

# ChemElectroChem

Supporting Information

## **Nitrate Radical Facilitates Indirect Benzyl Alcohol Oxidation on Bismuth(III) Vanadate Photoelectrodes**

Bradley D. Terry, John L. DiMeglio, John P. Cousineau, and Bart M. Bartlett\*

## Table of Contents

Experimental Methods and Procedures	S2
<i>Fig. S1.</i> Diffuse reflectance plot and Tauc plot for BiVO <sub>4</sub>	S5
<i>Fig. S2.</i> X-ray diffractograms of as-made BiVO <sub>4</sub> and FTO substrate	S6
<i>Fig. S3.</i> CPC of PhCH <sub>2</sub> OH in MeCN	S7
<i>Fig. S4.</i> CPC of PhCH <sub>2</sub> OH with Bu <sub>4</sub> NNO <sub>3</sub> in MeCN	S8
<i>Fig. S5.</i> XPS analysis of Bi and V features pre- and post-CPC	S9
<i>Fig. S6.</i> LSV comparison of Bu <sub>4</sub> NNO <sub>3</sub> and HNO <sub>3</sub> accounting for water	S10
<i>Fig. S7.</i> LSVs of nitric acid with benzyl alcohol in acetonitrile	S11
<i>Fig. S8.</i> CPC under optimized conditions and GC-FID spectra	S12
<i>Fig. S9.</i> LSV traces recorded in air and under N <sub>2</sub> atmosphere	S13
<i>Fig. S10.</i> LSV traces of substituted benzyl alcohols	S14

## 1. Experimental Methods and Procedures

Solvents (acetonitrile, ethanol, benzyl alcohol) were purchased from Sigma Aldrich and used without additional purification. *P*-benzoquinone was purchased from Fisher and sublimed to remove impurities. Bismuth nitrate pentahydrate, vanadyl acetylacetonate, deuterated benzyl alcohol, potassium iodide and lactic acid solution ( $\geq 85\%$ ) were obtained from Sigma Aldrich and used without further purification. All aqueous solutions were made using Millipore water ( $18.2 \Omega \text{ cm}^{-1}$ ). Nylon syringe filters (25 mm, 0.2 mm membrane) were purchased from VWR. Fluorine-doped tin oxide glass (NSG TEC 15) was purchased from Pilkington North America.

**Preparation of BiVO<sub>4</sub> Electrodes.** Fluorine-doped tin oxide (FTO) was cleaned by sonication in acetone, followed by Millipore water with detergent, then ethanol for 20 minutes each before rinsing with Millipore water and drying under N<sub>2</sub>. The deposition solution for BiOI was made using previously reported methods, with the final pH set to 3.41 – 3.43 for the most consistent results between batches.<sup>13</sup> Due to solid formation in the Vycor frit of Ag/AgCl reference electrodes, the open-circuit potential was measured between a platinum disk working and the Ag/AgCl reference, showing a stable potential near 0.314 V vs RE; the Pt disk was then used as a stable reference electrode for BiOI growth on FTO and showed a static open-circuit potential. The same two-step electrochemical deposition was used ( $-0.35 \text{ V vs Ag/AgCl}$  for 20 s, followed by  $-0.1 \text{ V vs Ag/AgCl}$  until  $370 \text{ mC cm}^{-2}$  passed) with the open circuit between Pt disk working and Ag/AgCl reference electrodes accounted for ( $-0.664 \text{ V}$  and  $-0.414 \text{ V vs Pt disk reference}$  respectively). Films were rinsed with ethanol and dried gently under a stream of N<sub>2</sub>. The BiOI was converted to BiVO<sub>4</sub> using a thermal treatment process, where  $50 \mu\text{L cm}^{-2}$  of 0.2 M VO(acac)<sub>2</sub> in DMSO were drop-casted onto BiOI films before heating at  $2 \text{ }^\circ\text{C min}^{-1}$  to  $450 \text{ }^\circ\text{C}$ , holding for 2 hours, and cooling back to room temperature over 45 minutes. Excess V<sub>2</sub>O<sub>5</sub> was dissolved off by gentle

stirring in a dish of 1 M NaOH<sub>(aq)</sub> for 40 minutes. These films were rinsed with Millipore water and dried with air.

**Characterization Details.** UV-vis spectra of BiVO<sub>4</sub> films were gathered using a Cary 5000 UV-vis spectrophotometer (Figure S1). Powder X-Ray diffraction data were collected on a Panalytical Empyrean diffractometer with a power of 1.8 kW (40 mA, 45 kV) using a Cu K $\alpha$  radiation source ( $\lambda = 0.15418$  nm). A position-sensitive 1D diffractometer (X'Celerator Scientific) equipped with a with Bragg-Brentano<sup>HD</sup> X-ray optic that ensured delivery of only K $\alpha$  radiation was used (Figure S2). Surface images were obtained on an EMAL JEOL JSM-7800FLV field-emission scanning electron microscope (SEM) instrument with an accelerating voltage of 10 keV and a working distance of 10 mm in The Robert B. Mitchell Electron Microbeam Analysis Lab. Additional surface analysis was performed with X-ray photoelectron spectroscopy (XPS) with data collected on a Kratos Axis Ultra X-ray photoelectron spectrometer. Monochromatic Al K $\alpha$  X-rays (1486.7 eV) were used inside an analysis chamber with a pressure of  $1 \times 10^{-9}$  Torr. Charging effects on semiconductor substrates were mitigated through compensation with an electron flood gun. A step size of 0.1 eV and pass energy of 20 were used to collect high-resolution spectra. Adventitious carbon (284.8 eV) was used to calibrate peak positioning for Bi 4f and V 2p peaks.

**Photoelectrocatalysis.** The light source was a single Royal Blue ( $\lambda_{\text{max}} = 447.5$  nm) High Power LED from Mouser Electronics (Lumileds LXML-PR02-A900) powered by XP-603 Elenco Precision 0 – 30 V Variable Benchtop Power Supply. The light fixture was kept cool with an Arctic Alpine M1 low speed fan. A custom 2-compartment cell was constructed in-house supporting a quartz window and a 1  $\mu\text{m}$  polypropylene frit to separate compartments. The compartment with the quartz window was fitted with a glass side arm to contain the Ag reference electrode at a fixed distance from the central column where a BiVO<sub>4</sub> film was supported. A Pt coil counter electrode

was used in all electrochemical measurements. A 15 mL aliquot of solution was placed in the working/reference electrode compartment along with 6.7 mL in the counter to match solution levels and prevent solution transfer due to gravity. A Teflon stir bar was placed in the working electrode side to ensure solution mixing during electrolysis. Light intensity was applied at a constant  $100 \text{ mW cm}^{-2}$  for all light-based experiments and the reaction vessel was sealed by compression with *o*-rings with screw caps. A Metrohm Autolab electrochemical station and a CH Instruments Electrochemical Workstation 660C were used for all electrochemical measurements.

**Detection of Metal Leaching.** A Perkin-Elmer Nexion 2000 Inductively-Coupled Plasma Mass Spectrometer was used to detect concentrations of bismuth and vanadium in pre- and post-photoelectrolysis conditions. A rotary evaporator was used to remove volatile organics (acetonitrile) yielding a crude. Washes with Millipore water ( $3 \times 2 \text{ mL}$ ) were used to extract the metals in the crude to create stock samples from which serial dilutions were prepared for analysis on the ICP-MS. Diluted samples were referenced to a Pt external standard and concentrations of Bi and V were determined via calibration curves containing equimolar concentrations of Bi and V from independent  $1000 \text{ }\mu\text{g/mL}$  sources (GFS Chemicals and Fisher respectively).

**Density Functional Theory.** Ground-state energy calculations were performed with B3LYP functionals with the 6-31G\* basis set in polar solvent using the software *Spartan'18* Wavefunction, Inc. Irvine, CA. Reference: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A. Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **8**, 3172 (2006).

## 2. Supplementary Data

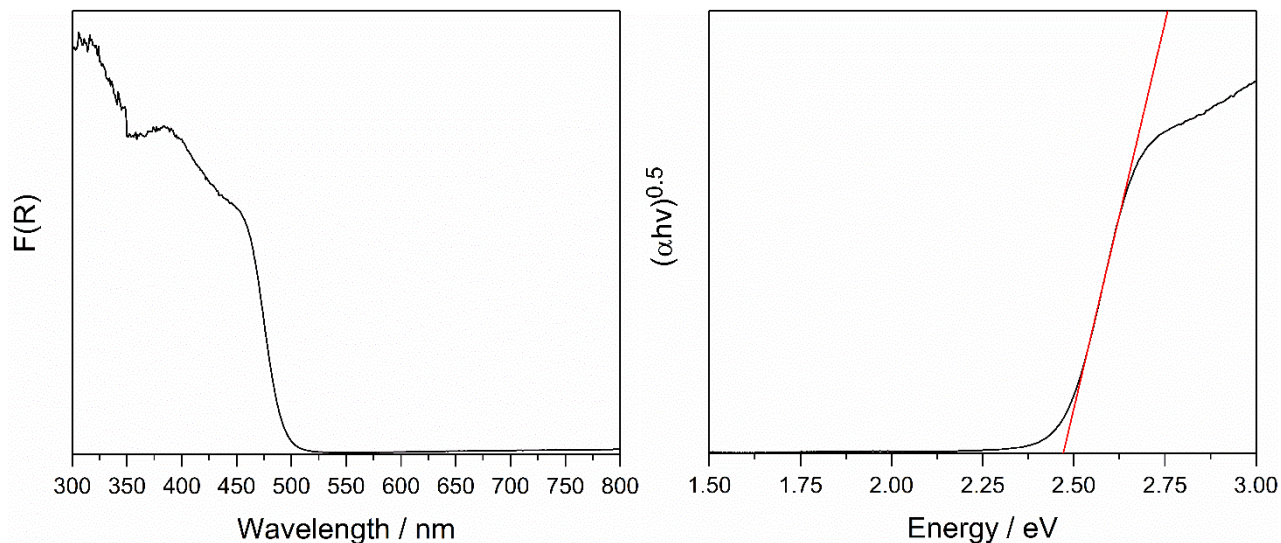


Figure S1.  $F(R)$  transformation of diffuse reflectance measurements on as-made  $\text{BiVO}_4$  films via Kubelka-Munk Theory given by the following equation (left). Tauc analysis treating  $\text{BiVO}_4$  as an indirect band gap material (right).

Where  $R_\infty$  is the absolute reflectance measured by the integration sphere of the Cary 5000 UV-vis-NIR spectrophotometer.

$$F(R) = \frac{(1 - R_\infty)^2}{2R_\infty}$$

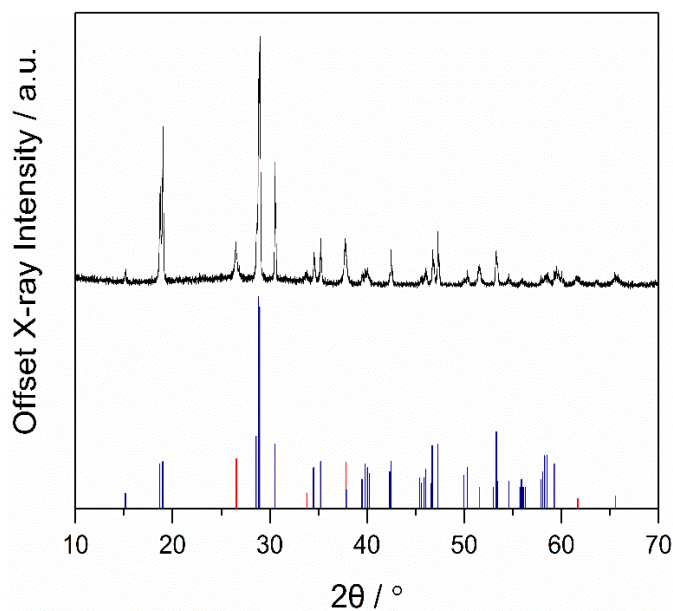


Figure S2. X-ray diffractogram containing diffraction patterns for as-made  $\text{BiVO}_4$  films (black pattern, top), fluorine-doped tin oxide glass substrate (red droplines, bottom) and Jade database reference pattern (PDF#14-0688) for monoclinic  $\text{BiVO}_4$  (navy droplines, bottom).

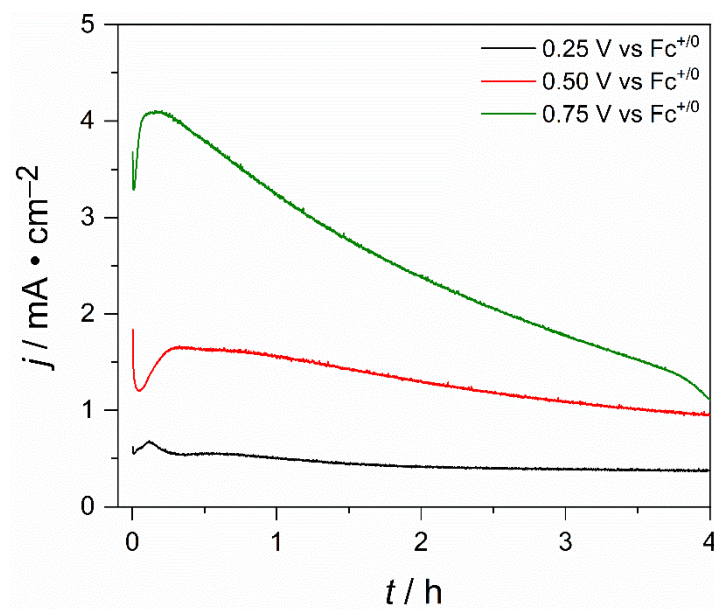


Figure S3. Current vs time plot during CPC experiments with 250 mM PhCH<sub>2</sub>OH in 100 mM Bu<sub>4</sub>NPF<sub>6</sub> (MeCN). A constant potential was held on the BiVO<sub>4</sub> working electrode while stirring the solution in the presence of 100 mW cm<sup>-2</sup> Royal Blue LED ( $\lambda_{\text{max}} = 448$  nm).



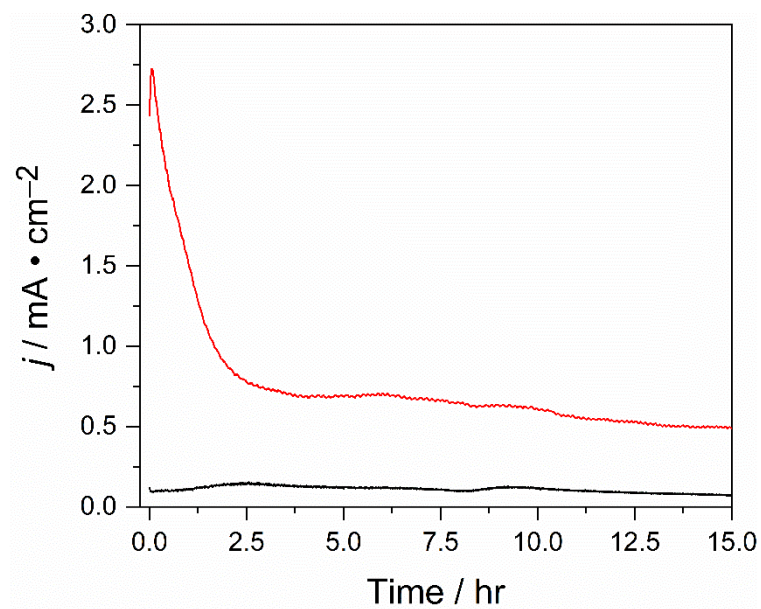


Figure S4. Current vs time plot during CPC experiments for solution containing 250 mM PhCH<sub>2</sub>OH in 100 mM Bu<sub>4</sub>NPF<sub>6</sub> (MeCN) with (red trace) and without (black trace) 100 mM Bu<sub>4</sub>NNO<sub>3</sub>. A constant potential of 0 V vs Fc<sup>+0</sup> was held on the BiVO<sub>4</sub> working electrode while stirring the solution in the presence of 100 mW cm<sup>-2</sup> Royal Blue LED ( $\lambda_{\text{max}} = 448$  nm).

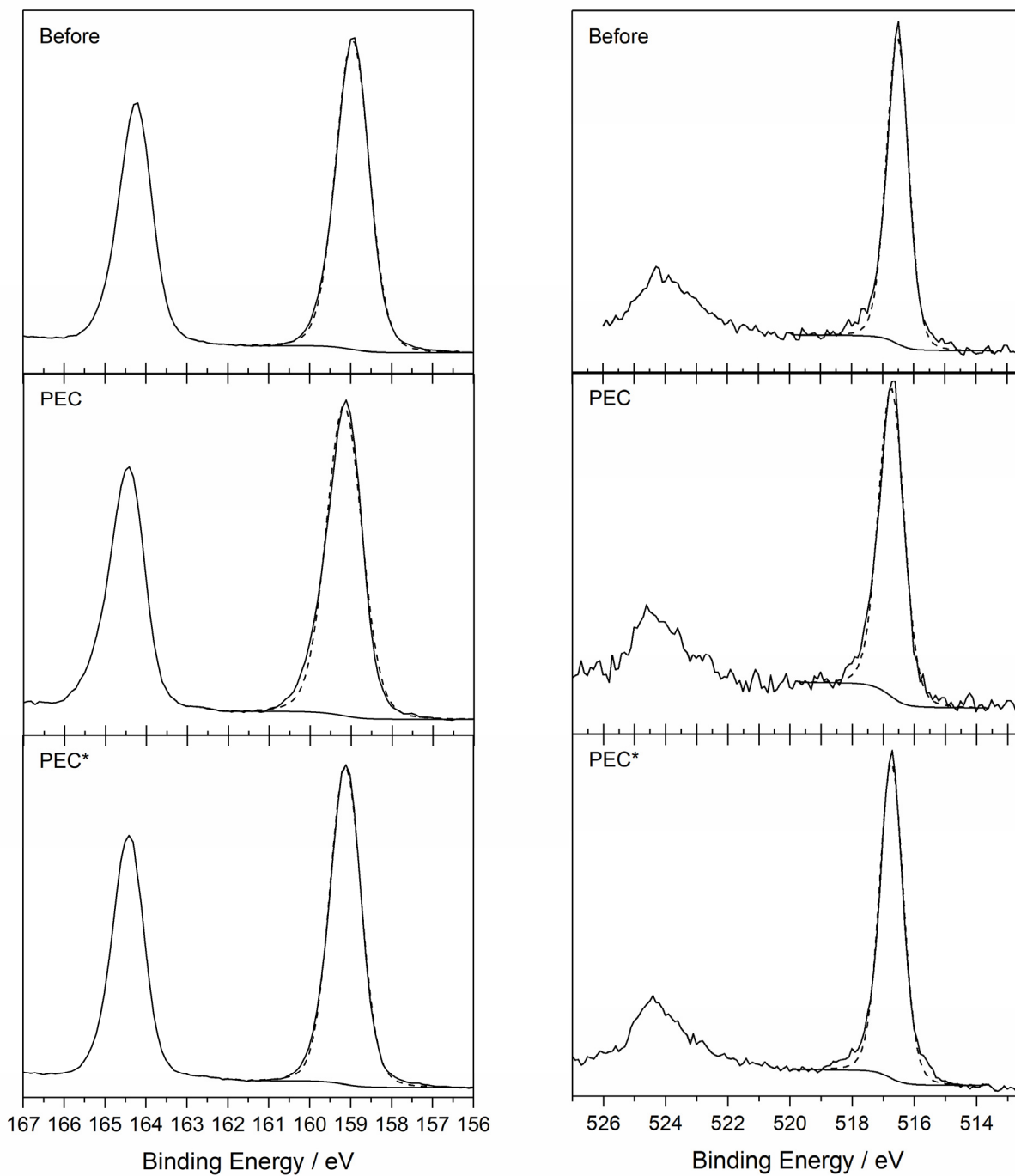


Figure S5. XPS spectra of the bismuth 4f doublet (left) along with vanadium 2p doublet (right) using as-made BiVO<sub>4</sub> (top), and after CPC under PEC—main text Table 1, entry 3— and PEC\*—main text Table 1, entry 4—conditions in the table above.

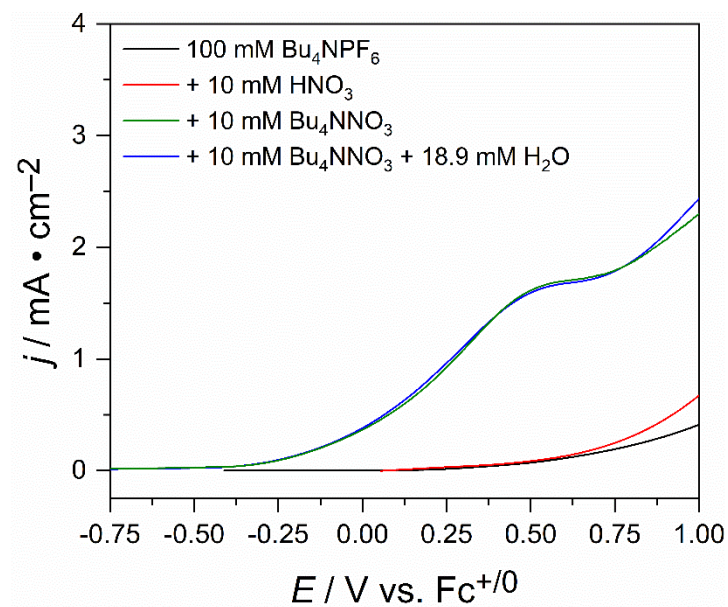


Figure S6. LSVs in solutions containing 10 mM TBANO<sub>3</sub> or 10 mM HNO<sub>3</sub> (Note: Millipore water was added to TBANO<sub>3</sub> (red trace) to account for the water introduced by adding 65% HNO<sub>3</sub> solution in water). Scan rate: 10 mV s<sup>-1</sup>, illumination: 100 mW cm<sup>-2</sup> of 447.5 nm Royal Blue LED illumination in a single-compartment PEC cell with a Pt coil cathode and Ag wire reference electrode (protected by Vycor frit).

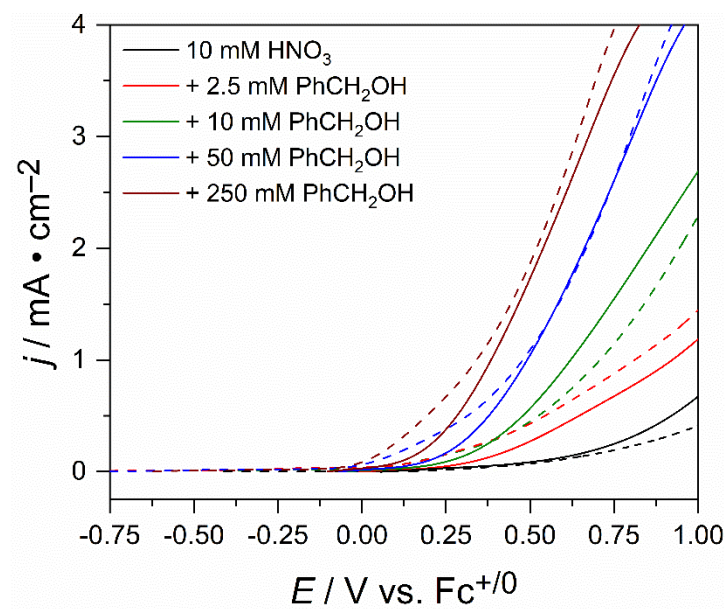


Figure S7. Solid lines: varying concentrations of benzyl alcohol with 10 mM HNO<sub>3</sub> introduced. Dashed lines: Same concentration of benzyl alcohol without HNO<sub>3</sub> present (Presented in main text Figure 1). Scan rate: 10 mV s<sup>-1</sup>, illumination: 100 mW cm<sup>-2</sup> of 447.5 nm Royal Blue LED illumination in a single-compartment PEC cell with a Pt coil cathode and Ag pseudo reference to Fc<sup>+0</sup> (protected by Vycor frit).

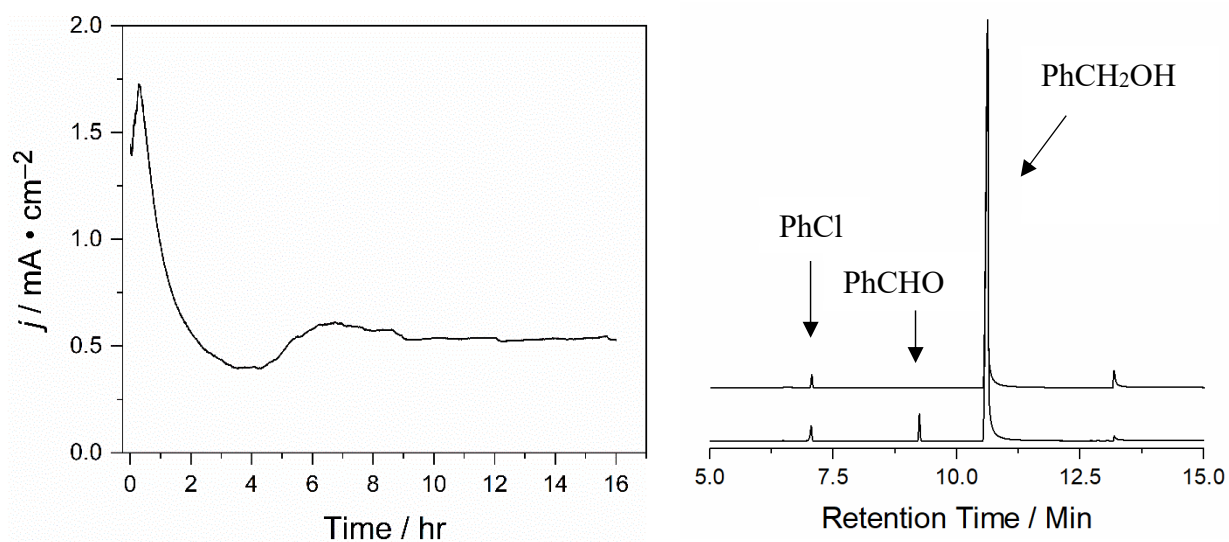


Figure S8. 16-hour bulk electrolyses on  $\text{BiVO}_4$  while stirring in  $100 \text{ mW cm}^{-2}$  448 nm Royal Blue LED illumination. Solution consisted of  $100 \text{ mM Bu}_4\text{NPF}_6$  supporting electrolyte with  $50 \text{ mM Bu}_4\text{NNO}_3$  and  $500 \text{ mM PhCH}_2\text{OH}$  in acetonitrile (left). Representative GC-FID traces used for product analysis and FE determination. The top trace is a before electrolysis and the bottom is after the same solution after CPC for 16 hours at  $0 \text{ V vs Fc}^{+/0}$  (right).

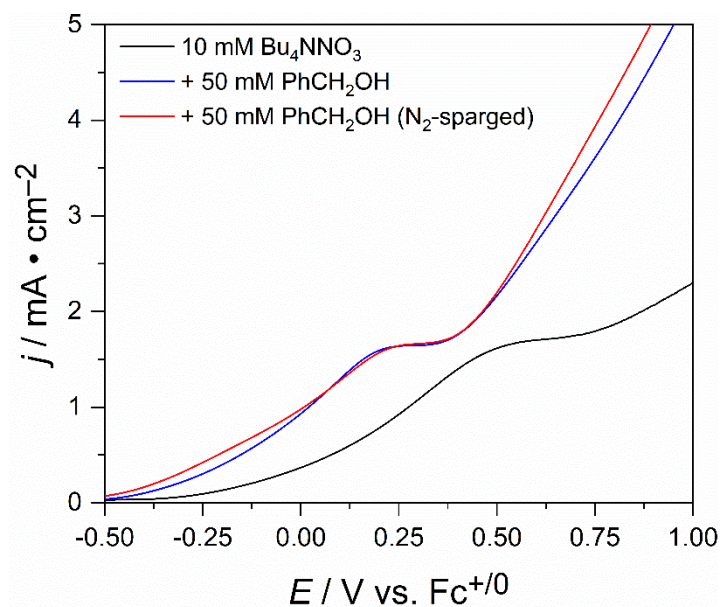


Figure S9. LSVs on  $\text{BiVO}_4$  in solutions containing 10 mM  $\text{TBANO}_3$  and 50 mM  $\text{PhCH}_2\text{OH}$ .  $\text{N}_2$  sparged into solution for 1 hour while sealed and stirring solution (volume  $\sim 15$  mL) Scan rate:  $10 \text{ mV s}^{-1}$ , illumination:  $100 \text{ mW cm}^{-2}$  of 447.5 nm Royal Blue LED illumination in a single-compartment PEC cell with a Pt coil cathode and Ag wire reference electrode (protected by Vycor frit).

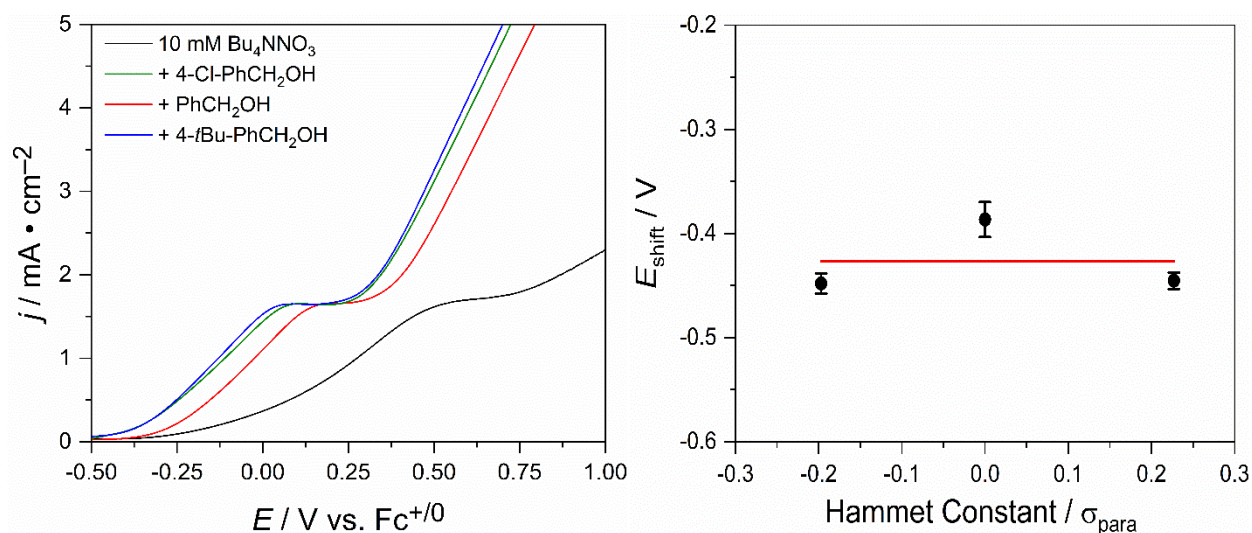


Figure S10. LSVs on BiVO<sub>4</sub> in solutions containing 10 mM TBANO<sub>3</sub> and 50 mM of a benzyl alcohol derivative as labeled (left). Scan rate: 10 mV s<sup>-1</sup>, illumination: 100 mW cm<sup>-2</sup> of 447.5 nm Royal Blue LED illumination in a single-compartment PEC cell with a Pt coil cathode and Ag wire reference electrode (protected by Vycor frit). Average  $E_{\text{shift}}$ —potential at middle of plateau—plotted as a function of para-substituted sigma Hammett parameters for 4-*t*Bu-benzyl alcohol ( $\sigma_{\text{para}} = -0.20$ ), 4-Cl-benzyl alcohol ( $\sigma_{\text{para}} = +0.23$ ) relative to benzyl alcohol ( $\sigma_{\text{para}} = 0$ ) (right). Sigma values obtained from reference 1.

Ref 1: D. H. McDaniel, H. C. Brown, *J. Org. Chem.* **1958**, *23*, 420–427.