# Supporting Information

# Inverse-opal $CuCrO_2$ photocathodes for $H_2$ production using organic dyes and a molecular Ni catalyst

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**Table S1**. Dye properties determined using UV-Vis spectroscopy, fluorescence spectroscopy, and cyclic voltammetry.[1–3]

| Dye | $\lambda_{max}$ (nm) | $\varepsilon$ ($M^{-1}$ $cm^{-1}$) | $E_{00}$ (eV) | $E_{S^*/S^-}$ (V *vs.* RHE) | $E_{S/S^-}$ (V *vs.* RHE) |
|---|---|---|---|---|---|
| **PMI-P** | 536 | $3.8 \times 10^4$ | 2.20 | 1.47 | −0.73 |
| **DPP-P** | 496 | $2.6 \times 10^4$ | 2.27 | 1.57 | −0.70 |

**Table S2.** Quantities of dye and catalyst loaded on the photocathodes.

| Photocathode | Dye Loading (nmol $cm^{-2}$) | **NiP** Loading (nmol $cm^{-2}$) Pre-catalysis | **NiP** Loading (nmol $cm^{-2}$) Post-catalysis[a] |
|---|---|---|---|
| IO-$CuCrO_2$\|**PMI-P/NiP** | 11.4 ± 1.8 | 4.5 ± 0.9 | 3.9 ± 1.5 |
| IO-$CuCrO_2$\|**DPP-P/NiP** | 14.8 ± 1.6 | 4.5 ± 0.4 | 3.3 ± 1.1 |
| Sol-Gel $CuCrO_2$\|**DPP-P/NiP**[b] | 2.6 ± 0.7 | 0.8 ± 0.4 | 0.4 ± 0.3 |

[a] Conditions for catalysis: Visible light illumination (100 mW $cm^{-2}$, AM 1.5G, $\lambda$ > 420 nm) for 2 h with the cell maintained at 25 °C, applied potential of 0.0 V *vs.* RHE, aqueous $Na_2SO_4$ (0.1 M, pH 3). [b] Taken from previous report.[1]

## Supporting Figures

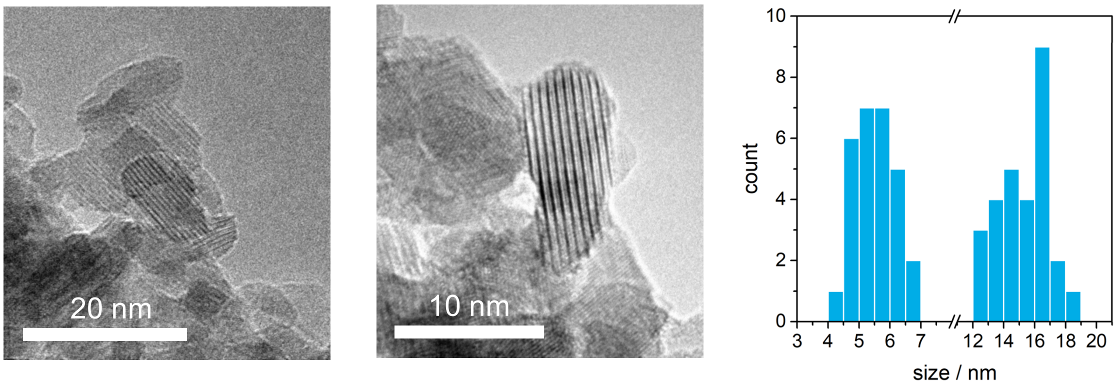



**Figure S1.** TEM images of as-prepared $CuCrO_2$ nanoparticles with measured diameter and length distribution.

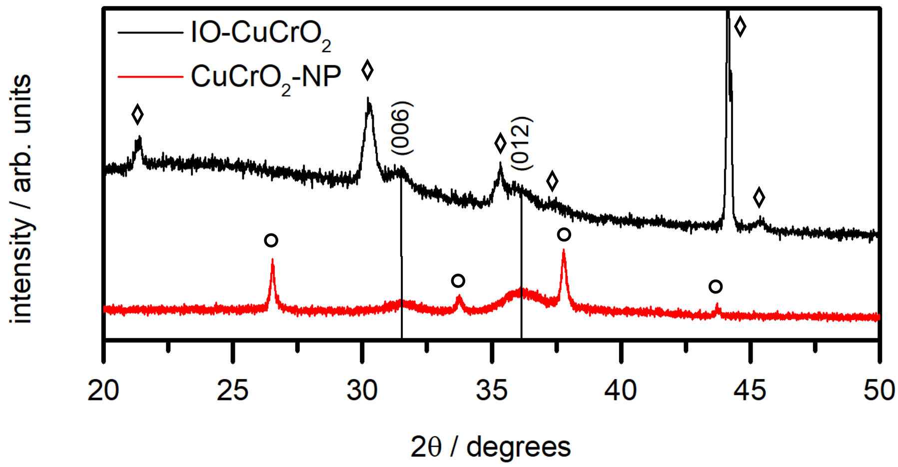



**Figure S2**. XRD patterns of $CuCrO_2$-NPs and IO-$CuCrO_2$ films. Diamonds represent ITO-glass background and circles the $SiO_2$ reference.

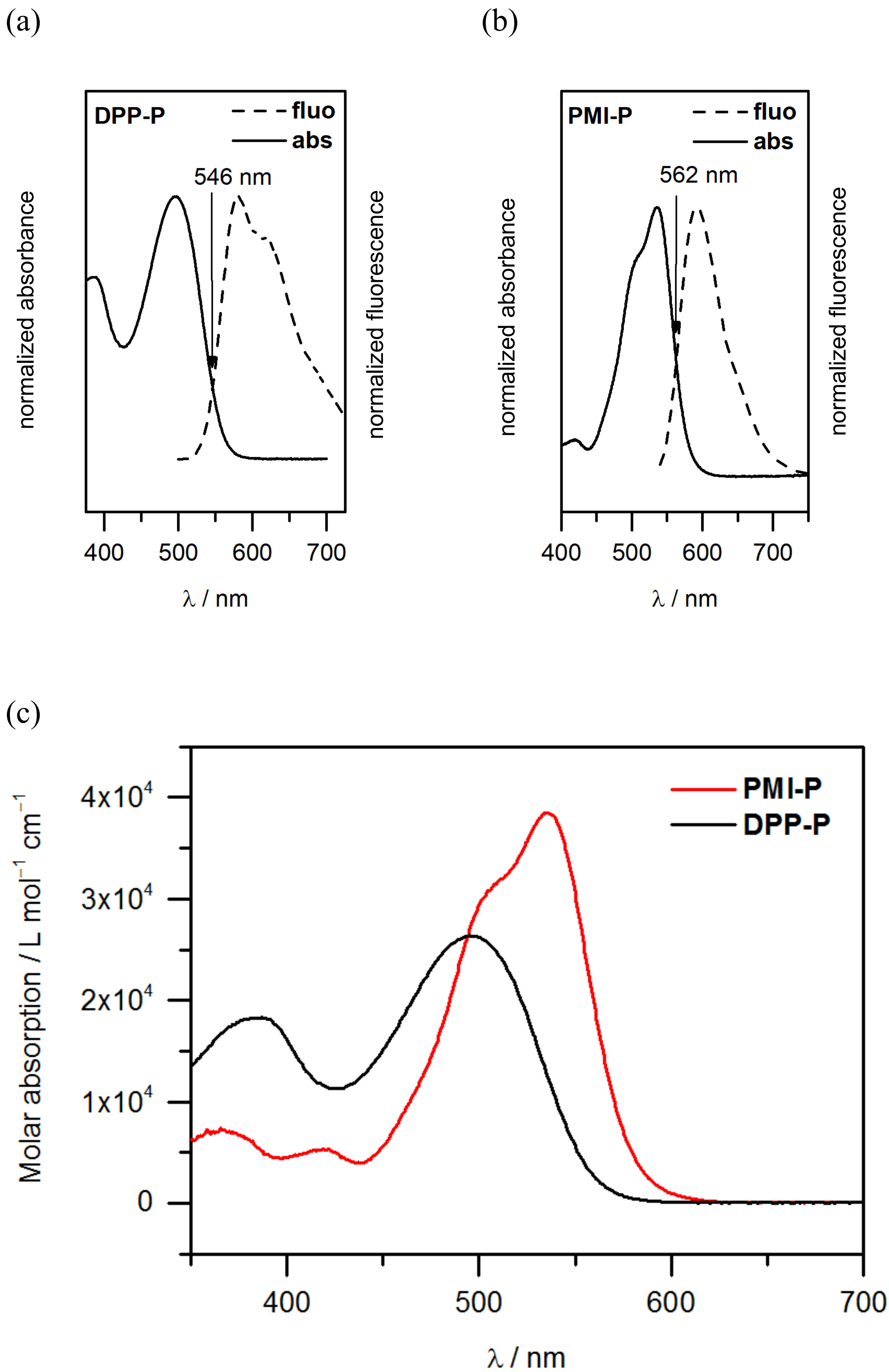
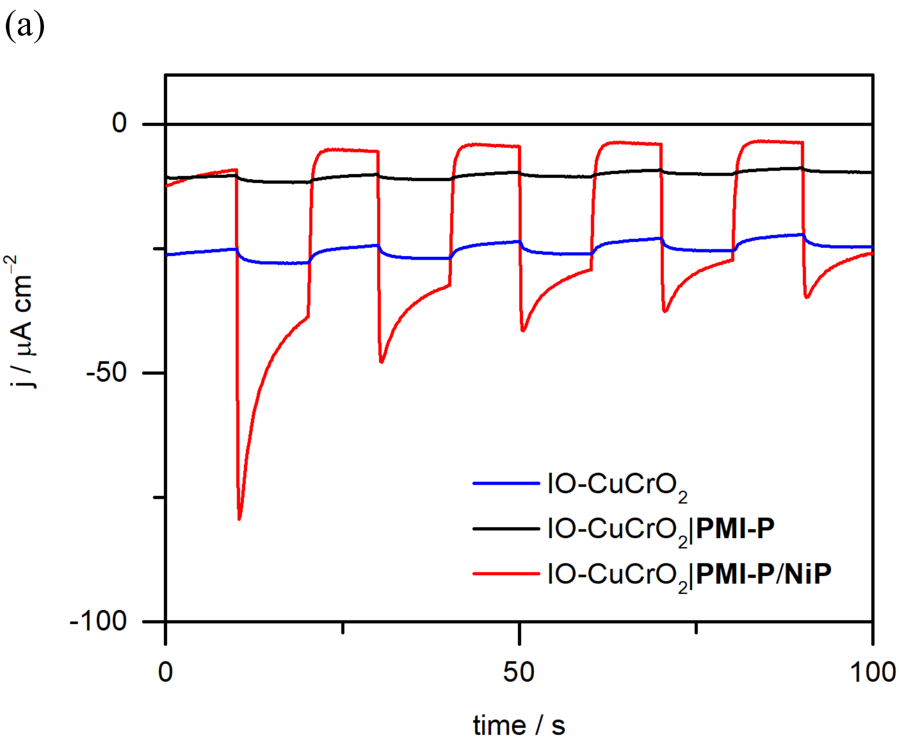



**Figure S3**. Normalized absorption and emission spectra of (a) **PMI-P** and (b) **DPP-P** in DMF, (c) UV-Vis spectra of **PMI-P** (red) and **DPP-P** (black) recorded in DMF.[2,4]



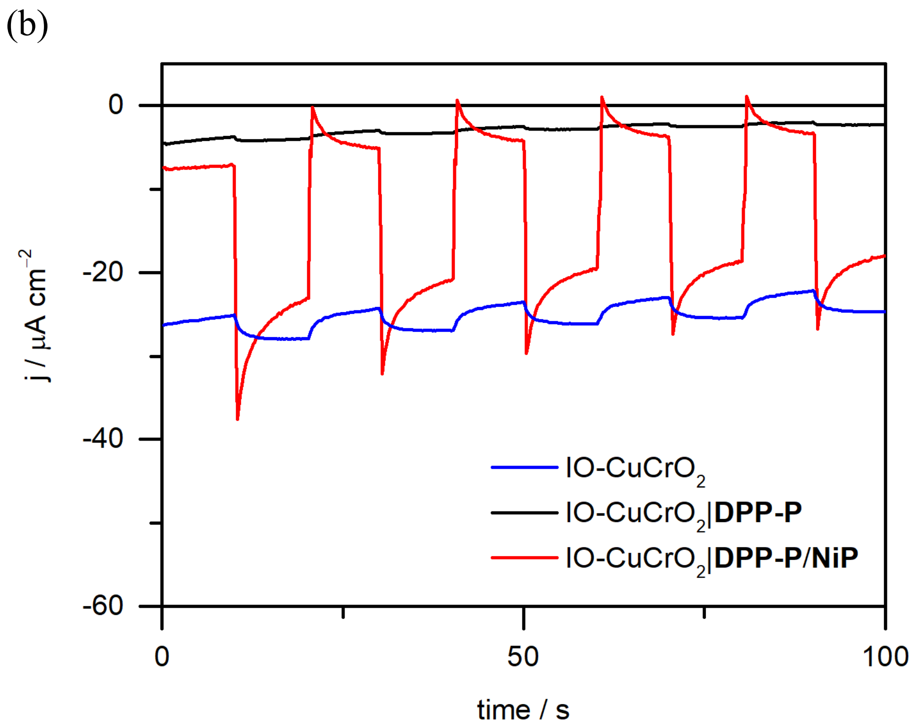




**Figure S4.** Chronoamperometry results at 0.0 V *vs.* RHE under chopped light illumination upon loading of separate components for (a) IO-$CuCrO_2$|**PMI-P**/**NiP** and (b) IO-$CuCrO_2$|**DPP-P**/**NiP** photocathodes. Conditions: aqueous $Na_2SO_4$ (0.1 M, pH 3), chopped visible light illumination (100 mW $cm^{-2}$, AM 1.5G, $\lambda > 420$ nm). A geometric electrode area of 0.25 $cm^2$ was used for all experiments.

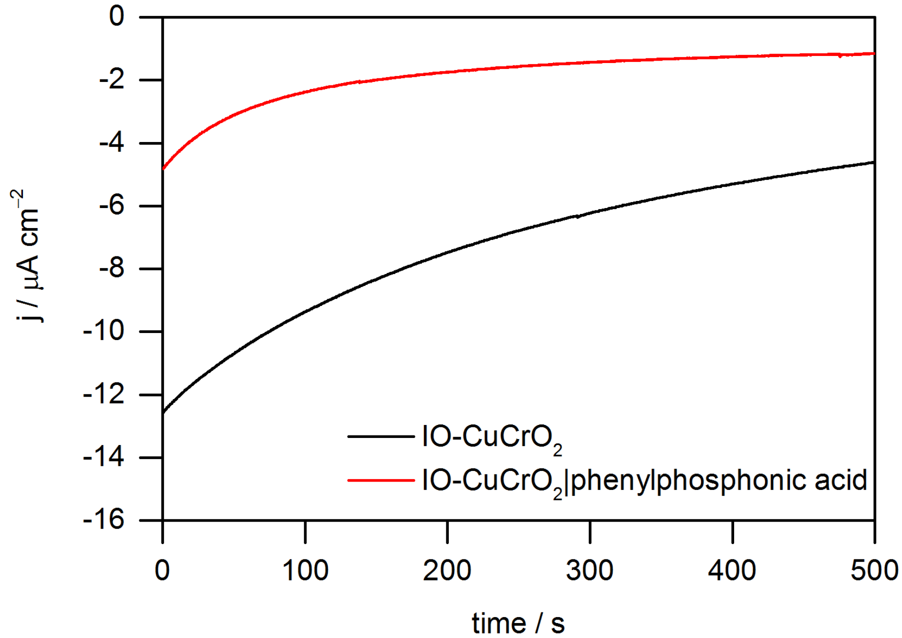



**Figure S5.** Chronoamperometry at 0.0 V *vs.* RHE in the dark for IO-$CuCrO_2$ and IO-$CuCrO_2$|phenylphosphonic acid electrodes. Conditions: aqueous $Na_2SO_4$ (0.1 M, pH 3). A geometric electrode area of 0.25 $cm^2$ was used.

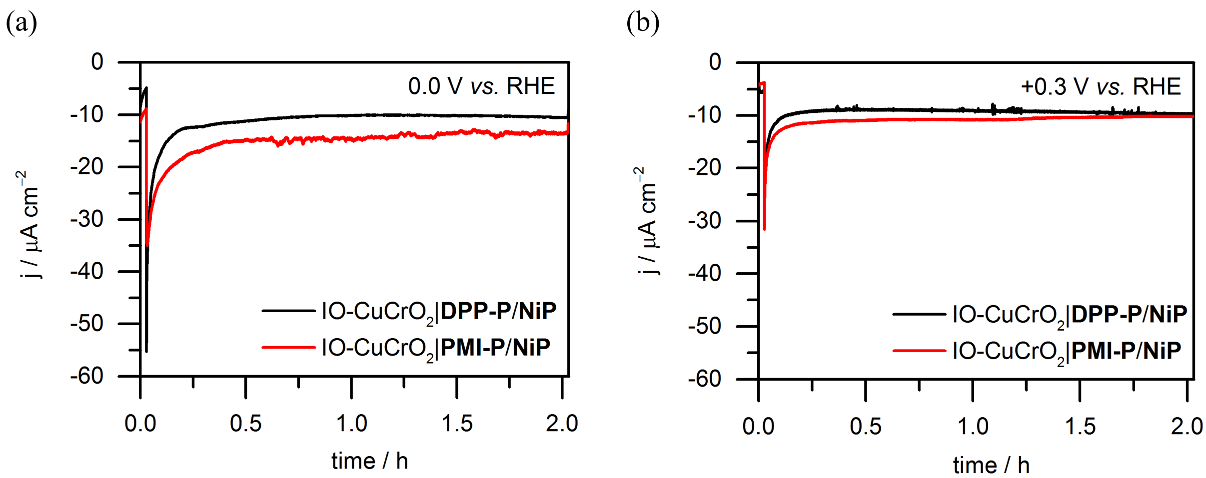



**Figure S6.** Controlled potential photoelectrolysis at (a) 0.0 V *vs.* RHE and (b) + 0.3 V *vs.* RHE under constant light illumination for IO-$CuCrO_2$|**PMI-P**/**NiP** (red) and IO-$CuCrO_2$|**DPP-P**/**NiP** (black) photocathodes. Conditions: aqueous $Na_2SO_4$ (0.1 M, pH 3), illumination (100 mW $cm^{-2}$, AM 1.5G, $\lambda >$ 420 nm). A geometric electrode area of 0.25 $cm^2$ was used for all experiments.

## Supporting References


(1) Creissen, C. E.; Warnan, J.; Reisner, E. Solar $H_2$ Generation in Water with a $CuCrO_2$ Photocathode Modified with an Organic Dye and Molecular Ni Catalyst. *Chem. Sci.* **2018**, *9*, 1439–1447.

(2) Warnan, J.; Willkomm, J.; Farre, Y.; Pellegrin, Y.; Boujtita, M.; Odobel, F.; Reisner, E. Solar Electricity and Fuel Production with Perylene Monoimide Dye-Sensitised $TiO_2$ in Water. *Chem. Sci.* **2019**, *10*, 2758–2766.

(3) Farré, Y.; Maschietto, F.; Föhlinger, J.; Wykes, M.; Planchat, A.; Pellegrin, Y.; Blart, E.; Ciofini, I.; Hammarström, L.; Odobel, F. Manuscript in Preparation.

(4) Warnan, J.; Willkomm, J.; Ng, J. N.; Godin, R.; Prantl, S.; Durrant, J. R.; Reisner, E. Solar $H_2$ Evolution in Water with Modified Diketopyrrolopyrrole Dyes Immobilised on Molecular Co and Ni Catalyst–$TiO_2$ Hybrids. *Chem. Sci.* **2017**, *8*, 3070–3079.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