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Light-Driven Catalytic Upgrading of Butanol in a Biohybrid Photoelectrochemical System

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Abstract

This paper reports the design and preparation of a biohybrid photoelectrochemical cell (PEC) that can drive the tandem enzymatic oxidation and aldol condensation of *n*-butanol (BuOH) to C₈ 2-ethylhexenal (2-EH). In this work, BuOH was first oxidized to *n*-butyraldehyde (BA) by the alcohol oxidase enzyme (AOx), concurrently generating hydrogen peroxide (H₂O₂). To preserve enzyme activity and increase kinetics nearly 2-fold, the H₂O₂ was removed by oxidation at a bismuth vanadate (BiVO₄) photoanode. Organocatalyzed aldol condensation of C₄ BA to C₈ 2-EH improved the overall BuOH conversion to 6.2 ± 0.1% in a biased PEC after 16 h. A purely light-driven, unbiased PEC showed 3.1 ± 0.1% BuOH conversion, or ~50% of that obtained from the biased system. Replacing AOx with the enzyme alcohol dehydrogenase (ADH), which requires the diffusional nicotinamide adenine dinucleotide cofactor (NAD⁺/NADH), resulted in only 0.2% BuOH conversion due to NAD⁺ dimerization at the photoanode. Lastly, the application of more positive biases with the biohybrid AOx PEC led to measurable production of H₂ at the cathode, but at the cost of lower BA and 2-EH yields due to both product overoxidation and decreased enzyme activity.

Keywords

Bismuth vanadate; Alcohol oxidase; Aldol condensation; Green chemistry

INTRODUCTION

Multiple strategies, including water splitting¹⁻⁸ or CO₂ reduction with solar energy,⁹⁻¹⁶ have been developed to produce electrical energy or fuels from renewable energy sources,

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01849. UV-vis spectra of BiVO₄, LSV measurements, product extraction partitioning coefficients curves, ¹H NMR spectra of extracted products, ADH reaction results, hydroxyl radical formation verification tests, AOx reaction yields at varying biases, BiVO₄ electrodeposition data, the gas chromatograph calibration curve, enzyme control experiments, and a summary of results table (PDF)

The authors declare no competing financial interest.

including biological sources such as plants or microbes.¹⁷⁻²⁰ In addition to these strategies, alternative methods using mediated electron transfer between enzymes and electrodes have been employed to generate electrical power or fuel conversion.²¹⁻²⁴ While biofuels, including ethanol and *n*-butanol (BuOH), may be obtained from natural organisms or engineered strains, there remain significant challenges in separating and isolating the products directly from aqueous media.²⁵⁻²⁷ This problem is further exacerbated by the wide range of products obtained from a biological single source, including carboxylic acids, ketones, and alcohols.²⁸ One strategy to improve separation is to convert small molecules of interest to larger, hydrophobic molecules for simple liquid–liquid extraction. Because chain lengthening of substrates requires energy input, the upgrading process would ideally only utilize light as an energy source without any sacrificial reagents. While semiconductor nanocrystals have shown promise as photo-catalysts, the absorption of high-energy photons and oxidation of capping ligands are known to greatly reduce nanoparticle stability, thereby significantly reducing catalyst activity or eliminating it entirely.²⁹ For example, we recently used a CdS nanocrystal as a photocatalyst to help upgrade a C₄ alcohol to a larger C₈ hydrocarbon, but the reaction was limited to shorter time scales due to photodegradation and the eventual precipitation of the nanoparticles from solution.³⁰

Here, we show how the judicious choice of catalysts, reaction conditions, and electrode materials in a photoelectrochemical cell (PEC) provides continuous upgrading of C₄ alcohols to C₈ aldehydes under many hours of constant illumination. In this reaction (Scheme 1), C₄ BuOH is first converted to C₄ *n*-butyraldehyde (BA) by enzymatic oxidation, followed by aldol condensation to produce C₈ 2-ethylhexenal (2-EH). Enzymes are well-suited for oxidizing alcohols to aldehydes without overoxidation, but enzyme choice is critical for sustaining activity over extended periods. Additionally, because of the wide range of fermentation products generated from biological sources, the promiscuity of substrates that the enzymes can oxidize can be an important factor for improving the versatility of this process. In this work, we first show that alcohol oxidase (AOx) can continuously oxidize short-chain alcohols to aldehydes by removing the formed H₂O₂ to prevent accumulation and enzyme inhibition.³¹⁻³³ For this, we first demonstrate that BiVO₄, a promising semiconductor material that shows long-term stability and absorption in the visible spectrum (~2.4 eV), can remove the H₂O₂ photoelectrochemically at low applied potentials which we also show is critical for maintaining enzyme stability and activity.³⁴⁻³⁶ Then, using a BiVO₄/Pt cell with AOx, we show that BuOH can be converted to butyraldehyde (BA) with 5.2 ± 0.1% conversion after 16 h of photoirradiation. In the absence of light, the enzyme alone showed only 2.8 ± 0.1% BuOH oxidation to BA, demonstrating that the photoanode helped to increase enzyme kinetics by continuous removal of the formed H₂O₂. Next, the organo-catalyst β -alanine, to run the carbon–carbon coupling of BA to the C₈ 2-EH, was added to yield a mild increase in BuOH conversion. Finally, while no hydrogen gas was produced at 0 V or more negative biases, at applied biases >0 V, measurable amounts of hydrogen were generated, though with lower BA and 2-EH yields.

RESULTS AND DISCUSSION

The BiVO₄ photoanode was prepared on indium–tin–oxide-coated (ITO-coated) glass electrodes using the electrodeposition method developed by Kim and Choi.³⁵ Briefly, a

bismuth oxyiodide (BiOI) layer was formed on ITO from a solution of KI, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and *p*-benzoquinone. A potential of -0.1 V vs Ag/AgCl (3.0 M KCl) was applied until a total charge of 0.13 C cm^{-2} was passed. The resulting orange-brown BiOI layer was then rinsed with water and air-dried before deposition in a solution of vanadyl acetylacetonate in DMSO, followed by annealing at 450°C for 2 h. Excess V_2O_5 was removed by soaking the electrodes in aqueous 1 M NaOH for 30 min. UV-vis spectroscopy of the BiVO_4 electrode showed strong absorbance at 550 nm with a band gap ~ 2.25 eV (Figure S1). The photocurrent response was then measured using linear sweep voltammetry (LSV) at 5 mV s^{-1} under chopped illumination (9 W, 465 ± 30 nm light-emitting diode (LED), 4.5 W cm^{-2}) in 0.1 M phosphate buffer (PB) at pH 7.5. As shown in Figure S2, the anodic onset of the BiVO_4 electrode was seen at -0.4 V vs Ag/AgCl in Ar-purged PB. Next, LSV measurements of the BiVO_4 photoanode in the presence of H_2O_2 were run at 5 mV s^{-1} (Figure 1) in unpurged PB. Upon photoirradiation, the anodic onset began at 0 and -0.4 V in PB alone and 15 mM H_2O_2 , respectively, and current densities increased linearly with H_2O_2 concentrations ranging from 5 to 15 mM.

The BiVO_4 electrodes were next tested for oxidizing H_2O_2 generated by the enzyme AOX during conversion from BuOH to BA. For this, a three-electrode-compartment cell composed of a BiVO_4 photoanode, a Ag/AgCl reference, and Pt counter electrode was fabricated (Figure S3). The three compartments were separated by 0.3 cm wide porous glass frits ($15\text{--}50 \mu\text{m}$) with a total reaction volume of 15 mL. The starting concentration of BuOH was set at 50 mM ($750 \mu\text{mol}$) to mimic the typical yields of BuOH produced either from *Clostridium acetobutylicum* or engineered *Escherichia coli*.³⁷⁻³⁹ The enzyme, AOX, was then added at a final concentration of $0.4 \mu\text{M}$ (25 units) to the compartment holding the BiVO_4 electrode; despite being small enough to diffuse through the porous frits, the enzyme was not found in the neighboring compartment during product extraction. After 15 min in the dark to allow for H_2O_2 accumulation by AOX oxidation of BuOH, the BiVO_4 anode was photoirradiated (9 W, 465 ± 30 nm LED) at a constant potential of 0 V for 2, 8, 16, and 24 h. Initially, 0 V was utilized because LSV studies with the BiVO_4 electrodes showed the largest difference in photocurrent at this bias in the presence of H_2O_2 as compared to PB alone (Figure 1). First, transient BiVO_4 photocurrents (Figure 2a) showed high photostability and repeatability over the 24 h reaction. In triplicate measurements, photocurrents peaked after 3 h to $246 \pm 6 \mu\text{A}$, which is 2.4 and 1.8 times greater than BiVO_4 photocurrents in the presence of PB or 50 mM BuOH in PB, respectively. The higher photocurrents in the presence of AOX and BuOH show the oxidation of H_2O_2 at the photoanode generated by AOX *in situ*. After 6 h, the photocurrents gradually decreased, which is attributed to the loss of AOX activity over time, until a steady-state current was reached after 10 h. Upon completion, an aliquot of the reaction mixture in each compartment was extracted with deuterated chloroform (CDCl_3), and BA formation was quantified by ^1H NMR spectroscopy using tetramethylsilane (TMS) as an internal standard. Since complete BA extraction is difficult to achieve because of equilibration to the hydrate,⁴⁰ the amount of oxidized BuOH was determined using partition coefficient standards (Figure S4a). As shown in Figure 2b, photo-illuminating BiVO_4 in the presence of AOX and BuOH nearly doubled the enzyme activity from 218 to 405 h^{-1} over 16 h. After 16 h of irradiation, the BA yield peaked at $38.8 \pm 0.7 \mu\text{mol}$, which decreased slightly to $36.8 \pm 1.5 \mu\text{mol}$ after 24 h. In contrast, when the

reactions were run under photoirradiation but without AOx, only $5.0 \pm 0.4 \mu\text{mol}$ of BA formed along with trace amounts of butyric acid (BTA) after 16 h. These results suggest that after a period of time the AOx loses its activity, which reduces the production of H_2O_2 , causing the BA present to be subsequently oxidized to the acid. The product yields with and without photoirradiation for this biohybrid PEC are summarized in Table S1.

To study the effect of higher AOx concentrations, $0.8 \mu\text{M}$ (50 units) of AOx was next tested with the BiVO_4/Pt PEC. After 16 and 24 h, 43.0 ± 1.9 and $50.6 \pm 1.3 \mu\text{mol}$ of BA were detected. While AOx activity slows considerably between 16 and 24 h, we did not observe the decrease in BA after 24 h that we saw with 25 units. Because a significant increase in the total BuOH conversion to BA was not observed, even with double the enzyme concentration, we next tested the activity of AOx with BuOH in the PEC in the absence of photoirradiation. As shown in Figure 2b, when $0.4 \mu\text{M}$ AOx was allowed to react for 48 h without photoirradiation, the measured BA yield was $35.2 \pm 2.2 \mu\text{mol}$, which closely matches the 16 h yields with light. Additionally, after 64 h only $42.6 \pm 2.4 \mu\text{mol}$ of BA was measured, which suggests that AOx undergoes significant deactivation after converting roughly 35–40 μmol of BuOH to BA independently of photoirradiation. Control experiments starting with BA in solution did not show AOx inhibition, which suggests that an additional deactivation mechanism is occurring. A previous report with AOx showed that, during methanol oxidation in the presence of catalase, deactivation occurs at a “significant rate” after high turnovers, but because of the formation of turbidity, a specific chemical event could not be identified.⁴¹

In an effort to shift reaction equilibria, improve BuOH conversion, and generate products of higher energy, the organocatalyst β -alanine was next incorporated into the PEC to convert the C_4 BA to C_8 2-EH through aldol condensation.⁴² For this, 550 mM β -alanine organocatalyst was added to the PB electrolyte while the AOx and BuOH concentrations were kept constant. After the AOx was allowed to react in the dark for 15 min, the BiVO_4 anode was photoirradiated and maintained for 8, 16, and 24 h at 0 V bias. As before, the solutions were extracted with CDCl_3 , and the amount of BA and 2-EH formed was quantified by ^1H NMR spectroscopy using partition coefficient standards (Figure S4a,b). A typical ^1H NMR spectrum of BA and 2-EH products is shown in Figure S5. After 24 h of irradiation, starting from 50 mM BuOH, the amounts of BA and 2-EH at 0 V were measured to be 27.5 ± 1.4 and $12.1 \pm 0.9 \mu\text{mol}$, respectively, which correspond to $51.5 \pm 3.1 \mu\text{mol}$ ($6.9 \pm 0.4\%$) overall BuOH conversion (Figure 3a). Under identical conditions, without photoirradiation, overall BuOH conversion was $19.9 \pm 2.2 \mu\text{mol}$ ($2.6 \pm 0.3\%$), which is $61.4 \pm 1.9\%$ lower than that obtained with light. As compared to the amount of BuOH oxidized in the absence of organocatalyst, BuOH conversion improved with the addition of β -alanine by only $19.2 \pm 0.3\%$ after 16 h. Transient measurements showed that aldol condensation proceeded slowly in the first 8 h because of either insufficient amounts of BA present or the previously identified low turnover frequencies (TOFs) of β -alanine for aldol condensation in water (Figure 3a,b).³⁰ Only after 8 h, when BA yields were greater than $17.9 \pm 1.1 \mu\text{mol}$ ($1.2 \pm 0.1 \text{ mM}$), did we see a 5-fold increase in 2-EH yields to $12.1 \pm 0.9 \mu\text{mol}$ from 8 to 24 h. These results may explain why the addition of β -alanine did not significantly improve BuOH conversion. Since aldol coupling only occurs after significant BA accumulation, the enzyme

AOx has already turned over many times. Thus, by the time BA has converted to 2-EH, less BuOH oxidation to form BA is occurring since the enzyme has already become deactivated.

Unbiased BiVO₄/Pt experiments were also performed to investigate product yields from a purely light-driven PEC. On the basis of previous unbiased PEC work,¹⁶ these experiments were performed with a 1 kΩ resistor connected between the photoanode and the Pt cathode. The full reaction with AOx/BuOH/ β -alanine generated 16.1 ± 0.3 μ mol of BA and 3.5 ± 0.3 μ mol of 2-EH after 16 h of photoirradiation. Although the unbiased results show ~50% less conversion than the biased system, the unbiased PEC showed ~30% better conversion than the biased, dark reaction (Figure 4). These unbiased results illustrate the effectiveness of this biohybrid PEC for light-driven BuOH upgrading without the need for electrical biasing.

As a comparison to using the promiscuous AOx enzyme in the PEC, a more substrate-specific enzyme, ADH (alcohol dehydrogenase), was also studied.³³ While ADH is also known to perform alcohol oxidation, it is dependent on the diffusional cofactor NAD⁺/NADH rather than a bound FAD.³⁰ In the case of NAD⁺-dependent ADH, the reaction thermodynamics heavily favor the alcohol, requiring continuous regeneration of NAD⁺ via NADH oxidation for increased BA production.⁴³ From LSV measurements, the BiVO₄ photoanode showed a strong photocurrent response for NADH oxidation from -0.4 to +0.1 V vs Ag/AgCl (Figure S6). However, PEC reactions with analogous loadings (25 units of ADH (0.1 μ M), 1 or 5 mM NAD⁺, and 0 V bias) produced <2 μ mol of BA and 0 μ mol of 2-EH after 16 h (Figure S7a). In addition, we observed a yellowing of the ADH/NAD⁺/NADH solution (Figure S7b), which we attributed to the overoxidation of NADH and formation of NAD-dimer complexes induced by hydroxyl radical formation by the BiVO₄ photoelectrodes.⁴⁴⁻⁴⁶ The presence of these radicals was confirmed using aminophenyl fluorescein (APF), a fluorogenic sensor for hydroxyl radicals (Figure S8). Despite the incorporation of radical scavengers and testing of other electrolytes, the BA and 2-EH yields could not be improved.

Finally, the formation of H₂ at the Pt cathode in the AOx-containing PEC was also measured. The reason to do this is to explore the possibility of hydrogenating the α,β -unsaturated aldehydes formed by aldol condensation to enable continued carbon-carbon coupling or to produce higher-energy (saturated) products. For this, since the conduction band edge of BiVO₄ is just below the redox potential of H₂, it was difficult to detect any H₂ at potentials below 0 V or unbiased. However, at potentials greater than 0 V, even in the unpurged electrolytic solution, H₂ could be detected in the gas phase over a 3 h period (Figure S9a). However, BA and 2-EH formation also decreased, which was likely due to the overoxidation of BA to BTA and AOx deactivation due to electrostatic interactions with the anode, since the reported isoelectric point of AOx is 6.1.⁴⁷ A summary of BA and 2-EH yields after 24 h are shown in Figure S9b at potentials ranging from -0.2 to 0.4 V.

CONCLUSION

In conclusion, we have demonstrated the fabrication and testing of a biohybrid PEC for catalytically upgrading a low-molecular-weight C₄ alcohol to a longer-chain C₈ product, thus converting a common water-soluble cell metabolite to an oil-extractable product with

higher-energy content. Photoirradiation of a BiVO₄ anode promoted the oxidation of BuOH to BA catalyzed by AOx. Because the H₂O₂ product was removed by photooxidation, the rate of enzyme activity increased by 1.9-fold over that of the reaction in the dark after 16 h. The addition of the organocatalyst, β -alanine, showed a mild increase in BuOH conversion through carbon–carbon coupling of the enzyme-derived BA to the final C₈ product, 2-EH. It was found, however, that because the AOx activity reduced over 16–24 h and because of slow aldol condensation rates, adding β -alanine did not show significant gains in BuOH conversion. However, in comparison to AOx, the NAD-dependent ADH showed only 0.2% BuOH conversion, presumably due to NAD⁺ dimerization and subsequent ADH inactivation. Lastly, since H₂ could be formed at the Pt cathode, the AOx/BuOH/ β -alanine PEC was tested for H₂ generation at varying biases. Because of the overall potentials of the BiVO₄/Pt electrodes, while little-to-no H₂ was detected at 0 V, more positive biases resulted in the detection of H₂ in the gas phase over a period of 3 h. However, the increasing bias also reduced product yields and AOx activity, necessitating PECs that can function with light alone for catalytic upgrading. Future studies will investigate the fabrication and testing of other photoanodes and photocathodes for this application.

EXPERIMENTAL SECTION

General Information.

All chemicals and solvents were analytical grade and used as-received from commercial sources. Alcohol oxidase solution from *Pichia pastoris* (AOx, 1.1.3.13), alcohol dehydrogenase from *Saccharomyces cerevisiae* (ADH, 1.1.1.1), β -nicotinamide adenine dinucleotide sodium salt (NAD⁺), phosphate buffer solution (PB), β -alanine, n-butylaldehyde (BA), bismuth(III) nitrate penta-hydrate (Bi(NO₃)₃·5H₂O), vanadyl acetylacetonate (VO(acac)₂), and deuterated chloroform (CDCl₃) containing 0.03% (v/v) trimethylsilane (TMS) were purchased from Sigma-Aldrich. ADH is reported to have 369 units/mg on the basis that one unit converts 1.0 μ mol of ethanol to acetaldehyde per minute at pH 8.8 and 25 °C. Similarly, AOx is reported to oxidize 1.0 μ mol of methanol to formaldehyde per minute at pH 7.5 at 25 °C. β -Nicotinamide adenine dinucleotide disodium salt hydrate (NADH) and 2-ethylhexenal (2-EH) were purchased from TCI Chemicals. *p*-Benzoquinone was purchased from Alfa Aesar. Nitric acid (HNO₃) was purchased from Macron Chemicals. Butanol (BuOH) and potassium iodide (KI) were purchased from Fisher Scientific. Unpolished float glass, 9 × 22 × 1.1 mm³, SiO₂ passivated/indium–tin–oxide (ITO) electrodes were purchased from Delta Technologies, Ltd. Double-distilled water (dd-H₂O) used as a reaction solvent was deionized using a Milli-Q Advantage A-10 water purification system (Millipore). UV–vis spectra were acquired on a DU 730 spectrophotometer (Beckman Coulter).

BiVO₄ Electrodeposition.

Nanoporous BiVO₄ photoanodes were produced as previously reported by Kim and Choi.³⁵ In detail, a 25 mL solution containing 0.4 M KI, adjusted to pH 1.7 with HNO₃, was prepared. Bi(NO₃)₃·5H₂O was then dissolved into this solution to yield 0.04 M Bi(NO₃)₃. The resulting solution was mixed with 10 mL of 0.23 M *p*-benzoquinone in absolute ethanol (100%) and vigorously stirred for at least 5 min. Electrodeposition was performed using a

three-electrode cell with an ITO working electrode, Ag/AgCl (3.0 M KCl) reference electrode, and a platinum foil counter electrode. Before electrodeposition, the ITO working electrode was cleaned ultrasonically in ethanol and then dried using an oven at 100 °C. Cathodic deposition was performed potentiostatically at -0.1 V vs Ag/AgCl at room temperature until a total charge of 0.13 C cm⁻² was passed. The current and charge profile is shown in Figure S10a. Upon completion, the orange-brown BiOI electrodes were gently rinsed with dd-H₂O and air-dried. 100 μ L of a 0.2 M VO(acac)₂ DMSO solution was placed on the BiOI film and then annealed at 450 °C for 2 h (2 °C min⁻¹). Once the electrodes were slowly cooled to room temperature, they were soaked in a 1 M NaOH solution for 30 min with gentle stirring. The resulting BiVO₄ electrodes were rinsed with dd-H₂O and dried at room temperature before measurements. Figure S10b-d shows the electrodes throughout the synthesis procedure.

Photoelectrochemical Measurements.

Photoelectrochemical measurements were performed using a Metrohm-Autolab potentiostat (Model PGSTAT204) using Nova 2.1 software. LSV measurements were performed in a one-compartment cell in which Pt foil was used as the counter electrode and Ag/AgCl (3.0 M KCl) was used as the reference electrode. For all chronoamperometry experiments, a custom-built three-electrode PEC was used (Figure S3), where the total volume was 15 mL of unpurged, 0.1 M phosphate buffer at pH 7.5. In all photocatalysis experiments, a 9 W, 465 $\pm$ 30 nm LED was utilized with back illumination on the photoanode with gentle stirring in this compartment. In unbiased experiments, the BiVO₄ photoanode was connected to the Pt cathode by copper wire with a 1 k Ω resistor in series.

NMR Spectroscopy.

¹H NMR spectroscopy was performed by using a 400 MHz Bruker AV III spectrometer. For a typical measurement, an aliquot (1 mL) from each of the three compartments was extracted with 200 μ L of CDCl₃ containing 0.03% (v/v) TMS three times for a total CDCl₃ volume of 600 μ L. Product concentrations were integrated by using MestreNova software 10.0.2 (Mestrelab Research) after the phase was corrected, the drift correction was changed to 0%, and the zero-filling was changed to 128 K. The integrations were determined by comparing the absolute values of the integration to that of the internal standard, TMS (2.2 mM). A typical ¹H NMR spectrum of BA and 2-EH products is shown in Figure S5.

GC Measurements.

H₂ amounts were recorded using an HP/Agilent 6890 (G1540A) system equipped with a 5 Å column and a thermal conductivity detector by injecting a 100 μ L sample from the 35 mL headspace. H₂ was quantified using the calibration curve shown in Figure S11.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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ABBREVIATIONS

PEC	photoelectrochemical cell
BuOH	<i>n</i> -butanol
BA	<i>n</i> -butyraldehyde
2-EH	2-ethylhexenal
BTA	butyric acid
AOx	alcohol oxidase
FAD	flavin adenine dinucleotide
ADH	alcohol dehydrogenase
NAD⁺	β -nicotinamide adenine dinucleotide
NADH	β -nicotinamide adenine dinucleotide (reduced)
PB	phosphate buffer
TMS	tetramethylsilane
APF	aminophenyl fluorescein

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Figure 1. Linear sweep voltammogram (5 mV s⁻¹) of the BiVO₄ photoanode under illumination at λ = 465 nm in unpurged, 0.1 M phosphate buffer (PB) at pH 7.5. The inset shows the increase in current with H₂O₂ concentration at 0 V vs Ag/AgCl.

Figure 2.

(a) Photocurrent summary over 24 h of the 0.4 μM AOx and 50 mM BuOH reaction with and without photoirradiation on the BiVO_4 photoanode in unpurged, 0.1 M PB at pH 7.5 with an applied bias of 0 V vs Ag/AgCl. (b) Transient BA yield profiles from reaction conditions described in Figure 2a. Error bars indicate one standard deviation (SD) from triplicate measurements.

Figure 3.

(a) Transient BA and 2-EH yield profile with (8, 16, and 24 h) and without (16 and 24 h-L) light and (b) 24 h photocurrent profile starting from 0.4 μM AOx, 50 mM BuOH, and 550 mM β -alanine on the BiVO_4 photoanode in unpurged, 0.1 M PB at pH 7.5 with an applied bias of 0 V vs Ag/AgCl. Error bars indicate one SD from triplicate measurements.

Figure 4.

Comparison of unbiased BA and 2-EH yields with light to 0 V vs Ag/AgCl biased results with and without light after 16 h starting from 0.4 μM AOx, 50 mM BuOH, and 550 mM β -alanine in unpurged, 0.1 M PB at pH 7.5. Error bars indicate one SD from triplicate measurements.

Scheme 1. Overall Reaction Scheme for Light-Driven *n*-Butanol (BuOH) Upgrading to *n*-Butyraldehyde (BA) to 2-Ethylhexenal (2-EH) in a Biohybrid Photoelectrochemical Cell (PEC)^a
^aBuOH oxidation to BA catalyzed by alcohol oxidase (AOx) produces hydrogen peroxide (H₂O₂). H₂O₂ is removed by oxidation on the bismuth vanadate (BiVO₄) photoanode and H₂ generation at the Pt cathode under biases >0 V vs Ag/AgCl. The BA product is then upgraded via aldol condensation and is catalyzed by β -alanine to 2-EH.