Inverse Opal CuCrO$_2$ Photocathodes for H$_2$ Production Using Organic Dyes and a Molecular Ni Catalyst

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INTRODUCTION

Solar conversion of water into chemical energy carriers offers a sustainable alternative to fossil fuels. Dye-sensitized photoelectrochemical (DSPEC) cells are an emerging approach to producing solar fuels. The recent development of delafossite CuCrO$_2$ as a p-type semiconductor has enabled H$_2$ generation through the coassembly of catalyst and dye components. Here, we present a CuCrO$_2$ electrode based on a high-surface-area inverse opal (IO) architecture with benchmark performance in DSPEC H$_2$ generation. Coimmobilization of a phosphonated diketopyrrolopyrrole (DPP-P) or perylene monoimide (PMI-P) dye with a phosphonated molecular Ni catalyst (NiP) demonstrates the ability of IO-CuCrO$_2$ to photogenerate H$_2$. A positive photocurrent onset potential of approximately +0.8 V vs RHE was achieved with these photocathodes. The DPP-P-based photoelectrodes delivered photocurrents of $-18 \mu$A cm$^{-2}$ and generated 160 ± 24 nmol of H$_2$ cm$^{-2}$, whereas the PMI-P-based photocathodes displayed higher photocurrents of $-25 \mu$A cm$^{-2}$ and produced 215 ± 10 nmol of H$_2$ cm$^{-2}$ at 0.0 V vs RHE over the course of 2 h under visible light illumination (100 mW cm$^{-2}$, AM 1.5G, $\lambda > 420$ nm, 25°C). The high performance of the PMI-constructed system is attributed to the well-suited molecular structure and photophysical properties for p-type sensitization. These precious-metal-free photocathodes highlight the benefits of using bespoke IO-CuCrO$_2$ electrodes as well as the important role of the molecular dye structure in DSPEC fuel synthesis.

KEYWORDS: dye-sensitized, molecular catalyst, photocatalysis, solar fuels, p-type semiconductor, delafossite

ABSTRACT: Dye-sensitized photoelectrochemical (DSPEC) cells are an emerging approach to producing solar fuels. The recent development of delafossite CuCrO$_2$ as a p-type semiconductor has enabled H$_2$ generation through the coassembly of catalyst and dye components. Here, we present a CuCrO$_2$ electrode based on a high-surface-area inverse opal (IO) architecture with benchmark performance in DSPEC H$_2$ generation. Coimmobilization of a phosphonated diketopyrrolopyrrole (DPP-P) or perylene monoimide (PMI-P) dye with a phosphonated molecular Ni catalyst (NiP) demonstrates the ability of IO-CuCrO$_2$ to photogenerate H$_2$. A positive photocurrent onset potential of approximately +0.8 V vs RHE was achieved with these photocathodes. The DPP-P-based photoelectrodes delivered photocurrents of $-18 \mu$A cm$^{-2}$ and generated 160 ± 24 nmol of H$_2$ cm$^{-2}$, whereas the PMI-P-based photocathodes displayed higher photocurrents of $-25 \mu$A cm$^{-2}$ and produced 215 ± 10 nmol of H$_2$ cm$^{-2}$ at 0.0 V vs RHE over the course of 2 h under visible light illumination (100 mW cm$^{-2}$, AM 1.5G, $\lambda > 420$ nm, 25°C). The high performance of the PMI-constructed system is attributed to the well-suited molecular structure and photophysical properties for p-type sensitization. These precious-metal-free photocathodes highlight the benefits of using bespoke IO-CuCrO$_2$ electrodes as well as the important role of the molecular dye structure in DSPEC fuel synthesis.

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INTRODUCTION

Solar conversion of water into chemical energy carriers offers a sustainable alternative to fossil fuels. Dye-sensitized photoelectrochemical (DSPEC) cells are a promising technology for solar water splitting due to their flexibility, ease of modification, and assembly. In these systems, semiconductor-immobilized molecular dyes harvest solar light and transfer charge to a catalytic site, facilitating the synthesis of solar fuels. Significant progress with dye-sensitized photocathodes (DSPCs) and photoanodes has been made possible through a deeper understanding of charge transfer processes and performance-limiting recombination routes. Although efficiency has improved in recent years, DSPCs still suffer from low photocurrents and poor catalytic activity, representing a bottleneck in state of the art DSPEC devices.

In DSPCs, light absorption by the dye is typically followed by hole injection into the semiconductor, creating a reduced dye that can transfer an electron to the coimmobilized catalyst. The steady-state photocurrent is representative of the kinetic interplay between productive charge transfer and detrimental recombination pathways. Therefore, higher photocurrents can be achieved by blocking the dominant recombination mechanisms between holes in the p-type semiconductor and (1) the reduced dye (geminate recombination) or (2) the reduced catalyst. Methods to minimize catalyst recombination in DSPCs through layer-by-layer assemblies and molecular dye–catalyst dyad complexes have shown some success, but the photocatalytic activity is still limited. Modular assembly through a coimmobilization route is generally preferred, as it provides flexibility in the construction of the electrode, avoiding complex synthetic modification and permitting the use of already established molecular species. The undesirable geminate recombination pathway can be rationally addressed through engineering of the dye structure. Charge transfer from an immobilized dye to a semiconductor is highly dependent on the spatial separation. Consequently, localizing charge...
density in the photoreduced dye (i.e., the ground state LUMO) away from the semiconductor surface reduces charge recombination kinetics. Such strategies have proven beneficial in p-type dye-sensitized solar cells (p-DSSCs) to effectively increase the photocurrent and photovoltage.\textsuperscript{16,44,45} In particular, organic dyes have proven to be proficient rivals to conventional precious-metal dyes, commonly displaying favorable qualities for p-type sensitization such as high extinction coefficients and internal acceptor units.\textsuperscript{16,46–48} The two dyes used in this study are based on diketopyrrolopyrrole (DPP) and perylene monomide (PMI) chromophores, both of which exhibit beneficial characteristics for incorporation in DSPCs.

Nonetheless, the key component in both recombination routes is the semiconductor. NiO is currently the dominant wide-bandgap p-type semiconductor in DSPCs owing to its simple preparation using solution-based techniques.\textsuperscript{26,49} However, problems associated with the high density of traps and low hole mobility have been identified,\textsuperscript{53–55} which account for the scarcity of reports of H\textsubscript{2} generation with coimmobilized dye and catalyst components.\textsuperscript{20,21,38,56–59} Improved DSPCs can be realized through the development of alternative wide-bandgap p-type semiconductors. Delafossite structures are suitable candidates due to their solution processability, high hole mobility, and metal oxide character.\textsuperscript{60–63} CuGaO\textsubscript{2} and CuCrO\textsubscript{2} have been employed in DSPCs, both enabling an early photocurrent onset due to their highly anodic valence band positions.\textsuperscript{32,64–66} In particular, CuCrO\textsubscript{2} formed using a sol–gel method was able to generate H\textsubscript{2} in a coimmobilized molecular dye/catalyst assembly.\textsuperscript{67} The DSPC outperformed an analogous NiO-based photocathode, but low dye and catalyst loadings limited product generation. This issue can in principle be addressed through development of meso- and macroporous architectures such as inverse opal (IO) structures, which has previously proven effective for the incorporation of dye and catalyst components on metal oxides.\textsuperscript{27,28,67–75} Here, IO-CuCrO\textsubscript{2} electrodes are reported through a bottom-up templating method using organic microsphere templates and delafossite CuCrO\textsubscript{2} particles. Two organic dyes (DPP-P\textsuperscript{76} and PMI-P,\textsuperscript{77} Figure 1) were explored in this study and coimmobilized with a DuBois-type molecular Ni catalyst\textsuperscript{78–82} (NiP, Figure 1). Photoelectrochemical (PEC) H\textsubscript{2} generation was used to demonstrate the influence of the novel CuCrO\textsubscript{2} morphology and dye structure on performance.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of IO-CuCrO\textsubscript{2} Electrodes.** IO-CuCrO\textsubscript{2} electrodes were constructed using a bottom-up templating method using mixtures of preformed CuCrO\textsubscript{2} nanoparticles (NPs) with polystyrene (PS) beads (750 nm diameter). CuCrO\textsubscript{2}-NPs were synthesized using a modified hydrothermal synthesis procedure.\textsuperscript{53} In brief, Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (6.25 mmol) and Cr(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O (6.25 mmol) were stirred in Milli-Q H\textsubscript{2}O (70 mL) and NaOH (5 g) was added. The resulting alkaline solution was placed in a PTFE-lined autoclave and heated to 240 °C for 60 h. The NPs were washed consecutively with dilute HCl and EtOH three times and then dried in vacuo. Transmission electron microscopy (TEM) analysis showed that crystalline particles of approximately 15 nm in length and 5 nm in diameter were obtained (Figure S1) with a Brunauer–Emmett–Teller (BET) surface area of 86 m\textsuperscript{2} g\textsuperscript{−1}. Powder X-ray diffraction (XRD) analysis confirmed the 3R delafossite structure (Figure S2).

The CuCrO\textsubscript{2}-NPs were dispersed in a 4/1 H\textsubscript{2}O:MeOH mixture by sonication. The PS beads were washed with MeOH, and a portion of the CuCrO\textsubscript{2}-NP mixture was added. The dispersion was sonicated and drop-cast on precleaned ITO-coated glass confined to a circular area with Parafilm and left to dry under ambient conditions. The Parafilm was removed, and the PS template was dissolved in toluene. The films were subsequently washed with acetone and dried before being sintered at 500 °C for 1 h under argon. Scanning electron microscopy (SEM) analysis showed that the IO-CuCrO\textsubscript{2} films were approximately 2 μm thick with macropores roughly 600–700 nm in diameter (Figure 2a,b). XRD patterns of the IO-CuCrO\textsubscript{2} films displayed peaks consistent with the 3R delafossite polytype (Figure S2).

**Dye and Catalyst Properties.** DPP-P\textsuperscript{76} and PMI-P,\textsuperscript{77} and NiP\textsuperscript{86} were synthesized as previously reported. The phosphonic acid anchoring groups facilitate immobilization on metal oxide surfaces, and both dyes have previously been employed in colloidal dye-sensitized photocatalysis systems with TiO\textsubscript{2}-NPs and NiP using sacrificial reagents.\textsuperscript{76,77,81} DPP-P was previously shown to be an effective dye in a CuCrO\textsubscript{2} photocathode with NiP and is therefore a suitable choice for comparative purposes in this study.\textsuperscript{64} PMI dyes are renowned for their high stability and intense visible light absorption.\textsuperscript{35} PMI-based photocathodes have been established with heterogeneous catalysts\textsuperscript{85} and with molecular catalysts in solution,\textsuperscript{86} but no examples with an immobilized molecular catalyst currently exist.

The two dyes exhibit similar electrochemical properties in solution (Table S1). Importantly, both dye anions exhibit sufficient thermodynamic driving force (\(E_{\text{Fe/dye}} \approx -0.7\) V vs RHE) to reduce NiP to a catalytically active state (\(E_{\text{NiP,onset}} = -0.21\) V vs RHE).\textsuperscript{78} Hole injection into the valence band of CuCrO\textsubscript{2} (\(E_h \approx +1.0\) V vs RHE) is facilitated by the highly anodic excited state reduction potentials (\(E_{\text{DPP-P*/DPP-P}} = +1.57\) V vs RHE and \(E_{\text{PMI-P*/PMI-P}} = +1.47\) V vs RHE).\textsuperscript{64,87} PMI-P displays a broad and intense absorption signal from 450

\[ \text{NiP} \rightarrow \text{Ni}^{2+} + 2e^- \]

\[ \text{DPP-P} \rightarrow \text{DPP-P}^- + e^- \]

\[ \text{PMI-P} \rightarrow \text{PMI-P}^- + e^- \]
DMF and then H2O. The resulting IO-CuCrO2 electrodes were soaked in a solution of the dye followed by the catalyst. IO-CuCrO2 electrodes were dried under N2 and then immersed in a NiP solution (1 mM, MeOH, 3 h) under a N2 atmosphere to form IO-CuCrO2/NiP electrodes (see the Experimental Section for details).

Photocathode Assembly. Photocathodes were constructed through sequential anchoring of the dye followed by the catalyst. IO-CuCrO2 electrodes were soaked in a solution of PMI-P or DPP-P (0.2 mM, DMF, 15 h) before rinsing with DMF and then H2O. The resulting IO-CuCrO2 dye electrodes were dried under N2 and then immersed in a NiP solution (1 mM, MeOH, 3 h) under a N2 atmosphere to form IO-CuCrO2 dye/NiP electrodes (see the Experimental Section for details).

The color of the IO-CuCrO2 electrodes changed from light green to red or orange for the PMI-P- or DPP-P-sensitized electrodes, respectively (Figure 2c). UV−vis spectra of the films showed the characteristic visible light absorption profiles of the dyes. IO-CuCrO2|PMI-P electrodes displayed higher intensity for the peak at 536 nm than at 536 nm as opposed to the solution-based experiments—this could be attributed to the underlying absorption of CuCrO2 or to the presence of aggregates (Figure 2d).

The loading of each dye was quantified following desorption in basic solution by electronic absorption spectrophotometry, and the amount of catalyst was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Table S2). The high-surface-area IO-CuCrO2 electrodes loaded approximately 20 nmol cm−2 of the combined molecular species with a dye/catalyst ratio of approximately 3/1. The loading corresponds to a 5-fold increase over the previously reported sol−gel CuCrO2 electrodes (loading approximately 4 nmol cm−2).

Photoelectrochemical H2 Generation. PEC analysis was conducted in aqueous Na2SO4 solution (0.1 M, pH 3) under chopped visible light illumination (100 mW cm−2, AM 1.5G, λ > 420 nm). Mildly acidic conditions are optimal for the catalytic H2 generation performance of NiP. Linear sweep voltammograms (LSVs) showed that cathodic photocurrents were obtained for IO-CuCrO2/DPP-P/NiP and IO-CuCrO2/PMI-P/NiP electrodes with an onset potential of approximately +0.8 V vs RHE (Figure 3a). Chronoamperometry analysis conducted at 0.0 V vs RHE displayed higher photocurrents for the PMI-P photocathodes (j ≈−25 μA cm−2) than the corresponding DPP-P electrodes (j ≈−18 μA cm−2) (Figure 3b). The enhancement can be assigned to the red-shifted, more intense, and broader absorption profile of the PMI dye.

Transient photocurrent spikes were observed for both photocathodes, which are representative of charge accumulation at the semiconductor/electrolyte solution interface. Previous systems have also associated such spikes with recombination, but the exact origin is not easily identifiable because both dominant recombination routes can contribute to the effect. In this study, the PMI-P-based photocathodes generate the highest cathodic spikes, suggesting substantial charge accumulation at the interface. Kinetic modeling could provide further insight into the exact mechanism and has been successfully applied in similar systems but is beyond the scope of the current study.

All electrodes displayed a dark current previously assigned to a CuII/I redox couple and associated oxygen intercalation in LSVs. Interestingly, the dark current decreased upon immobilization of the individual dye and catalyst components.

Figure 2. (a) Top-down and (b) cross-sectional SEM images of IO-CuCrO2 electrodes. (c) Photographs and (d) diffuse reflectance UV−vis spectra of the dye- and catalyst-loaded electrodes.

Figure 3. (a) LSVs and (b) chronoamperometry analysis of IO-CuCrO2 electrodes at 0.0 V vs RHE. (c) IPCE plots of IO-CuCrO2 electrodes at +0.3 V vs RHE with monochromatic light intensity maintained at 0.8 mW cm−2. Conditions (a−c): aqueous Na2SO4 (0.1 M, pH 3), chopped visible light illumination (100 mW cm−2, AM 1.5G, λ > 420 nm), scan rate 5 mV s−1 for voltammograms, 25 °C cell temperature maintained. A geometric electrode area of 0.25 cm2 was used for all experiments.

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CuCrO$_2$/DPP-P/NiP photocathodes preserved only 50% of the catalyst, suggesting that the immobilized NiP is stabilized against desorption by the IO-CuCrO$_2$ structures.

**Comparison with State of the Art.** The photocathodes presented here display high activities for coimmobilized molecular DSPCs. Incorporation of a coumarin 343 dye coimmobilized with a bimetallic iron-based catalyst on NiO generated photocurrents of $\sim$10 $\mu$A cm$^{-2}$ at $+0.16$ V vs RHE with a FE of 50% but was extremely short lived due to degradation of the catalyst with a final TON $\leq$ 3.$^{37}$ A cobalt diimine-dioxime system featuring a coanchored push–pull dye on NiO generated photocurrents of $\sim$7.5 $\mu$A cm$^{-2}$ at $+0.14$ V vs RHE, producing H$_2$ with an FE of 10%.$^{38}$ Immobilization of the same push–pull dye with a cobaloxime catalyst on CuGaO$_2$ boosted H$_2$ generation, increasing the FE to 74%; this further stresses the importance of altering the semiconductor unit in DSPCs.$^{66}$ The high photocurrents, FEs, and TONs of the PMI-P ($\sim$25 $\mu$A cm$^{-2}$, FE = 41%, TON = 48) and DPP-P ($\sim$18 $\mu$A cm$^{-2}$, FE = 40%, TON = 36) photocathodes presented here highlight the benefits of using CuCrO$_2$. Furthermore, the first example of a PMI-sensitized DSPC with an immobilized molecular catalyst is presented. The high performance of the PMI system directs research toward modification of similar chromophores that benefit from high extinction coefficients and favorable structural properties for sensitization of p-type semiconductors.

NiP has previously been incorporated as the catalyst in DSPCs. Layer-by-layer assembly of a phosphonated Ru-polypyriddylic dye and NiP on NiO using a Zr$^{IV}$ linker facilitated H$_2$ generation but with low activity.$^{26}$ Incorporation of a donor–dye–catalyst assembly with a Ru-based dye reported photocurrents of $\sim$56 $\mu$A cm$^{-2}$ at $+0.05$ V vs RHE with a TON of $\sim$16 and an FE of 53%.$^{27}$ A subsequent trilayered NiO/ITO assembly without the donor assembly enhanced the FE to 90%.$^{28}$ The PMI and DPP photocathodes in the current study avoid precious-metal components but retain high activity. Although not as efficient as the best Ru-dye NiP-based examples, they are competitive despite the simple coimmobilization strategy. Layer-by-layer assemblies using organic dyes with CuCrO$_2$ could further reduce catalyst recombination to enhance activity in future studies.

The benefits of modifying NiO through doping and defect passivation/elimination has been outlined in previous reports.$^{26,27,28}$ Similar improvements to CuCrO$_2$ electrodes are expected to result in enhanced performance. Here, the development of our previous CuCrO$_2$ system through altering the semiconductor morphology increased photocurrents and product yields. The amount of H$_2$ generated is 70% higher with the IO-CuCrO$_2$ electrodes, the enhanced performance being assigned to higher molecular loadings (500% increase) of dye and catalyst in the extended IO network. The sustained photocurrent of the IO-CuCrO$_2$ photocathode is approximately twice that of the previous CuCrO$_2$ system; however, the lower TON achieved is likely due to a significant amount of each species that is grafted on the electrode but does not contribute to catalysis. Significant light scattering/absorption of the IO films is another likely cause, where light harvesting from dye molecules buried within the film is highly limited. The issue could be addressed through pore size modification and thickness control to rationally tailor the IO network for a specific dye/catalyst combination without significantly reducing the molecular loading. Similar approaches to increase the

Table 1. PEC H$_2$ Generation with Corresponding TON$_{NiP}$ and FE for IO-CuCrO$_2$/PMI-P/NiP and IO-CuCrO$_2$/DPP-P/NiP Photocathodes at Different Applied Potentials over the Course of 2 h

| Electrode | H$_2$ (nmol cm$^{-2}$) | TON$_{NiP}$ | FE (%) |
|-----------|----------------------|-------------|--------|
| IO-CuCrO$_2$/PMI-P/NiP | +0.3 V vs RHE | 184 ± 22 | 41 ± 5 | 45 ± 6 |
| | +0.0 V vs RHE | 215 ± 10 | 48 ± 2 | 41 ± 8 |
| IO-CuCrO$_2$/DPP-P/NiP | +0.3 V vs RHE | 72 ± 9 | 16 ± 2 | 25 ± 1 |
| | +0.0 V vs RHE | 160 ± 24 | 36 ± 5 | 40 ± 14 |

*Conditions: aqueous Na$_2$SO$_4$ (0.1 M, pH 3), UV-filtered simulated solar light (100 mW cm$^{-2}$), AM 1.5G, $\lambda$ > 420 nm (Table 1 and Figure S6). IO-CuCrO$_2$/NiP electrodes were conducted with each electrode at applied potentials of 0.0 and +0.3 V vs RHE in aqueous Na$_2$SO$_4$ (0.1 M, pH 3) over the course of 2 h under constant light illumination (100 mW cm$^{-2}$, AM 1.5G, $\lambda$ > 420 nm) (Table 1 and Figure S6). IO-CuCrO$_2$/NiP electrodes were conducted with each electrode at applied potentials of 0.0 and +0.3 V vs RHE in aqueous Na$_2$SO$_4$ (0.1 M, pH 3) over the course of 2 h under constant light illumination (100 mW cm$^{-2}$, AM 1.5G, $\lambda$ > 420 nm) (Table 1 and Figure S6). IO-CuCrO$_2$/NiP electrodes were conducted with each electrode at applied potentials of 0.0 and +0.3 V vs RHE in aqueous Na$_2$SO$_4$ (0.1 M, pH 3) over the course of 2 h under constant light illumination (100 mW cm$^{-2}$, AM 1.5G, $\lambda$ > 420 nm) (Table 1 and Figure S6). IO-CuCrO$_2$/NiP electrodes were conducted with each electrode at applied potentials of 0.0 and +0.3 V vs RHE in aqueous Na$_2$SO$_4$ (0.1 M, pH 3) over the course of 2 h under constant light illumination (100 mW cm$^{-2}$, AM 1.5G, $\lambda$ > 420 nm) (Table 1 and Figure S6).
surface area could prove effective with other p-type semiconductors in future studies.

The advantage of bypassing synthetically challenging complexes through coimmobilization increases the diversity of available photocathodes. Well-studied organic chromophores such as the two employed here can be integrated with the established range of Earth-abundant molecular catalysts, enabling inexpensive and efficient reduction reactions. Future developments of dye–catalyst assemblies based on IO-CuCrO₂ could provide an understanding of the catalysis-limiting processes in DSPCs.

## CONCLUSIONS

We report two inverse opal CuCrO₂ photocathodes using different organic dyes with a coimmobilized molecular Ni bis(diphosphine) catalyst. The IO architecture enables high loadings of molecular species, resulting in a 70% enhancement in H₂ generation over a previously reported analogous sol–gel CuCrO₂ photocathode. This PMI-sensitized CuCrO₂ electrode benefits from a broad and intense absorption profile, ensuring that a large portion of visible light can be effectively harvested. Both IO-CuCrO₂|PMI-P/NiP and IO-CuCrO₂|DPP-P/NiP photocathodes generate photocurrents of ~25 and ~18 μA cm⁻², respectively, at 0.0 V vs. RHE under visible light illumination (100 mW cm⁻², AM 1.5G, λ > 420 nm). The photocurrent onset potential was approximately +0.8 V vs RHE for both architectures. DPP-P- and PMI-P-sensitized photocathodes produce appreciable amounts of H₂ over the course of 2 h CPPE. The IO-CuCrO₂|PMI-P/NiP photoelectrodes perform best, producing 215 ± 10 nmol of H₂ cm⁻² at 0.0 V vs RHE with an FE of 41 ± 8% and a TONNiP of 48 ± 2. Under the same conditions, IO-CuCrO₂|DPP-P/NiP generates 160 ± 24 nmol of H₂ cm⁻² with a FE of 40 ± 14% and a TONNiP of 36 ± 5. The high performance of PMI-P reflects the favorable molecular structure and absorption spectrum, which is well-suited for sensitization of p-type semiconductors.

The novel IO-CuCrO₂ morphology emphasizes the importance of high-surface-area structures and more suitable p-type semiconductors in DSPCs. Coimmobilization of catalyst and dye components proves to be a viable method to form DSPCs with CuCrO₂, avoiding the need for a complicated synthetic protocol. Furthermore, the procedure enables control over pore size through the use of different-sized template spheres, which could assist the development of DSPCs in future studies. Integration of CO₂ reduction catalysts and development of dyes tailored for this CuCrO₂ surface could provide vital advancements for delafossite-based photocathodes. The novel and transferable IO-CuCrO₂ structure presented here extends the range of materials available for fuel-generating DSPCs.

## EXPERIMENTAL SECTION

### Materials and Methods

NiP,⁷⁶ DPP-P,⁷⁶ and PMI-P⁷⁷ were synthesized as previously reported. Milli-Q H₂O (R > 18.2 MΩ cm) was used for all electrochemical and analytical measurements. Cu(NO₃)₂·3H₂O (Sigma-Aldrich, ≥99%), Cr(NO₃)₃·9H₂O (Sigma-Aldrich, ≥99%), and anhydrous NaOH pellets (Sigma-Aldrich, ≥98%) were used for the CuCrO₂-NP preparation.⁵⁵ PS beads (Polysciences Inc., 750 nm, 2.6% w/v) were used for IO-CuCrO₂ synthesis. ITO-coated glass sheets (VisionTek Systems Ltd., R = 12 Ω cm⁻², thickness of 1.1 mm) were cut into 1 × 3 cm² slides prior to cleaning.

### Synthesis of CuCrO₂-NPs

Cu(NO₃)₂·3H₂O (1.51 g, 6.25 mmol) and Cr(NO₃)₃·9H₂O (2.50 g, 6.25 mmol) were stirred in Milli-Q H₂O (70 mL), and NaOH (5.0 g) was added (final solution pH 13). The solution was stirred at room temperature for 2 h, and then 12 mL was decanted into a PTFE-lined autoclave (23 mL total volume). The autoclave was heated to 240 °C for 60 h before the CuCrO₂-NPs were removed. The particles were washed with HCl (0.1 M, 15 mL) and centrifuged (8000 rpm, 5 min), and the supernatant was removed. They were then washed with EtOH (15 mL) and recentrifuged, and the supernatant was removed. The washing steps were repeated for a total of three washes before the CuCrO₂-NPs were dried in vacuo. The dry NPs were ground using a pestle and mortar and stored under vacuum before use.

### Synthesis of IO-CuCrO₂ Electrodes

PS beads (750 nm, 2.6% w/v suspension in H₂O, 0.5 mL) were centrifuged, and the supernatant was removed; the beads were then washed with MeOH and centrifuged again to give a PS pellet. A dispersion of CuCrO₂-NPs (7.5 wt %, MeOH/H₂O 1/4, 140 μL) was added to the PS pellet and sonicated (5 min at <10 °C). The solution was drop-cast (4 μL) onto ITO-coated glass (0.5 cm², confined with Parafilm) and dried in air for 3 h. The Parafilm was removed and the PS template dissolved in toluene for 15 h before being rinsed with acetonitrile and washed with H₂O and dried in vacuo. Annealing under Ar (500 °C, 5 °C min⁻¹ ramp rate, 1 h, 150 scm flow rate) using a tube furnace fitted with a quartz tube, end seals, and insulation plugs (Carbolite Gero) was required to sinter the particles to form the final IO-CuCrO₂ structures.

### Physical Characterization

A Tescan MIRA3 FEG-SEM was used to obtain all SEM images. TEM analysis was conducted using a FEI Phillips Technai F20-G2 TEM, operating at an accelerating voltage of 200 kV (Electron Microscopy Suite, Cavendish Laboratory, University of Cambridge). XRD measurements were taken with a PANalytical BV X'Taper Pro X-ray diffractometer. UV–vis absorption spectra were acquired using a Varian Cary 50 spectrophotometer operated in transmission mode or with a diffuse reflectance accessory (Barrelino) for powder samples. Emission spectra were recorded on a Fluoromax-4 Horiba Jobin Yvon spectrophuorimeter (PMI) or with an Edinburgh Instruments FSS spectrophuorimeter (DPP). N₂ gas adsorption measurements were carried out using a Micromeritics 3 Flex instrument (Micromeritics, Norcross, GA, USA) with powder samples. Samples were degassed for 10 h at 100 °C, and measurements were carried out in liquid N₂. BET specific surface area values were obtained from fitting N₂ isotherms using the Microactive software.

### Immobilization of Dyes and Catalyst

The dye species were immobilized through soaking in a bath containing DPP-P or PMI-P (0.2 mM) for 15 h in DMF, maintained at 25 °C. The IO-CuCrO₂|dye electrodes were rinsed with DMF and water before being dried under N₂. These electrodes were then soaked in NiP (1 mM, MeOH) for 3 h under a N₂ atmosphere. The IO-CuCrO₂|dye/NiP electrodes were rinsed with MeOH and then water and dried under N₂ in the dark. All electrodes were used directly after immobilization. A bare IO-CuCrO₂ electrode was soaked in a solution of phenylphosphonic acid (0.5 M, DMF) for 2 h and then rinsed with DMF and H₂O for the comparative dark current study.
Quantification of Immobilized DPP-P and NiP. DPP-P and PMI-P loadings were quantified using UV–vis spectroscopy following desorption from IO-CuCrO$_2$/dye/NiP electrodes by scraping the CuCrO$_2$-NP powder from the surface (0.25 cm$^2$) and sonicating in tetrabutylammonium hydroxide (TBAOH) 30-hydrate (0.1 M, DMF, 1 mL) for 30 min. Higher TBAOH concentrations and longer sonication times were avoided to prevent dye decomposition. The absorption maximum at 500 and 536 nm for DPP-P and PMI-P electrodes, respectively, was determined and fitted to a calibration curve (conducted in 0.1 M TBAOH in DMF) to determine the loading values. NiP loading was determined by ICP-OES following overnight digestion of the electrodes (0.25 cm$^2$) in aqueous HNO$_3$ (70%, 1 mL) and subsequent dilution to 10% v/v with Milli-Q H$_2$O. Values for nitric acid solution, IO-CuCrO$_2$, IO-CuCrO$_2$/DPP-P, IO-CuCrO$_2$/PMI-P, and pre- and postelectrolysis CuCrO$_2$/DPP-P/NI and CuCrO$_2$/PMI-P/NI electrodes were determined in triplicate.

**Photoelectrochemical Measurements.** PEC measurements were conducted using an ivium CompactStat potentiostat in a custom two-compartment electrochemical cell featuring a flat quartz window and a Nafion membrane. A three-electrode setup was used with a Pt counter electrode, Ag/AgCl/KCl$\text{aq}$ reference electrode, and an IO-CuCrO$_2$-based working electrode (0.25 cm$^2$ active area). N$_2$-purged (15 min) aqueous Na$_2$SO$_4$ electrolyte solution (0.1 M, pH 3) was used for all measurements. Electrodes were illuminated from the front using a calibrated Newport Oriel solar light simulator (150 W, 100 mW cm$^{-2}$, AM 1.5G) with an IR water filter and a UQG Optics UV-Filter ($\lambda$ > 420 nm).

CPPE experiments with each photocathode were conducted in triplicate at +0.3 and 0.0 V vs RHE in a custom two-compartment electrochemical cell featuring a flat quartz window and a Nafion membrane. Both compartments were purged with 2% CH$_4$ in N$_2$ for 30 min prior to electrolysis, and the amount of H$_2$ was determined using a Shimadzu Traceria GC2010 Plus gas chromatograph using a barrier ionization detector and a mol sieve column (kept at 130 °C) with He as the carrier gas. All PEC cells were left for 2 h following electrolysis to allow solution-dissolved H$_2$ to equilibrate with the gas headspace. The partial pressure of H$_2$ was calculated to account for dissolved gas in the solution, and this was added to the amount of H$_2$ in the headspace to determine the total H$_2$ and Faradaic efficiency.

**IPCE Measurements.** A three-electrode setup with a Pt counter electrode, Ag/AgCl/KCl$\text{aq}$ reference electrode, and an IO-CuCrO$_2$/dye/NiP or IO-CuCrO$_2$ working electrode was used in a custom three-necked cell with a flat borosilicate glass window for IPCE measurements. The electrolyte solution was Na$_2$SO$_4$ (0.1 M, pH 3), and an applied potential of +0.3 V vs RHE was maintained for all measurements. Monochromatic light was supplied with a 300 W xenon lamp solar light simulator connected to a monochromator (MSH300, LOT Quantum design). The intensity was calibrated to 0.8 mW cm$^{-2}$ for each individual wavelength, and experiments with each electrode were conducted in triplicate with different electrodes using an active area of 0.25 cm$^2$. Photocurrents were determined at each recorded wavelength through light chopping using an ivium CompactStat potentiostat. Error bars represent standard deviation from the mean.

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