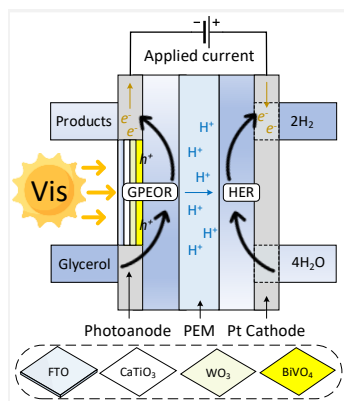


A novel multi-layered $\text{CaTiO}_3/\text{WO}_3/\text{BiVO}_4$ photoanode for enhanced glycerol valorization and hydrogen production

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This study explores the fabrication, characterization, and application of a novel multi-layered photoanode composed of calcium titanate (CaTiO_3), tungsten trioxide (WO_3), and bismuth vanadate (BiVO_4) (CWB). The photoanode was applied to glycerol oxidation, with simultaneous hydrogen (H_2) production using a platinum cathode. Characterization results revealed enhanced current densities for the CWB photoanode under visible light conditions, stating its photoactivity. At a current density of 10 mA cm^{-2} , glycerol was converted at the anode into dihydroxyacetone (DHA), glyceric acid (GEA), and formic acid (FA) with an overall Faradaic efficiency (FE) of 64%. Additionally, H_2 was produced at the cathode with a production rate of $0.55 \text{ mmol m}^{-2} \text{ s}^{-1}$. These findings indicate a promising advancement towards the sustainable production of valuable chemicals and fuels in photo-electrochemical (PEC) electrolyzers.

Introduction

The pursuit of sustainable and efficient energy conversion has attracted significant attention in coupling anodic and cathodic reactions in PEC electrolyzers for simultaneous organics oxidation to valuable products and hydrogen (H_2) production [1]. Multi-layered photoanodes composed of materials such as calcium titanate (CaTiO_3), tungsten trioxide (WO_3), and bismuth vanadate (BiVO_4) (e.g., $\text{CaTiO}_3/\text{BiVO}_4$ and $\text{BiVO}_4/\text{WO}_3$) have already been fabricated, demonstrating promising results for water splitting [2, 3]. Here, we present a novel multi-layered material composed of $\text{CaTiO}_3/\text{WO}_3/\text{BiVO}_4$ (CWB) in a 21:16:63 mass ratio. The new material was thoroughly characterized electrochemically and applied to glycerol photoelectro-oxidation reaction (GPEOR) simultaneously with hydrogen evolution reaction (HER).

Material and Methods

FTO-coated glass substrates with a geometric area of 10 cm^2 underwent ultrasonic cleaning and drying at $105 \text{ }^\circ\text{C}$. Catalyst inks were deposited onto the clean FTO-coated glass substrates via automated spray pyrolysis, with CaTiO_3 , WO_3 , and BiVO_4 powders loaded at 1, 0.75, and 3 mg cm^{-2} , respectively, using isopropanol as the solvent and Nafion D521 as the binder in a 70:30 ratio [2, 3]. The setup utilized for PEC characterization was an adapted filter-press flow reactor (Micro Flow Cell from ElectroCell, Denmark) with separated anodic and cathodic compartments by a Nafion[®] 117 proton exchange membrane (PEM). There was a window on the anode side for the photoanode irradiation. The

fabricated CWB photoanode was applied and irradiated with visible light ($\lambda_{\text{peak}} = 450 \text{ nm}$) at 100 mW cm^{-2} . A platinized-titanium plate acted as cathode for H_2 production. An Ag/AgCl reference electrode was placed in the catholyte compartment. For characterization purposes, both compartments were fed with a 0.5 M potassium bicarbonate (KHCO_3) solution at pH 8.7, flowing at 5.7 mL min^{-1} . For PEC experiments involving GPEOR, an aqueous solution containing 1.0 M glycerol and 0.5 M KHCO_3 was used as anolyte under single-pass operation [4] and the catholyte was 0.5 M KHCO_3 . On-off characterization included linear sweep voltammetry (LSV) between -1.7 and -0.8 V (vs. Ag/AgCl) at a scan rate of 50 mV s^{-1} ; chronopotentiometry (CP) at different current densities (j) of -10 , -45 , -90 , and -200 mA cm^{-2} for 60 min; and electrochemical impedance spectroscopy (EIS) at 0.8 V (vs. Ag/AgCl) over a frequency range of 100 kHz to 0.1 Hz . H_2 , dihydroxyacetone (DHA), glyceric acid (GEA), and formic acid (FA) contents were determined using chromatography techniques.

Results and Discussion

LSV results (Figure 1) show that the photocurrent density was higher than the current density under dark conditions, highlighting the positive effect of visible light illumination, especially at more negative potentials. At -1.56 V vs Ag/AgCl, the photocurrent density reached -152 mA cm^{-2} , a 28% improvement over the -119 mA cm^{-2} observed in the dark. These results were confirmed by CP values (Figure 2). A voltage of -1.45 V vs Ag/AgCl resulted in a photocurrent density of -200 mA cm^{-2} . In our previous

work [4], a $\text{CaTiO}_3/\text{BiVO}_4$ photoanode achieved only -71 mA cm^{-2} at a higher voltage of $-1.8 \text{ V vs Ag/AgCl}$. These results indicate that the novel photoanode configuration with three layers is more efficient, achieving better performance with less applied voltage.

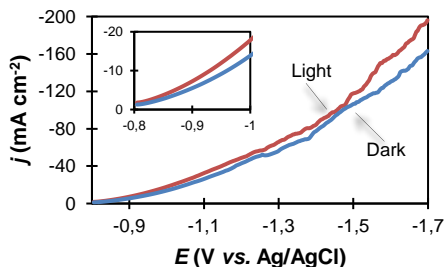


Figure 1. LSV curves for the CWB photoanode under light (100 mW cm^{-2}) and dark conditions using KHCO_3 as electrolyte (scan rate of 50 mV s^{-1}).

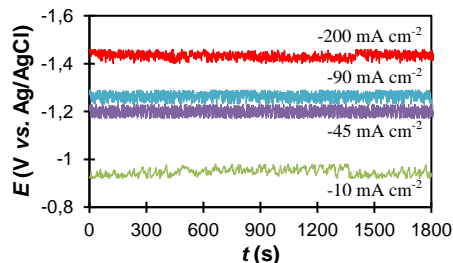


Figure 2. CP results (100 mW cm^{-2}) for the CWB photoanode for different fixed j using KHCO_3 as electrolyte.

EIS measurements (Figure 3) show a lower resistance under visible light irradiation compared to dark conditions both in the absence and presence of glycerol, suggesting more effective charge separation and electron transfer upon irradiation. Moreover, a larger semicircle diameter can be observed in the presence of glycerol, indicating a higher charge transfer resistance. This can be attributed to an increase of the viscosity in the presence of glycerol, which may have hindered the

Conclusions

The novel $\text{CaTiO}_3/\text{WO}_3/\text{BiVO}_4$ photoanode demonstrated enhanced photoactivity, promoting superior PEC performance for GPEOR and H_2 production. Glycerol acted as a donor of electrons for an improved H_2 generation while producing valuable products at the anodic compartment.

Acknowledgments

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efficiency of ion movement between the bulk solution and the surface of the catalyst, and vice versa [5].

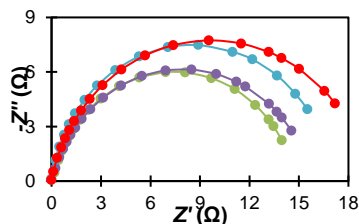


Figure 3. EIS results for the CWB photoanode under light (100 mW cm^{-2}) and dark conditions using different anolytes and KHCO_3 0.5 M as catholyte. Legend: (green) KHCO_3 0.5 M under light, (purple) KHCO_3 0.5 M in dark, (blue) KHCO_3 0.5 M + Glycerol 1.0 M under light, and (red) KHCO_3 0.5 M + Glycerol 1.0 M in dark.

PEC experiments for GPEOR and HER reactions were carried out during 40 min reaction at constant current density of 10 mA cm^{-2} , resulting in -0.94 V or $-0.96 \text{ V vs. Ag/AgCl}$ at the cathode under light or dark conditions, respectively. At the anode under light irradiation, valuable glycerol-derived products were formed, with production of $117 \pm 5 \text{ mg L}^{-1}$ of DHA, $52 \pm 2 \text{ mg L}^{-1}$ of GEA, and $69 \pm 4 \text{ mg L}^{-1}$ of FA, with a Faradaic efficiency (FE) of 64%. In the dark, $99 \pm 4 \text{ mg L}^{-1}$ of DHA, $28 \pm 1 \text{ mg L}^{-1}$ of GEA, and $64.40 \pm 0.04 \text{ mg L}^{-1}$ of FA were generated, which represents a FE of 49%. The introduction of light lowered the anodic potentials, thereby diminishing the impact of the oxygen evolution reaction (OER) as a competing reaction. Under the illumination of the anolyte compartment, the cathode achieved a H_2 production rate (r) of $0.55 \pm 0.02 \text{ mmol m}^{-2} \text{ s}^{-1}$, with an energy consumption (EC) of $383 \pm 15 \text{ kWh kmol}^{-1}$ and an energy efficiency (EE) of 64%. In the dark, the r was $0.54 \pm 0.01 \text{ mmol m}^{-2} \text{ s}^{-1}$, the EC was $504 \pm 6 \text{ kWh kmol}^{-1}$, and the EE was 61%. The performance of the PEC cell may have been enhanced by the presence of glycerol, which acts as a hole scavenger and electron donor, reducing electron-hole recombination [6].