Photoelectrochemical oxidation of organic substrates in organic media

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There is a global effort to convert sunlight into fuels by photoelectrochemically splitting water to form hydrogen fuels, but the dioxygen byproduct bears little economic value. This raises the important question of whether higher value commodities can be produced instead of dioxygen. We report here photoelectrochemistry at a BiVO₄ photoanode involving the oxidation of substrates in organic media. The use of MeCN instead of water enables a broader set of chemical transformations to be performed (e.g., alcohol oxidation and C-H activation/oxidation), while suppressing photocorrosion of BiVO₄ that otherwise occurs readily in water, and sunlight reduces the electrical energy required to drive organic transformations by 60%. These collective results demonstrate the utility of using photoelectrochemical cells to mediate organic transformations that otherwise require expensive and toxic reagents or catalysts.
interfacial photoelectrochemistry (PEC) at a semiconductor-liquid junction enables the direct conversion of light into chemical energy. The highly energetic electrons and holes that are created through the absorption of visible light by semiconducting electrodes are capable of driving the energetically demanding conversion of water into oxygen and hydrogen fuels. While there has been a large global effort to reduce the relatively large energy losses associated with producing oxygen at the anode, strikingly few photoanodes are known to be capable of both absorbing incident sunlight and mediating efficient and sustained water oxidation catalysis.

The technical challenges of using a photoanode to form dioxygen that has little economic value provides the imperative to explore alternative reactions that generate higher value products with lower energy input. Choi and coworkers recently demonstrated that the photoelectrochemical oxidation of 5-hydroxymethylurifural into 2,5-furandicarboxylic acid could be realized with a BiVO₄ photoanode in the presence of a redox mediator. A key challenge of this distinctive approach, however, is that the aqueous medium limits the scope of chemistry available and induces high rates of BiVO₄ photocorrosion. While photocorrosion in H₂O can be suppressed by a protective (electrocatalytic) layer (e.g., CoOₓ, NiOₓ, and FeOₓ) that tend to suppress the oxidation of organic compounds in favor of competitive oxygen evolution.

We therefore set out to explore conditions where the photoelectrochemically-driven oxidation of organic compounds in non-aqueous media could be achieved. Two classes of well known organic transformations were chosen to test this concept: alcohol oxidation and the more challenging C–H functionalization/oxidation (Fig. 1). The oxidation of alcohols can be readily achieved using chemical oxidizing agents that include transition metals, hypervalent iodine reagents, and activated sulfur trans-achieved using chemical oxidizing agents that include transition mediator. A key challenge of this distinctive approach, however, is that the aqueous medium limits the scope of chemistry available and induces high rates of BiVO₄ photocorrosion. While photocorrosion in H₂O can be suppressed by a protective (electrocatalytic) layer (e.g., CoOₓ, NiOₓ, and FeOₓ) that tend to suppress the oxidation of organic compounds in favor of competitive oxygen evolution.

Results

Photoelectrochemical stability of BiVO₄ in non-aqueous media. The BiVO₄ photoanodes used in this study were synthesized in accordance with documented procedures. Appropriate stoichiometric amounts of bismuth nitrate hexahydrate and vanadyl acetylacetone precursors dissolved in a solution of acetic acid and acetylacetone were spin-coated onto fluorine-doped tin oxide (FTO), annealed at 500 °C, and then subjected to ultraviolet (UV) irradiation (~10 mW cm⁻²) in air for 20 h. This UV radiation step renders higher activity for aqueous PEC. The UV-Vis absorption spectra, surface morphology, and powder X-ray diffractograms of the films are consistent with previous descriptions of BiVO₄ prepared by this protocol (Fig. 2).

The photoelectrochemical stability of BiVO₄ in aqueous and non-aqueous media was tested by measuring the absorptivity changes before and after 96 h of illumination under an applied potential. The photoanodes were immersed in 25 mL of H₂O containing 0.1 M NaHCO₃ or 25 mL of MeCN with 0.1 M LiClO₄ and exposed to simulated AM1.5 G sunlight for 24 h and an applied potential of 0.1 or 1.6 V, respectively (all potentials reported herein are referenced against Ag/AgCl). The anodes were then left in solution in the dark for 24 h at open-circuit prior to a subsequent 24 h of PEC electrolysis at these same potentials. UV-Vis absorption spectra of the photoanodes recorded after four successive cycles in H₂O (i.e. ~96 h of cumulative exposure to PEC conditions) showed a much more significant reduction in intensity over the 400–600 nm range than those in MeCN (Fig. 2a). This reduced absorptivity is consistent with a decrease in BiVO₄ film thickness, while the nominal changes in absorptivity of the photoanode in MeCN after PEC indicate insignificant photocorrosion. The solvent-dictated differences in photoanode stability were corroborated by photocurrent measurements of BiVO₄ before and after PEC in both solvents (Fig. 2b): The anode tested in H₂O exhibited a striking drop in photocurrent after 96 h of PEC electrolysis, whereas the photocurrents recorded in MeCN did not change. The

We report here the use of a PEC cell to mediate organic oxidation reactions using a photoanode immersed in organic media. The photoelectrochemical oxidation of benzyl alcohol, cyclohexene, and tetralin into their corresponding carbonyl compounds were demonstrated in a PEC cell containing a BiVO₄ photoanode immersed in MeCN containing appropriate reaction mediators (e.g., electrolyte, base, and electron transfer reagent). Product formation can be achieved using a 60% reduction in the applied voltage compared to a purely EC oxidation. Furthermore, no significant degradation of the photoanode was observed.

**Fig. 1** Summary of reaction conditions for alcohol oxidation and C-H functionalization. Three types of reaction conditions (chemical oxidation, EC oxidation at an electrode, and photoelectrochemical oxidation) that have been used for alcohol oxidation and C-H functionalization are shown. We report here C-H functionalization and oxidation by PEC.

**Fig. 2** Demonstration of lower BiVO₄ photocorrosion in MeCN than in H₂O. a) UV-Vis absorption spectra of BiVO₄ photoanodes before (black) and after 96 h of PEC in H₂O (blue) or MeCN (orange). b) Photocurrents of BiVO₄ photoanodes before (solid line) and after (dashed line) 96 h of PEC electrolysis in H₂O (blue) or MeCN (orange).
photoanodes tested in MeCN with increasing amounts of water also showed an increasing propensity for photocorrosion (Supplementary Table 1). The accelerated photocorrosion of BiVO₄ in H₂O was confirmed by scanning electron microscope (SEM) images of photoanodes before and after 96 h of PEC. Full coverage of FTO by spherical grains of BiVO₄ (Supplementary Fig. 2) are retained for the photoanodes subjected to 96 h of PEC electrolysis in MeCN, with visible FTO providing evidence for less uniform coverage in films exposed to aqueous PEC. This morphology change during PEC electrolysis in H₂O is widely known. While organic solvents increase the resistance of the PEC cell (~10−20 Ω with MeCN c.f. <10 Ω using water), merely ~30 mV in additional voltage is required at the low currents (~3 mA) relevant to this study. This additional voltage represents a modest energy penalty for the much higher photoanode stability.

**Photoelectrochemical alcohol oxidation.** Having validated the photostability of BiVO₄ in MeCN, we tested the oxidation of organic substrates using a PEC cell. All experiments were carried out in MeCN containing LiClO₄ electrolyte. Other organic solvents (e.g. acetone and CH₃NO₂) and electrolytes (e.g. Bu₄NClO₄ and Bu₄NPF₆) were tested but did not yield any discernible benefit in photocurrent or product yield. MeCN was utilized as the solvent because because the boiling point (82 °C) is sufficiently high to minimize evaporation during electrolysis and sufficiently low to circumvent interfering with the gas chromatography-mass spectrometry (GC-MS) analysis. LiClO₄ was selected on the basis of it being a cheap electrolyte that is soluble in organic media.

Linear sweep voltammetry (LSV) was measured under AM1.5 G light prior to performing PEC electrolysis (Fig. 3). Photocurrent profiles recorded on the BiVO₄ working electrode in 25 mL of MeCN containing 0.1 M LiClO₄, a glassy carbon counter electrode (CE), and an Ag/AgCl reference electrode (RE), generated nominal current below ca. 1 V. For each of the organic reactions in this study, pyridine served as the requisite base to accommodate deprotonation of N-hydroxysuccinimide (NHS), a soluble, transparent, and electrochemically active species that proved effective at mediating hole transfer from the electrode to the organic substrate. Baseline photocurrent profiles were measured prior to addition of 0.5 mmol of substrate: 4 equiv. pyridine (162 μL, 2 mmol) caused a small but detectable change in LSV photocurrent below 1 V (Fig. 3), while the subsequent addition of 40 mol% NHS (23 mg, 0.2 mmol) caused a more dramatic rise in current. The shoulder at 0.8 V (indicated by the vertical dashed lines in Fig. 3) is assigned to the oxidation of NHS⁻ to electrochemically-active NHS⁺. All organic oxidation reactions in this report were therefore carried out under an applied voltage of 0.8 V (denoted V_app), which is sufficiently low to avoid solvent and pyridine oxidation yet sufficiently positive to generate the NHS⁺ species required for oxidation of the organic substrates. The BiVO₄ photoanodes after 96 h of PEC with substrate exhibit minor differences in absorptivity and LSV photocurrents consistent with negligible photocorrosion (Supplementary Figs. 2 and 3), but not to a degree that compromises these experiments.

The facile oxidation of benzyl alcohol to benzaldehyde was selected as a proof-of-concept experiment because alcohol oxidation was previously shown to proceed at a BiVO₄ photoanode in H₂O. The photocurrent increased after the addition of 0.5 mmol benzyl alcohol to the PEC cell described above (Fig. 3a). This increase is assumed to be due to the consumption of NHS⁺ (which oxidizes benzyl alcohol) driving a faster NHS⁺ oxidation. The oxidation of benzyl alcohol into benzaldehyde was confirmed by GC-MS, with a reaction yield of 41% after 8 h of PEC electrolysis (Supplementary Fig. 4). While further optimization is still needed to make the yield of benzaldehyde competitive with the best available synthetic methods, the result demonstrates the viability of performing PEC in a non-aqueous medium. These experiments also demonstrate that NHS can act as a useful redox mediator in tandem with a BiVO₄ photoanode.

**Photoelectrochemical C-H oxidation.** With evidence of a successful photoelectrochemical oxidation in non-aqueous media, we next explored the more synthetically challenging oxidation of cyclohexene to cyclohexenone (Fig. 3b) and tetralin to 1-tetralone (Fig. 3c). In addition to using NHS as a redox mediator, an external oxygen source, tert-butyl hydroperoxide (‘BuOOH), is used to form the requisite ‘Bu peroxy-substrate adduct. (Supplementary Fig. 8) Prior to addition of 0.5 mmol of substrate,
η oxidation can be calculated by the following relationship:

\[
\eta = J^* (1.23 V - V_{app})/P_{in}, \quad J = \text{photocurrent density, } 1.23 V = E^0 (\text{O}_2/H_2O), \quad V_{app} = \text{applied potential in the PEC cell, and } P_{in} = \text{power density of illumination (100 mW cm}^{-2} \text{ in this study).}
\]

State-of-the-art BiVO₄ photoanodes that mediate PEC water oxidation at a V_{app} of 0.6 V generate \( J = 2.73 \text{ mA cm}^{-2} \) and therefore yield \( \eta = 1.7\% \). In our experiments in MeCN, the PEC cell was driven at 0.8 V to produce \( J = 3.8 \text{ mA/cm}^2 = 1.3 \text{ mA cm}^{-2} \). Our EC cell required 1.8 V to yield the same \( J \) value of 1.3 mA cm\(^{-2}\), and thus we assumed 1.8 V to effectively be the pseudo standard potential of NHS. Given that our illuminated photoanode area was 3 cm\(^2\) and our light intensity was 100 mW cm\(^{-2}\), the \( \eta \) of our cell is therefore 1.3\%. This analysis shows that our PEC organic oxidation system offers higher-valued organic products at approximately the same energy efficiency as traditional PEC water oxidation.

In summary, we have demonstrated that illumination of BiVO₄ immersed in organic media drives both alcohol oxidation and C-H activation/oxidation. The use of light can reduce the applied voltage of an EC oxidation process by 1 V. The use of organic media in place of water affords markedly higher semiconductor photostability, thereby enabling sustained photochemical conversion over at least 1 day. This alternative PEC cell design highlights the potential to generate higher-value small molecules compared to traditional PEC cells.

**Methods**

**Materials.** Bismuth nitrate hexahydrate (98%), vanadyl acetylacetonate (98%), and tungsten hexachloride (99%) were purchased from Strem Chemicals and used as received. All other chemicals were purchased from commercial vendors (Acros Organics, Alfa Aesar, Fisher Scientific, or Sigma-Aldrich) and used as received. FTO substrates (TEC 15) were purchased from Hartford Glass Co. Glassy carbon electrodes were purchased from Alfa Aesar.

**Electrode preparation.** BiVO₄ photoanodes were prepared in accordance with previously reported procedures. Bismuth nitrate hexahydrate (0.346 g, 0.713 mmol), vanadyl acetylacetonate (0.176 g, 0.663 mmol), and tungsten hexachloride (0.02 g, 0.035 mmol) were added to a 10 mL mixture of acetic acid and acetylacetone (1.8 v/v). The solution was sonicated for 15 min and then spin-coated onto a FTO substrate at 1000 rpm for 30 s. Each of the successive 16 coats was annealed at 500 °C for 10 min prior to a final 8 h annealing step at 500 °C. The BiVO₄ samples were irradiated with UV light (Model #: GPH4365TVH, Atlantic Ultraviolet Co.; \( \lambda_{\text{max}} = 254 \text{ nm and 185 nm; flux = 10 mW cm}^{-2} \) at 5.5 cm in our experiment) for 20 h. The geometric surface areas of all working electrodes (BiVO₄ photoanodes and glassy carbon electrodes) in this study were 3 cm\(^2\).

**Photoelectrochemical and electrochemical oxidation.** PEC and EC electrolyses were performed with a CHI 660D potentiostat in a three-electrode photoelectrochemical cell with a BiVO₄ photoanode (for PEC experiments) or glassy carbon (electrochemistry experiments) as the working electrode. Ag/AgCl as the RE, and glassy carbon as the CE. PEC measurements and electrolyses were conducted under AM1.5 G simulated sunlight with an Oriel 94011A-ES solar simulator integrated with a 100-W xenon arc lamp and AM1.5 G filter. An infrared water filter was applied to prevent the solution from heating up during PEC electrolysis. Experiments were performed in 0.1M LiClO₄ in 25 mL MeCN or 0.1M NaHCO₃ in H₂O (buffered to pH 7). Potentials were measured vs. Ag/AgCl, which was calibrated to 0.196 V vs. NHE in aqueous media. For the dark and photocurrent measurements, LSV was measured prior to performing electrolysis, and the scan rate was maintained at 10 mV s\(^{-1}\). For PEC and EC oxidations of organic substrates: pyridine (2 mmol, 4 equiv.), NHS (0.2 mmol, 40 mol%), \( \text{BuOOH} = 70\% \text{ in H}_2\text{O, 1.5 mmol, 3 equiv. for cyclohexene and tetralin oxidations) were added to 10 mL of 0.5 M MeCN solutions. Substrate oxidations were performed for 16 h in a 100-W xenon arc lamp and AM1.5 G filter. An infrared water filter was applied to prevent the solution from heating up during PEC electrolysis.}

**Gas chromatography-mass spectrometry**. Samples were taken during and after electrolysis and carvone was added as an internal standard. GC-MS measurements were run on an Agilent GC-MS instrument with a HP-5ms GC column and electron ionization ion source. A 1-μL aliquot was injected with a split sampling mode with a ratio of 20:1, and carvone was used as an internal standard. The oven temperature started at 60 °C for 1 min, then ramped from 100 to 150 °C at 20 °C min\(^{-1}\) and from 150 to 250 °C at 40 °C min\(^{-1}\). Detection was not performed for the first 1.75 min of the run, or the solvent delay time. GC-MS
peaks were identified using the NIST Mass Spectrometry Data Center database (all peak identifications exhibited a probability match of >90%) and compared with peaks in standard solutions. For quantitative analysis, a series of standard solutions with known concentrations of reactants and products were prepared and carvone was added as an internal standard. Standard solutions were run by GC-MS using the same method, and the relative peak areas of reactants and products were normalized to the internal standard peak. Linear calibration curves were plotted to quantify the concentrations of reactants and products.

**Physical methods.** Absorptivity measurements of BiVO₄ samples were collected with a PerkinElmer Lambda 35 UV-Vis spectrometer with a solid sample holder accessory. Baseline scans were recorded on clean FTO. X-ray diffraction characterization was conducted using a Bruker F8 Focus X-ray diffractometer. Data were collected between 2θ angles of 5° and 90° with a step size of 0.04° and the step time was 0.6 s. Film morphologies were investigated using a Helios NanoLab 650 Focused Ion Beam SEM, with the accelerating voltage kept at 1 kV and the current at 50 pA for imaging.

**Data availability.** The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding author upon request.

Received: 18 March 2017 Accepted: 27 June 2017 Published online: 30 August 2017

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**Acknowledgements**

Funding from The University of British Columbia 4YF Program, Canada Foundation for Innovation, Canada Research Chairs, NSERC, and CIFAR is gratefully acknowledged. Dr. Yun Ling in UBC Mass Spectrometry Centre is gratefully acknowledged for help with the GC-MS instrument.

**Author contributions**

C.P.B. and G.M.S. supervised this project; T.L., T.K., G.M.S., and C.P.B. wrote the manuscript. Preliminary experiments, J.H. performed the EC oxidation and K.E.D. obtained SEM images; T.L., T.K., G.M.S., and C.P.B. designed the experiments; T.L. performed the PEC oxidations and GC-MS analysis, T.K. performed preliminary experiments, J.H. performed the EC oxidation and K.E.D. obtained SEM images; T.L., T.K., G.M.S., and C.P.B. wrote the manuscript.

**Additional information**

Supplementary Information accompanies this paper at doi:10.1038/s41467-017-00420-y.

**Competing interests:** The authors declare no competing financial interests.

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