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Supporting Information

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Heterostructured Bismuth Vanadate/Cobalt Phosphate Photoelectrodes Promote TEMPO-Mediated Oxidation of 5-Hydroxymethylfurfural

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Contents:

- 1. Experimental Details
- 2. Additional Tables and Figures
- 3. References

1. Experimental Details

Materials: Boric acid (\geq 99.5%), dimethyl sulfoxide (DMSO, \geq 99.9%), nitric acid, potassium iodide (\geq 99%), anhydrous sodium sulfite (\geq 99%), and sulfuric acid were purchased from Fisher Scientific. Bismuth(III) nitrate pentahydrate (98%), cobalt(II) nitrate hexahydrate (\geq 98%), dimethyl sulfoxide (DMSO, \geq 99.5%), potassium dibasic phosphate (\geq 98%), potassium monobasic phosphate (\geq 99%), sodium hydroxide (\geq 97%), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) (98%), vanadyl acetylacetonate (98%), 1,4-benzoquinone (\geq 99%), 5-hydroxymethylfurfural (HMF, \geq 99%), 2,5-diformylfuran (DFF, \geq 99%), and 2,5-furandicarboxylic acid (FDCA, 97%) were purchased from Sigma-Aldrich. 5-hydroxymethyl-2-furancarboxylic acid (HFCA, \geq 99%) was purchased from Matrix Scientific. 5-formylfuran-2-carboxylic acid (FFCA, \geq 98%) was purchased from TCI America. All electrolytes were prepared using deionized water (18.2 M Ω cm).

Fabrication of BiVO₄ photoanodes: BiVO₄ films were synthesized by a procedure adapted from Kim et al.¹⁻² First, a 50 ml solution containing 0.4 M potassium iodide was adjusted to pH 1.7 with nitric acid, followed by the addition of 0.04 M bismuth(III) nitrate. The solution was mixed with a magnetic stir bar. After the bismuth precursor was fully dissolved, a 20 ml solution of 0.23 M 1,4-benzoquinone in ethanol was added. Electrodeposition was performed in a two-electrode configuration using fluorine-doped tin oxide (FTO) glass and platinum foil as working and counter electrodes, respectively. The area of FTO exposed to the electrolyte was approximately 5.75 cm². Deposition of bismuth oxyiodide (BiOI) was conducted at –4.0 mA for 328 s, corresponding to a charge transfer of approximately 0.23 C cm⁻². The BiOI films were washed with copious deionized water and dried under a nitrogen stream. A solution of 0.2 M vanadyl acetylacetonate in DMSO (0.8 ml) was drop-cast onto the top side of the BiOI film. Thermal treatment was performed in a muffle furnace (MTI) at 450 °C (ramp rate 2 °C per minute) for 2 h followed by naturally cooling to ambient temperature. Excess V₂O₅ was removed by placing the electrode in a stirred solution of 1.0 M sodium hydroxide for 30 min. The final BiVO₄ films were washed with deionized water and the precursor V₂O₅ was removed by placing the electrode in a stirred solution of 1.0 M sodium hydroxide for 30 min.

Electrodeposition of CoPi: CoPi was deposited onto BiVO₄ electrodes using the electrodeposition method described by Kanan and Nocera.³ CoPi layers were deposited from a solution of 0.5 mM cobalt(II) nitrate in 0.1 M potassium phosphate (pH 7.0) at 1.1 V versus a Ag/AgCl reference electrode. Deposition time was varied between 1 and 30 min. **Figure S3** shows the typical current density versus time plot for CoPi deposition. The photoanodes are designated BiVO₄/CoPi-*t*, in which *t* is the CoPi deposition time in minutes.

Characterizations: X-ray diffraction (XRD) patterns were collected with a Siemens D500 diffractometer operated with a Cu K_a source ($\lambda = 1.5418$ Å) at 45 kV and 30 mA and equipped with a diffracted beam monochromator (carbon). Diffuse transmittance (*T*) and reflectance (*R*) measurements were taken using Lambda 750 UV-vis spectrophotometer with a 100 mm integrating sphere. Absorbance (*A*) was calculated by the relationship: A = 1 - T - R. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed on an FEI Quanta 250 field-emission scanning electron microscope equipped with an Oxford Aztec EDS. SEM micrographs in **Figure 1** were collected with a backscattered electron detector. Samples for SEM were sputter-coated with Au films approximately 5 nm thick.

Photoelectrochemical experiments: Photoelectrochemical measurements were performed in a custommade undivided cell in a three-electrode configuration. Pt wire and Ag/AgCl (3.5 mm, Pine Research Instrumentation) served as counter and reference electrodes, respectively. Unless noted otherwise, all potentials (*E*) are reported versus the reversible hydrogen electrode (RHE), as calculated by eq. S1.

$$E(vs. RHE) = E(vs. Ag/AgCl) + 0.199 V + 0.059 V \cdot pH$$
 (S1)

Electrochemical measurements were conducted using a WaveDriver 20 system (Pine Research Instrumentation). Irradiation was achieved with a Sciencetech A1 Lightline solar simulator equipped with a 300 W xenon lamp and an AM1.5 filter. Light intensity was calibrated to approximately 1 sun equivalent (100 mW cm⁻²) using a reference cell certified by National Renewable Energy Laboratories (NREL), USA. The photoanodes were irradiated through the FTO glass substrate, i.e. "back-side" illumination. Photoanodes were masked with an aperture (1.0 cm diameter) to set the irradiated area to be the same as the area exposed to electrolyte. Current density values are reported with respect to geometric surface area (0.785 cm²). All experiments were performed in 0.2 M sodium borate buffer electrolyte (pH 9.2). Linear sweep voltammograms (LSVs) and cyclic voltammograms (CVs) were collected at a sweep rate of 10 mV s⁻¹. Transient photocurrent LSVs were collected using a mechanical shutter (4 s open, 4 s closed).

Oxygen quantification: The amount of evolved oxygen (O₂) was determined using an oxygen sensor system (NEOFOX-KIT-PROBE, Ocean Optics). Oxygen measurements were conducted in a glass H-type cell with an airtight silicone stopper on the anode chamber. The anode and cathode chambers were separated by an anion-exchange membrane (A-201, Tokuyama Corp.). The active area of the photoanode was approximately 5.75 cm². Irradiation passed through the glass wall of the reactor and electrolyte before striking the photoanode, so the light intensity was not exactly 1 sun equivalent. A fluorescence-based oxygen probe and thermistor were submerged into the anode electrolyte to measure the temperature-

Oxygen quantification (continued): compensated dissolved oxygen concentration. Before measurements, the cell was thoroughly purged with argon gas (99.99%, Airgas) and then sealed. The baseline oxygen concentration was monitored and subtracted from the measurements taken under photoelectrochemical conditions. The amount of O₂ produced (*no2*) was calculated by multiplying dissolved oxygen concentration by the electrolyte volume. The faradaic efficiency to OER was calculated by eq S2:

$$FE_{O2} = 4 n_{O2} / (FQ)$$
 (S2)

in which n_{02} is the measured amount of O₂ (mol), 4 is the electron transfer number for O₂ evolution, *F* is the Faraday constant (96,485.3 C mol⁻¹), and *Q* is the charge transferred in coulombs (C) calculated as the time integral of current. The theoretical amount of O₂ produced assuming 100% faradaic efficiency was calculated by eq S3:

$$n_{\rm O2,theoretical} = Q / (4F) \tag{S3}$$

The measured and theoretical amounts of O₂ produced were in good agreement when TEMPO was not present in the electrolyte, as shown in **Figure S5**.

Net charge injection efficiency: Net charge injection efficiency (ϕ_{inj}) is the fraction of the surfacereaching holes that are utilized for electrochemical reactions, rather than being lost to recombination processes. The total rate at which holes reach the surface can be estimated by measuring photocurrent in the presence of a hole accepter. Sodium sulfite is a good hole accepter capable of extracting nearly all holes that reach the semiconductor/electrolyte interface due to its fast, irreversible, oxidation kinetics.⁴⁻⁵ Therefore, the photocurrent measured for sulfite oxidation (*j*_{sulfite}) provides an estimate for the total rate of holes reaching the interface. Net charge injection efficiencies (ϕ_{inj}) for OER and TEMPO oxidation were determined by eqs S4–S5.

$$\phi_{\rm inj,OER} = j_{\rm OER} / j_{\rm sulfite} \tag{S4}$$

$$\phi_{\text{inj,TEMPO}} = j_{\text{TEMPO}} / j_{\text{sulfite}}$$
(S5)

Current density values were extracted from LSVs at 0.64 V vs. RHE. Current density for OER (*j*OER) was taken from LSVs measured in electrolyte without TEMPO or sodium sulfite present (cf. **Figure 3a**). Note that at 0.64 V vs. RHE, the contribution of OER to the total measured photocurrent (i.e. faradaic efficiency to OER) was negligible for BiVO4 and BiVO4/CoPi when TEMPO was present in the electrolyte (cf. **Figure 3c**). Therefore, it is reasonable to assume that the measured current density (*j*) was from TEMPO oxidation under that condition (i.e. $j = j_{\text{TEMPO}}$). The value of j_{sulfite} measured for BiVO4 was used in all calculations.

TEMPO-mediated photoelectrolysis: TEMPO-mediated photoelectrolysis of HMF was performed in a glass H-type cell at a constant potential of 0.64 V versus RHE. The anode and cathode chambers were separated by an anion-exchange membrane (A-201, Tokuyama Corp.). The anode electrolyte volume was 20 ml, and it contained 5.0 mM TEMPO and 1.0 mM HMF. Agitation was provided by a magnetic stirrer. The active area of the photoanode was approximately 5.25 cm². Irradiation passed through the glass wall of the reactor and electrolyte before illuminating the photoanode, and as a result the light intensity was not exactly equivalent to 1 sun. For BiVO₄/CoPi-30, the reaction was concluded when the amount of charge transferred reached 12 C, which occurred after about 2.7 h of reaction. This amount of charge corresponds to about 103% of the theoretical charge transfer required for complete conversion of HMF to FDCA (i.e. 11.59 C). Additional experiments were conducted using a BiVO₄ photoanode for a duration of 2.7 h.

Product analysis: Product analysis was performed with an Agilent 1200 high-performance liquid chromatograph, equipped with a Bio-Rad Aminex HPX-87H column (50 °C) and a variable wavelength detector (Agilent G1314F, 260 nm). The mobile phase was 0.01 M sulfuric acid with a flow rate of 0.5 ml min⁻¹. Reactants and products were identified and quantified by comparison with authentic samples. HMF conversion (*C*) was calculated by eq S6:

$$C = (n_{\rm HMF,initial} - n_{\rm HMF}) / n_{\rm HMF,initial}$$
(S6)

in which n_{HMF} is the amount of HMF (mol). The product selectivity (*S*) and yield (*Y*) were calculated for product *i* by eqs S7–S8:

$$S_i = n_i / (n_{\rm HMF, initial} - n_{\rm HMF})$$
(S7)

$$Y_i = n_i / n_{\rm HMF, initial} \tag{S8}$$

in which n_i is amount of product i (mol).

2. Additional Tables and Figures

Table S1. Relative abundance (at%) of Bi, V, Co, and P in BiVO₄ and BiVO₄/CoPi films determined by SEM-EDS.

	Bi	V	Со	Р
BiVO ₄	51.9	48.1	-	-
BiVO ₄ /CoPi-30	46.4	43.8	6.5	3.4

Table S2. Net charge injection efficiencies (ϕ_{inj}) for OER and TEMPO oxidation at 0.64 V vs. RHE.

	<i>joer</i> (mA cm ⁻²)	ϕ inj,OER (%)	<i>jтемро</i> (mA cm ⁻²)	ϕ inj,TEMPO (%)
BiVO ₄	0.098	6.3	0.033	2.1
BiVO4/CoPi-1 ^[a]	0.572	37.0	0.040	2.6
BiVO ₄ /CoPi-30	0.035	2.3	0.238	15.4

[a] BiVO₄/CoPi-1 is BiVO₄modified with CoPi deposition of 1 min.

Table S3. Product analysis of photoelectrochemical TEMPO-mediation HMF oxidation.^[a]

	$Q(C)^{[b]}$	C_{HMF} (%) ^[c]	$S_{ m DFF}$ (%) ^[d]	Sffca (%)	Sfdca (%)
BiVO ₄	0.52	15.2	50.9	30.6	0.7
BiVO ₄ /CoPi-30	12.0	98.8	0.2	3.8	89.0

[a] Conditions: 5.0 mM TEMPO and 1.0 mM HMF in 20 ml electrolyte; applied potential = 0.64 V vs. RHE; reaction duration 2.7 h. [b] Q is charge transferred in external circuit in coulombs. [c] C is HMF conversion [d] S is product selectivity.



Figure S1. XRD patterns of BiVO₄ and BiVO₄/CoPi-30 showing typical peaks for monoclinic scheelite structure (JCPDS No. 00-014-0688). Peaks from FTO substrate are indicated with asterisks (*).



Figure S2. UV-vis diffuse absorbance spectra for (a) BiVO₄ and (b) BiVO₄/CoPi-30 along with (c-d) corresponding Tauc plots.



Figure S3. Typical electrochemical CoPi deposition on a BiVO₄ electrode. Conditions: 1.1 V vs. Ag/AgCl in 0.1 M KPi buffer (pH 7.0) containing 0.5 mM cobalt(II) nitrate.



Figure S4. Top-view SEM micrographs (left) and cross-sectional SEM micrographs (right) for (a) BiVO₄ and (b) BiVO₄/CoPi-30 showing that no notable morphological changes were observed after electrochemical CoPi deposition. Top-view micrographs were collected with a backscattered electron detector, whereas cross-sectional micrographs were collected with a secondary electron detector.



Figure S5. Verification of O₂ quantification method for BiVO₄ photoanode at three applied potentials (V vs. RHE) in electrolyte without TEMPO present. Measured O₂ amounts are in good agreement with theoretical predictions assuming 100% faradaic efficiency to OER.

3. References

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