

3D-Printed Photoelectrochemical Cell and its Application in Evaluation of BiVO₄ Photoanodes: Supplementary

Material

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Materials and methods

Reagents

Bi(NO₃)₃•5H₂O, NH₄VO₃, ethylenediamine and p-benzoquinone were purchased from Acros Organics. Ethylene glycol, hydrazine hydrate, Triton X-100, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI) and vanadyl acetylacetonate were obtained from Fisher Scientific. Dimethyl sulfoxide (DMSO) was purchased from Fluorochem Ltd. All chemicals were analytical grade and were used without further purification. Solutions were prepared using ultrapure MilliQ water.

Photoelectrode preparation – Hydrothermal method

BiVO₄ catalyst was synthesised following four different methods adapted from literature procedures. Three of them were hydrothermal approaches, where BiVO₄ was synthesised with only the bismuth and vanadium precursors (referred to as HT photoanode in the results) or with the addition of hydrazine hydrate (HH) or ethylene glycol (EG). In the HT method (1), Bi(NO₃)₃•5H₂O (0.20 g, 0.44 mmol) and NH₄VO₃ (0.05 g, 0.43 mmol) were dissolved in a round bottom flask containing 100 mL of distilled water. As an alternative, 1 mL of ethylenediamine and 1 mL of hydrazine hydrate (80%) were added dropwise for the HH method (2). For the EG

method (3), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.25 g, 0.52 mmol) was dissolved in 5 mL ethylene glycol in continuous stirring. Then, NH_4VO_3 (0.06 g, 0.51 mmol) was added to the reactor and stirred until complete dissolution. The HT, HH and EG solutions were kept at 70 °C for 12 h and allowed to cool down to room temperature. For the EG method, 100 mL of distilled water were then added dropwise. The resulting yellow precipitates were collected and washed multiple times with distilled water and ethanol before drying at 70 °C under air for 10 h.

Fluorine tin oxide (FTO) electrodes (50 mm x 50 mm x 2.2 mm) (MSE supplies USA) were cleaned with acetone and allowed to dry at room temperature. Then the electrodes were fixed with adhesive tape leaving an uncovered surface of approximately 3 cm x 3 cm. Each BiVO_4 catalyst was mixed with 0.9 mL of either EMI (4) or Triton-X (5) to form a colloidal paste. The paste was spread over the FTO sheet by doctor-blading technique using an Elcometer (60 μm) and allowed to dry for a few minutes (< 5 min). The adhesive tape was then removed, and the electrodes were kept in a hot plate (Detlef Gestigkeit- model PR 5 3T) where the temperature was increased with a ramp rate of 5 °C·min⁻¹ to 450 °C, kept stable for 15 min, and then cooled down to room temperature.

Photoelectrode preparation – Electrodeposition method

The fourth photoanode (ED) was prepared by electrodeposition (6). A 0.04 M $\text{Bi}(\text{NO}_3)_3$ in 0.4 M aqueous KI (pH 1.7) solution and a 0.23 M p-benzoquinone in absolute ethanol solution were prepared. Then, the solutions were mixed thoroughly at a Bi-KI to a benzoquinone-ethanol ratio of 1.9 to obtain the electrodeposition solution. The FTO electrode was cleaned by sonication for 15 min in acetone and MilliQ water. After, it was connected to the potentiostat as a working electrode, whereas a platinum mesh was used as the counter electrode and Ag/AgCl was the reference electrode. A potential of -0.1 V vs Ag/AgCl was applied for 90 min to deposit the BiOI on the electrode surface. Then, 0.4 M vanadyl acetylacetonate was prepared in DMSO, and 810 μL of that solution was drop casted on the FTO after 90 min to obtain BiVO_4 . After dropcasting

the electrode was placed in hot plate and heated up to 450 °C (ramp rate of 5 °C·min⁻¹). Finally, the FTO was soaked in NaOH solution to wash out the excess vanadyl acetonate and dried at room temperature. The photos of electrode prepared through electrodeposition method are shown in Fig S9, the vanadyl acetylacetonate concentration and temperature ramp rate were optimised for the area of the electrode to obtain a homogenous film.

BiVO₄ photocatalyst characterisation

The X-ray diffraction (XRD) patterns of BiVO₄ were recorded on an Inel Equinox 6000 system with a 0.154056 nm Cu α -1 X-ray source. The morphologies of BiVO₄ were examined by a Hitachi S7400 scanning electron microscope. The photoelectrochemical properties were investigated using a Metrohm Autolab M204 potentiostat.

Photoelectrochemical cell set-up

The test cell used in this study (Figure S7) was specifically designed to ensure a reliable and replicable analysis of the photoelectrode. The frame, which was 3D printed in UV-cured resin material, consisting of a base and a top part square in shape (7 cm x 7 cm). The base had a chamber of approximately 20 mL volume hosting a 2 cm x 2 cm Pt-Ti mesh (Goodfellow, UK) as the counter electrode and an Ag/AgCl reference electrode (Alvatek, UK). Two more holes were also included to introduce the electrolyte and allow operation in flow-cell mode. The top part was designed to host 5 cm x 5 cm flat photoelectrodes and had a square hole of 3 cm x 3 cm to be exposed to illumination. The two parts were pushed on each other through a rubber gasket using steel rods and plastic screws to ensure leak-proof adhesion of the electrode.

Photoelectrode testing

The assembled cell was filled with approximately 20 mL of 0.1 M phosphate buffer containing 16.28 g·L⁻¹ K₂HPO₄ and 0.88 g·L⁻¹ KH₂PO₄ in ultrapure MilliQ water (pH 7, 23.3 mS·cm⁻¹ conductivity) and placed below a solar simulator (Pico G2V Optics, US), providing a standard

AM1.5G light spectrum. The distance between the lens of the solar simulator and the photoelectrode was fixed at 3 cm, as set by the solar simulator calibration data. Each photoelectrode was tested, in triplicate, in three-electrode configuration by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) using an Uniscan PG580 potentiostat under both dark and illuminated conditions. Several CV cycles were performed in the potential range 0.2 - 1.8 V *vs* SHE (50 mV·s⁻¹ scan rate) until a constant current response was obtained. Then, the LSV analyses were performed on the same potential range at 20 mV·s⁻¹ scan rate.

The CA tests were performed at 1.20 V *vs* SHE by stabilising the electrode for 10 min under dark conditions, followed by five cycles of alternate illumination (1 min light and 1 min dark). CA was also applied to test the long-term response on the most performing electrodes. These tests were performed in flow-cell mode by continuously re-circulating 70 mL phosphate buffer from the cell to a glass bottle (kept slightly open to avoid overpressure) at a 12 mL·min⁻¹ flow rate. The bottle was left open to avoid the accumulation of gas products during the tests. Selected photoelectrodes were also tested by electrical impedance spectroscopy (EIS) under dark and illuminated conditions using an Autolab M204 potentiostat (Metrohm, Switzerland) at an applied potential of 1.20 V *vs* SHE. The potential was chosen in a way that all the tested electrodes were photocatalytically active for the OER reaction (7). A sinusoidal wave with 10 mV amplitude was applied with a frequency range from 0.1 to 10⁵ Hz (10 steps per decade). The experimental data were fit to a Randles circuit to estimate ohmic drop, charge transfer resistance and pseudo-capacitance. All results were validated for causality, linearity and stability by applying the Kronig-Kramer test.

Supplementary table

Table S1 – Comparison of BiVO₄ photoanode performance using different synthesis methods, all tested at 100 mW·cm⁻². Photocurrent values obtained using chronoamperometry measurements.

Method	Photocatalyst	Potential applied	Electrolyte	Photocurrent (mA·cm ⁻²)	Ref
Electrodeposition	Bi/BiVO ₄	0.80 vs RHE	Sodium sulfate buffer (pH 7.35)	0.40	8
Spin coating	F:BiVO ₄ @Ar	1.23 vs RHE	Sodium sulfate buffer (pH 6.80)	1.15	9
Hydrothermal	F:FeOOH/BiVO ₄	1.23 vs RHE	Sodium sulfate buffer (pH 7.35)	2.70	10
Hydrothermal	BiVO ₄	1.20 vs SHE	Phosphate buffer (pH 7.00)	0.13	This work
Electrodeposition	BiVO ₄	1.20 vs SHE	Phosphate buffer (pH 7.00)	0.06	This work

Table S2. Photoelectrochemical parameters of the BVO-ED and BVO-HH electrodes prepared with Triton-X or EMI ink (average and standard deviation of triplicates). Ohmic resistance (R_s); charge transfer resistance (R_{CT}); pseudo-capacitance (C) and exponent (α) of the CPE. BVO-ED measurements done in one photoelectrode.

Photoanode	R_s (Ω)	R_{CT} (Ω)	C (μ F)	α
BVO-HH-Triton-X	22 ± 3	1700 ± 800	140 ± 10	0.83 ± 0.04
BVO-HH-EMI	20 ± 1	330 ± 10	93 ± 3	0.81 ± 0.01
BVO-ED	24	774	80	0.89

Supplementary figures

Fig. S1 – (left) Top view of the photoelectrochemical cell, using an FTO electrode; (right) photoelectrochemical cell in operation illuminated using a Pico G2V Optics solar simulator, located at 3 cm distance from the lens.

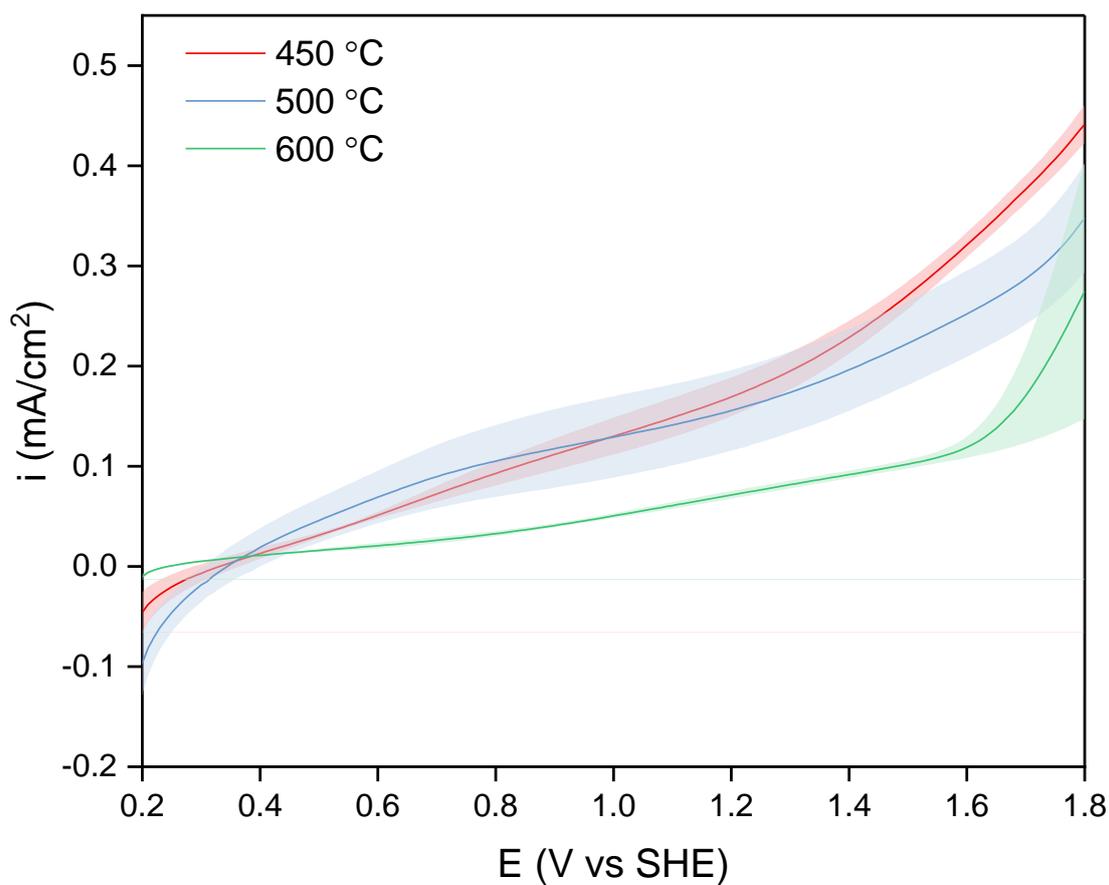


Fig. S2 – LSV analyses of the BVO-HH photoanodes produced with EMI ink at different annealing temperatures under AM1.5G illumination. The coloured lines and areas represent the average and interval of confidence obtained with three independent photoanodes.

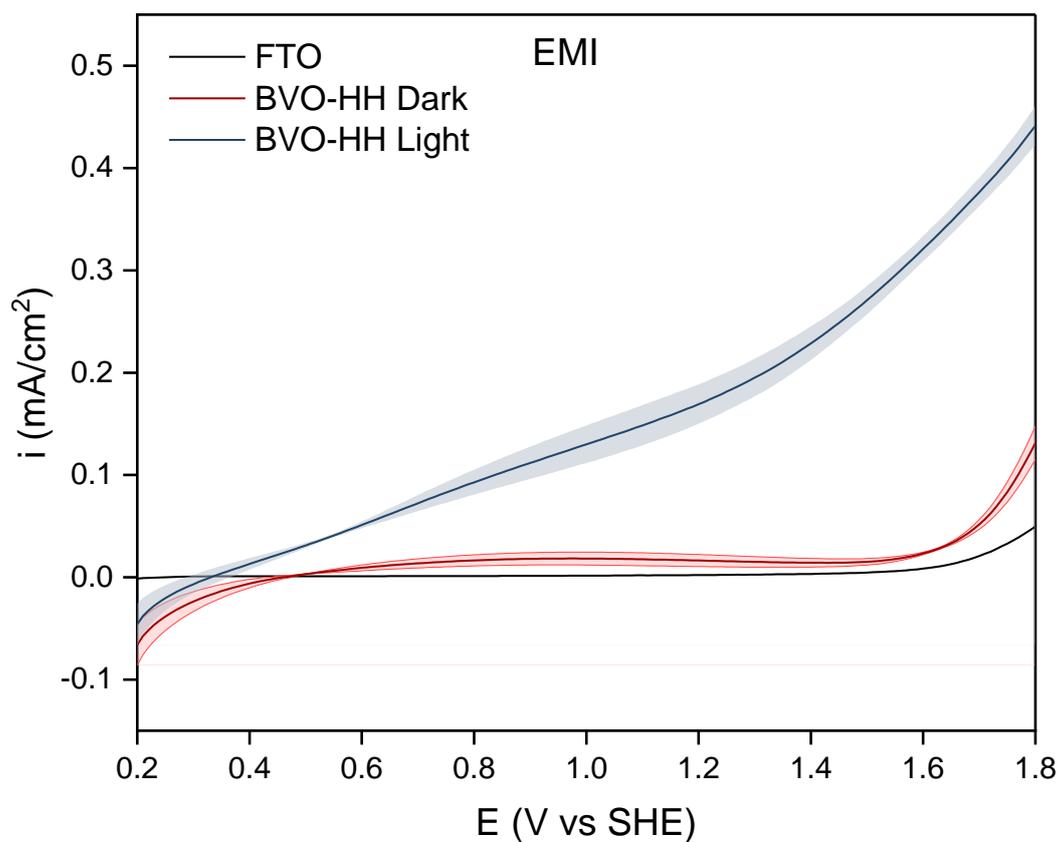


Fig. S3 – LSV analyses under dark and illuminated conditions of the BVO-HH photoanodes produced with the EMI ink. The coloured lines and areas represent the average and interval of confidence obtained with three independent photoanodes.

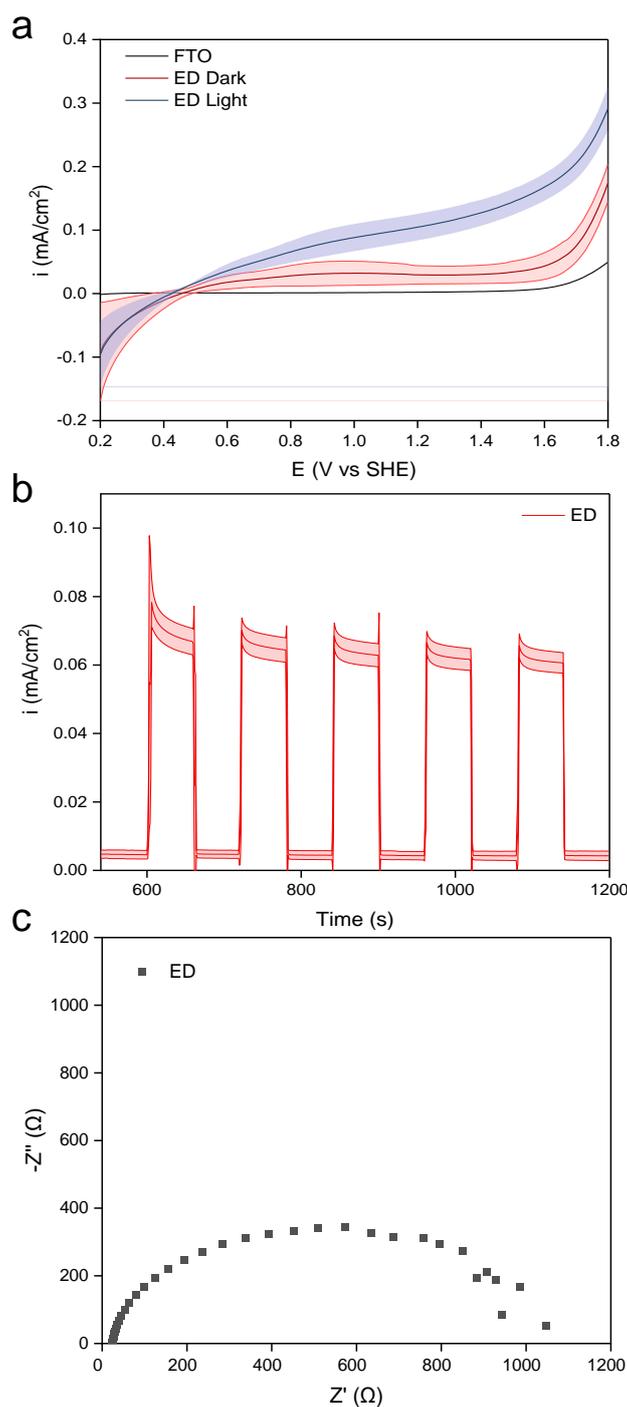


Fig. S4 – (a) LSV analyses of the ED photoanodes under AM1.5G illumination, the coloured lines and areas represent the average and interval of confidence obtained with three independent photoanodes; (b) CA analyses under the intermittent illumination of the ED photoanodes at 1.2 V vs SHE bias and AM1.5G illumination; (c) Nyquist plot describing the impedance behaviour of the ED photoanodes under illumination.

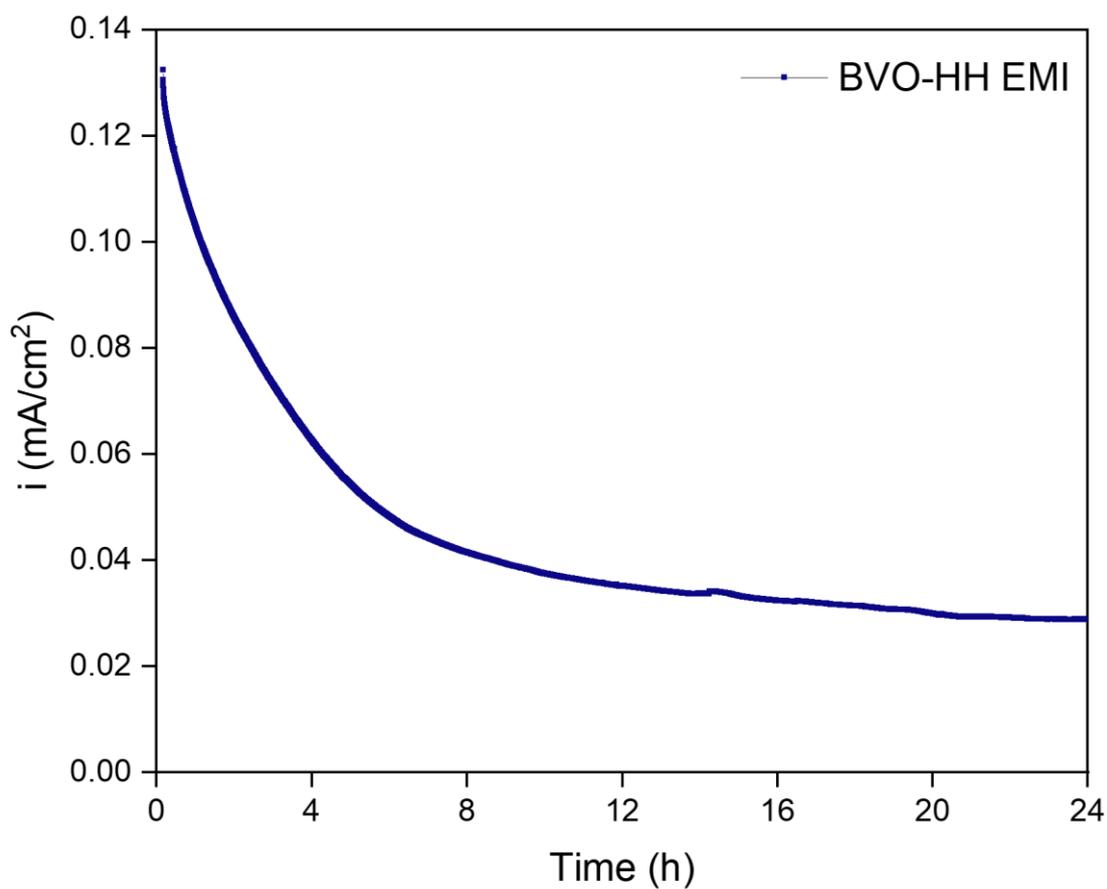


Fig. S5 – Stability test of the BVO-HH EMI photoanode under AM1.5G illumination with phosphate buffer (pH 7.00) at 1.20 V vs SHE.

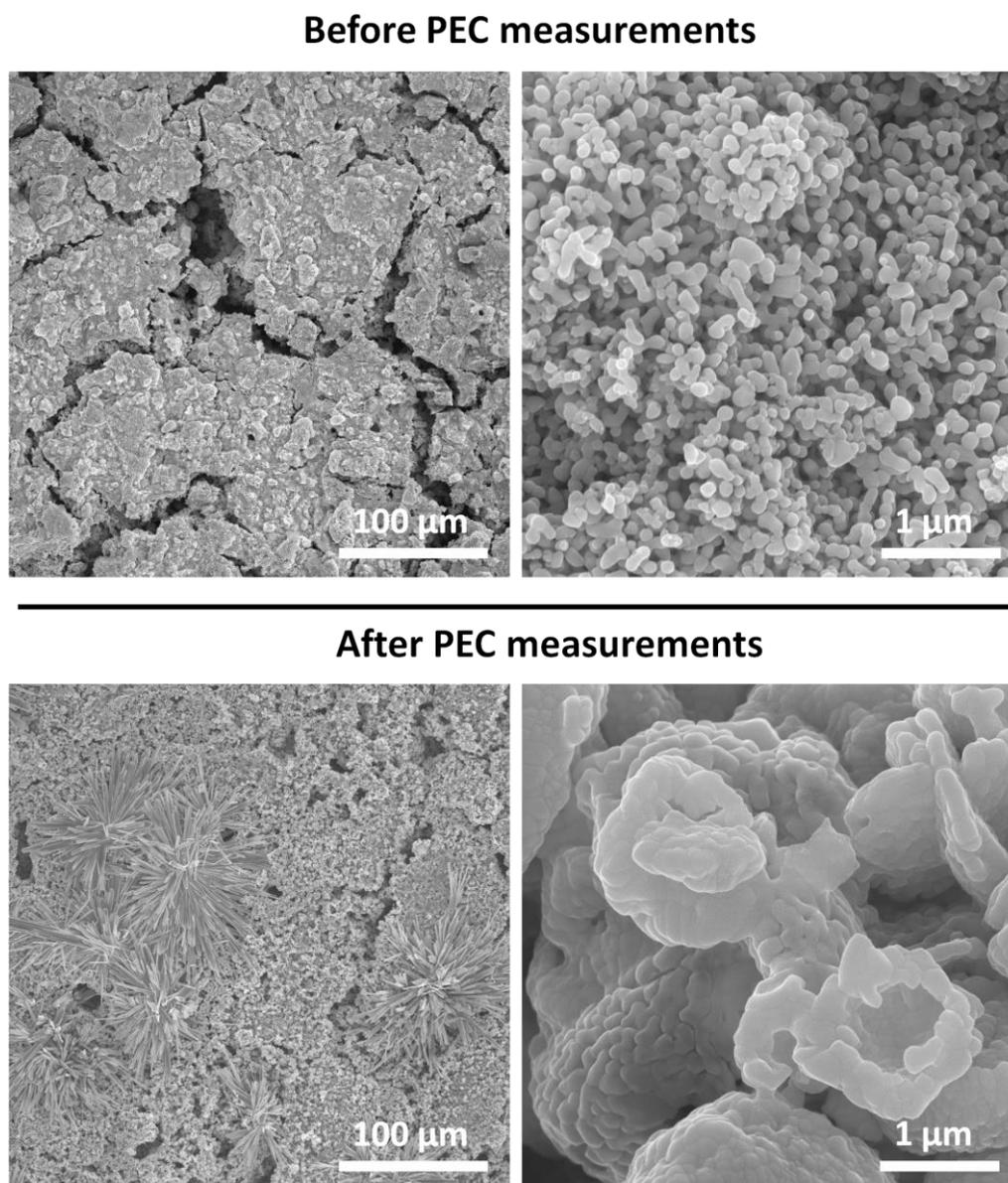


Fig. S6 – SEM images of the BVO slide by electrochemical deposition method before and after PEC measurements.

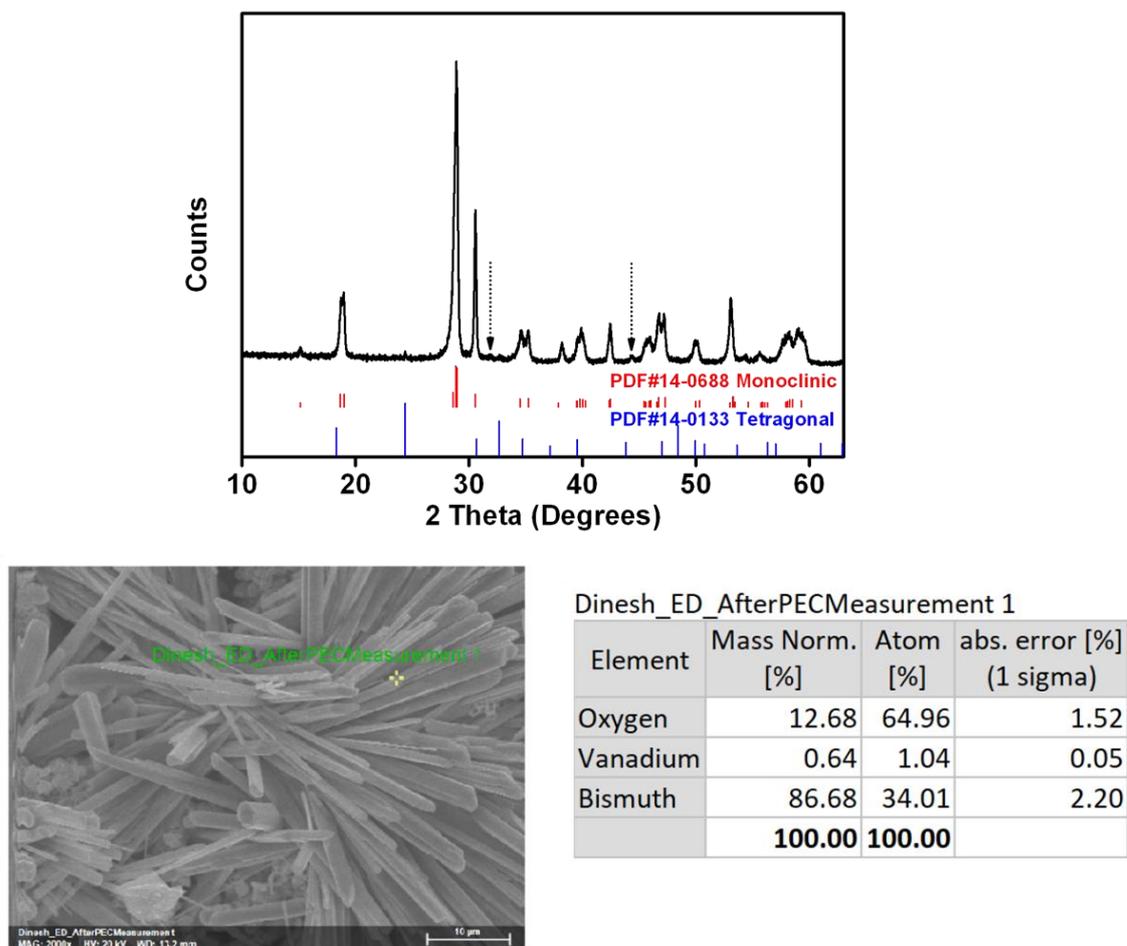


Fig. S7 – XRD pattern of the BiVO_4 powder scratched off the electrochemically deposited BVO slide after PEC measurements. The SEM image and EDX data are for the flower-like structures formed after PEC measurements on the electrochemically deposited BVO slide. The arrows in the XRD graph indicate the diffraction peaks from the impurities.

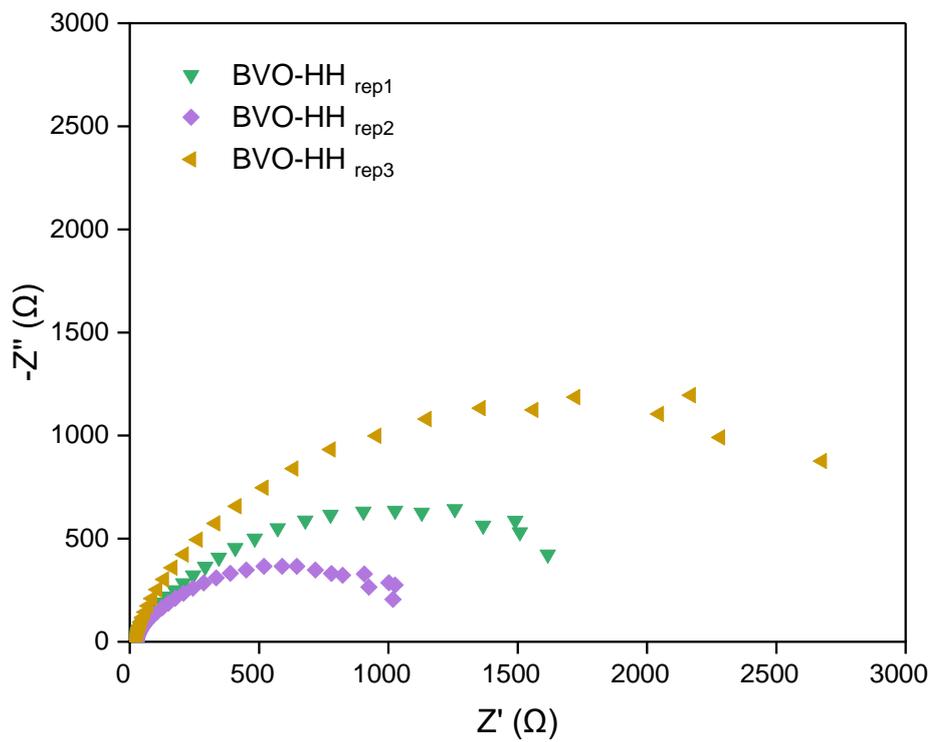


Fig. S8 – Nyquist plot describing the impedance behaviour of the BVO-HH Triton-X photoanodes under illumination.

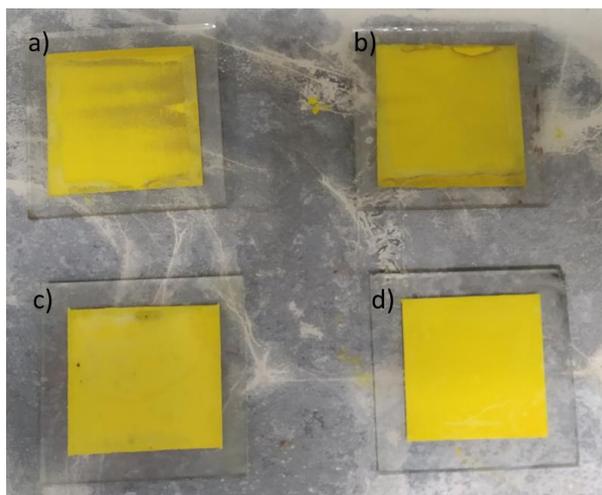


Fig. S9 – BiVO₄ photoanodes prepared by electrochemical deposition with varying concentration of vanadyl acetylacetonate calcinated at 450 °C. The deposition was accomplished with a uniform coverage of the electrode at a potential of -0.1V vs Ag/AgCl (3 M NaCl) under the conditions: a) 0.2 M vanadyl acetylacetonate with temperature ramp rate 5 °C/min; b) 0.2 M vanadyl acetylacetonate with ramp rate 2 °C/min; c) 0.3 M vanadyl acetylacetonate with ramp rate 5 °C/min; and d) 0.4 M vanadyl acetylacetonate with electrode ramp rate 5°C/min.

References

1. B.X. Lei, L.L. Zeng, P. Zhang, Z.F. Sun, W. Sun, & X.X. Zhang. *Adv. Powder Technol.*, 2014, **25**, (3), 946
2. M. Mousavi-Kamazani. *J. Mater. Sci. Mater. Electron.*, 2019, **30**, 17735
3. S. Nikam, & S. Joshi, *RSC Adv.*, 2016, **6**, (109), 107463
4. E.A. Mohamed, Z.N. Zahran, & Y. Naruta. *J. Mater. Chem. A*, 2017, **5**, (15), 6825
5. A.I. Kontos, A.G. Kontos, D.S. Tsoukleris, M.C. Bernard, N. Spyrellis, & P. Falaras. *J. Mater. Process. Technol.*, 2008, **196**, 243
6. K.R. Tolod, S. Hernández, M. Castellino, F.A. Deorsola, E. Davarpanah, & N. Russo. *Int. J. Hydrogen Energ.*, 2020, **45**, (1), 605.
7. S. Anantharaj, & S. Noda. *ChemElectroChem*, 2020, **7**, 2297
8. Q. Wang, J. He, Y. Shi, S. Zhang, T. Niu, H. She, & Y. Bi. *Chem. Eng. J.*, 2017, 326, 411-418.
9. M. Arunachalam, Y.J. Seo, S. Jeon, K.S. Ahn, C.S. Kim, & S.H. Kang, *S.H. Chem. Eng. J.*, 2020, 394, 125016.
10. H. She, P. Yue, J. Huang, L. Wang, & Q. Wang. *Chem. Eng. J.*, 2020, 392, 123703.