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Supporting Information for

Energetics and Efficiency Analysis of a Cobaloxime-Modified Semiconductor at Simulated Air Mass 1.5 Illumination

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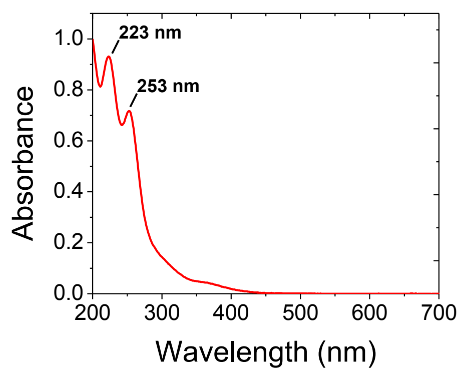

Figure S1. Absorbance spectrum of a model cobaloxime catalyst, $Co(dmgH)_2PyCl$, recorded as a solution in acetonitrile.

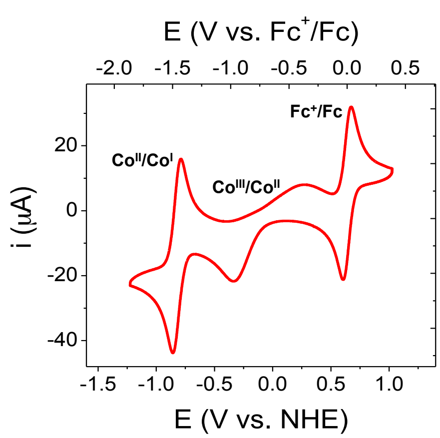

Figure S2. Cyclic votammogram of a model cobaloxime catalyst, $Co(dmgH)_2PyCl$, recorded in a 0.1 M $TBAPF_6$ acetonitrile solution using a glassy carbon working electrode and ferrocene as an internal standard.

Table S1. J-V response parameters, including the open circuit voltage V_{oc}, short-circuit current density J_{sc}, and fill factor FF, of working electrodes at pH =7 with illumination at 100 mW cm^{-2} using a Solar Light PV Cell Test Simulator.

Electrode	J_{sc}(mA cm^{-2})	V_{oc} (V vs. RHE)	FF
GaP	-0.42	0.69	0.15
PVP-GaP	-0.19	0.68	0.09
Co-PVP-GaP	-0.92	0.72	0.33

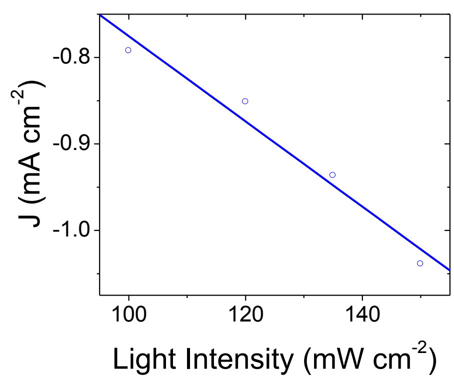

Figure S3. Photocurrent density (at -0.38 V vs. RHE) of a PVP-GaP electrode recorded at increasing illumination.

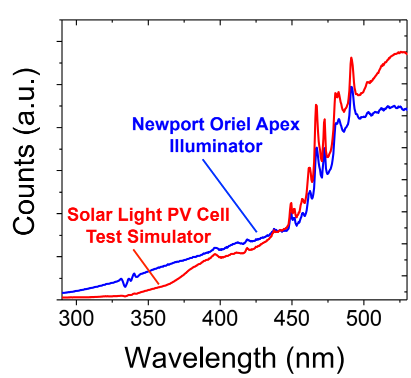

Figure S4. Spectral profile of the Solar Light PV Cell Test Simulator used in these experiments (red) and a Newport Oriel Apex Illuminator (blue), used as an illumination source in a previous report [10] The differences in illumination in the actinic region of the GaP substrates used in these experiments in part accounts for the difference in measured photocurrent densities when using these lamps. Figure S3 shows linear sweep voltammograms of Co-PVP-GaP electrodes using different lighting conditions and GaP substrates with different physical properties (e.g. resistivity, mobility and carrier concentration). These results show that the J-V response of the electrodes depends on the physical properties of the GaP semiconductor substrate as well as illumination conditions, indicating that illumination intensity and doping are important parameters for maximizing efficiency.

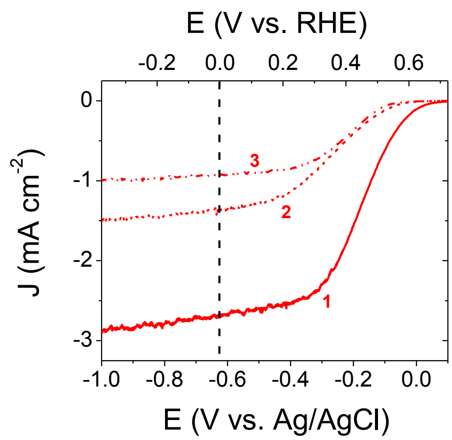

Figure S5. Linear sweep voltammograms of Co-PVP-GaP working electrodes collected using GaP substrates with the following properties and under the following illumination conditions: **1** (solid line) Zn doped p-GaP with a carrier concentration of 6.95×10^{17} cm^{-3}, under 100 mW cm^{-2} illumination using a Newport Oriel Apex Illuminator, **2** (dotted line) the same electrode described in **1** under 100 mW cm^{-2} illumination using a Solar Light PV Cell Test Simulator and **3** (dash-dot line) Zn doped p-GaP with a carrier concentration of 2.2×10^{18} cm^{-3} under 100 mW cm^{-2} illumination using a Solar Light PV Cell Test Simulator.

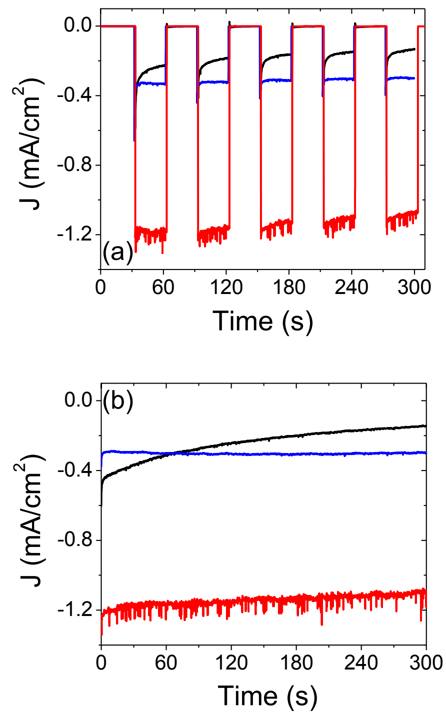

Figure S6. Three-electrode electrolysis measurements using GaP working electrodes with a carrier concentration of 6.95×10^{17} cm^{-3} following BHF treatment (black), polyvinylpyridine grafting (blue) and cobaloxime attachment (red), including data collected with (a) chopped (light on / light off) as well as (b) continuous simulated solar illumination. All measurements were performed at +0.17 V vs. RHE.