTRUCT}$  - CoHEC (blue, b) under illumination (400-780nm, 100 mW/cm<sup>2</sup>), 0.2 M phosphate buffer pH 6.7, under nitrogen. Dark currents have been substracted.

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