Supporting Information

Coupling CO_2 reduction with $2e^-$ water oxidation for simultaneous production of formate and H_2O_2

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MATERIALS AND METHODS

Electrode preparation. Bismuth dendrites deposited on Copper foil by the Dynamic hydrogen bubble template method (DHBT) were used as cathode. Commercially available copper foil (0.5 mm thick, area 1 cm^2) is taken as substrate. Before any electrochemical experiment, Copper was pre-treated with dilute HNO_3 for a few seconds followed by polishing the dried foil to remove the oxide layer on its surface. To prepare the anode, substrate FTO (Fluorine doped tin oxide) plates (area 1 cm^2) were washed by sonicating in a soap solution, acetone, water, and isopropyl alcohol; each for 20 minutes. A precursor solution for $BiVO_4$ was prepared by adding bismuth nitrate (0.05 moles), ammonium metavanadate (0.05 moles), and citric acid (0.01 moles) to 15 mL, 23.3 % HNO_3 solution. This solution was stirred for 30 min. Further, polyvinyl alcohol (0.08 g) and acetic acid (0.25 mL) were added to 1 mL of the aforementioned solution and the resultant solution was stirred for 4 hours. This solution was spin-coated on FTO plates with an acceleration time of 15 seconds to reach 4000 rpm and maintained for 30 seconds. Subsequently, these plates were dried at 90 °C for 1 hour followed by calcination in the furnace at 400 °C for 5 hours with a ramp rate of 2 ºC/min, and stored in a desiccator.

Characterization. Before electrochemical measurements, the two electrodes (Bi cathode and $BiVO_4$ anode) were characterized by performing powder X-ray diffraction (XRD) analysis under ambient conditions using PANalytical X'pert Pro MPD using monochromatic Cu Kα ($\lambda = 0.1547$ nm) radiation. The morphology, thickness and EDX measurements were done using scanning electron microscopy (Zeis Ultra FEG 55 SEM).

Electrochemical studies. For both oxidative and reductive reaction studies, a three-electrode setup was used. Both $BiVO_4$ and Bi were used as the working electrodes for oxidative and reductive reaction studies respectively. Platinum foil was used as a counter electrode.

For electrolyzer measurements, the electrochemical cell was equipped with a cathode and anode. Both compartments were separated by a proton exchange membrane (Nafion 117). In a separate experiment, individual electrode potentials were measured with the help of a multimeter, which was connected to each electrode and the reference electrode present in their particular compartments. All measurements were done in ice bath conditions except stability measurements and the electrolyte was purged for half an hour with CO_2 to obtain CO_2 saturated 1M $KHCO_3$ (pH 7-8) and during electrochemical experiments, CO_2 was continuously purged at a rate of 25 ml/min. To record an electrochemical response, Biologic potentiostat was used. Linear sweep voltammetry was performed at a scan speed of 20 mV/sec.

Analysis of products.

Formate quantification: By ^{1}H NMR (Bruker 800 MHz spectrometer), formate was identified based on obtained singlet at chemical shift value of (~ 8.4 ppm) and then quantified with Trimethylsilyl propanoic acid (TSP, 1 mM) as a reference, with the procedure as followed: After electrolysis, 540 μL electrolyte was mixed with 60 μL, 1mM TSP in D_2O, used as the internal standard, to quantify the moles of formate produced and ^{1}H NMR was done. Water suppression was performed to suppress the excess amount of water in the electrolyte.

The faradaic efficiency was calculated based on Eq. 1:

$$FE = (n \cdot N \cdot F \,/\, Q) \times 100\ \% \qquad \text{Eq. 1}$$

where N is the amount of the generated products in the process, mol; F is Faraday's constant (96485 C/mol); n is the number of electrons transferred in the Faradaic process (for formate it is 2); Q is the total charge passed through the whole reaction.

H_2O_2 quantification: The H_2O_2 was qualitatively identified with test strips (Quantofix-Sigma Aldrich) and the quantification was done by titrating 10 ml electrolyte after electrolysis, mixed with 5 mL H_2SO_4 (to make medium acidic) with freshly prepared standard potassium permanganate solution (5 mM solution, SDFCL) taken in syringe (1 mL). $KMnO_4$ reacts stoichiometrically with H_2O_2 in an acidic medium according to the following reaction.

$$2\,KMnO_4 + 5H_2O_2 + 6H^+ \rightarrow 2Mn^+ + 2K^+ + 5O_2 + 8H_2O$$

According to this equation, 1 mole of $KMnO_4$ reacts stoichiometrically with 2.5 moles of H_2O_2 and hence, moles of H_2O_2 can be calculated using Eq. 2:

$$M_{KMnO4} \text{ x } V_{KMnO4} = 2.5\,(M_{H2O2} \text{ x } V_{H2O2}) \qquad \text{Eq. 2}$$

The faradaic efficiency was calculated based on Eq. 1:

$$FE = (n \cdot N \cdot F \,/\, Q) \times 100\ \%$$

where N is the amount of the generated products in the process, mol; F is Faraday's constant (96485 C/mol); n is the number of electrons transferred in the Faradaic process (for H_2O_2, it is 2); Q is the total charge passed through the whole reaction.

Gaseous products quantification:

During the electrolysis of 10 min, the gaseous sample from the cathodic compartment was simultaneously collected in a container, and after electrolysis few microlitres of the collected sample were injected into micro GC, and also another sample was injected from the headspace of the electrochemical cell which still contains the residual gases. The addition of moles produced in both containers for a particular gas will represent the total production. For the anodic side, the same procedure was followed. For identification and quantification of the gases, standard runs were done which included a mixture of known concentrations of CO_2, CO, methane, H_2, N_2, ethane, ethene, and methane. A calibration curve was obtained from different standard runs differing in concentrations (100 ppm, 500 ppm, 1000 ppm, and 5000 pm) certified by Alchemie Gases and Chemicals Pvt. Ltd. The results suggested the production of hydrogen with traces of methane (< 5 %), in case of bismuth, at cathode side and oxygen at anodic side however, no other product was observed. Oxygen could not be measured accurately because of its presence in the environment.

H_2 quantification:

Let, the production of unknown sample hydrogen be obtained through calibration curves = x ppm

Hence, this suggests, a 1-litre gaseous volume will contain = x μL of H_2

Hence, the dead volume, V (L) will contain = (x V) μL of H_2

22.4×10^6 μL of H_2 corresponds to = 1mol of H_2

Hence, (x V) μL of H_2 corresponds to = $(xV/ 22.4 \times 10^6)$ mole of H_2

The faradaic efficiency was calculated based on Eq. 1:

$$FE = (n \cdot N \cdot F / Q) \times 100\ \%$$

where N is the amount of the generated products in the process, mol; F is Faraday's constant (96485 C/mol); n is the number of electrons transferred in the Faradaic process (for H_2, it is 1); Q is the total charge passed through the whole reaction.

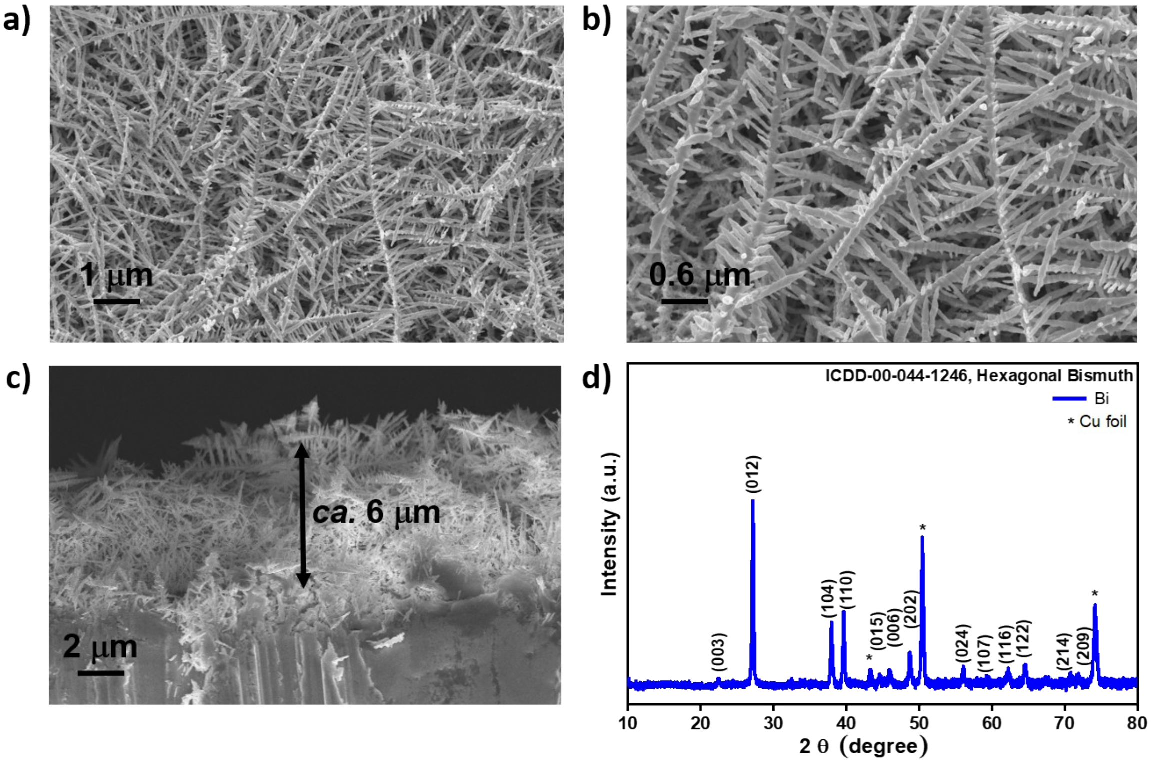


Figure S1. SEM of **(a, b)** top view and **(c)** cross-section of the deposited film (**d)** XRD pattern of the as-prepared cathode.

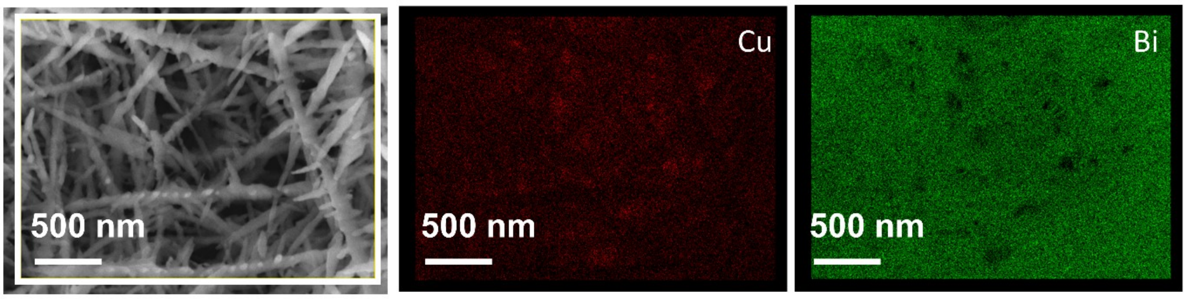


Figure S2. Elemental mapping plots of as-prepared Bi before the electrochemical experiment.

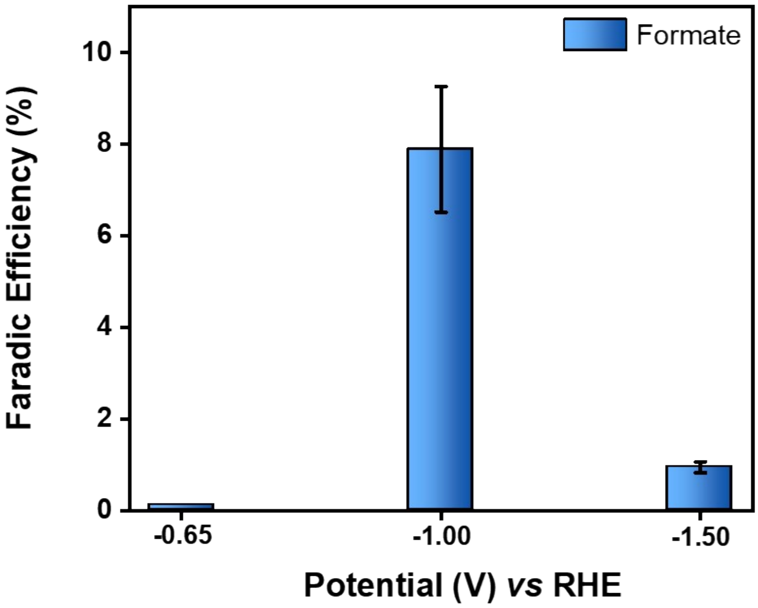


Figure S3. Faradaic Efficiency values of formate in the case of the Cu at different voltages. Counter Electrode - Platinum, Electrolyte: 1 M $KHCO_3$.

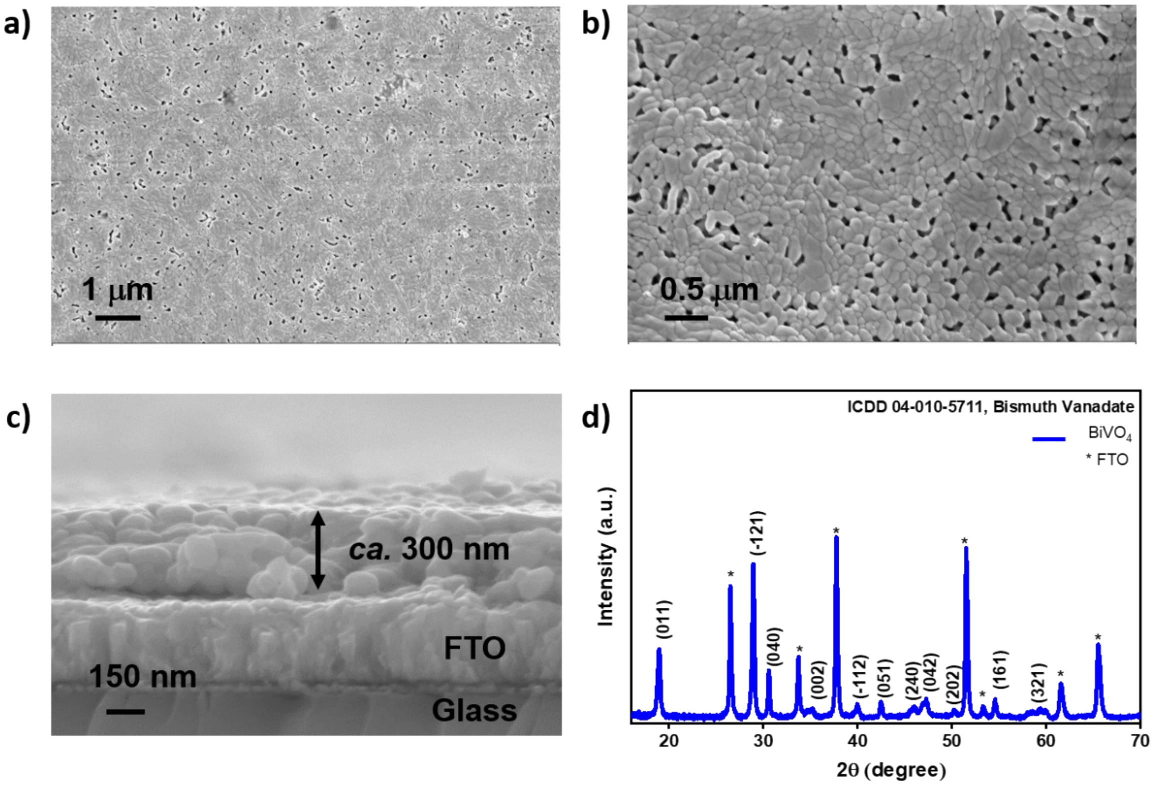


Figure S4 (a, b) SEM and **(c)** cross-section image of $BiVO_4$ and **(d)** XRD of as-synthesized $BiVO_4$

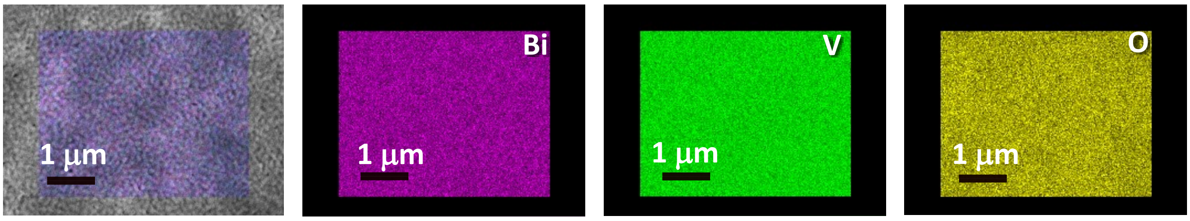


Figure S5. Elemental mapping plots of $BiVO_4$ (synthesized on FTO) before the electrochemical experiment.

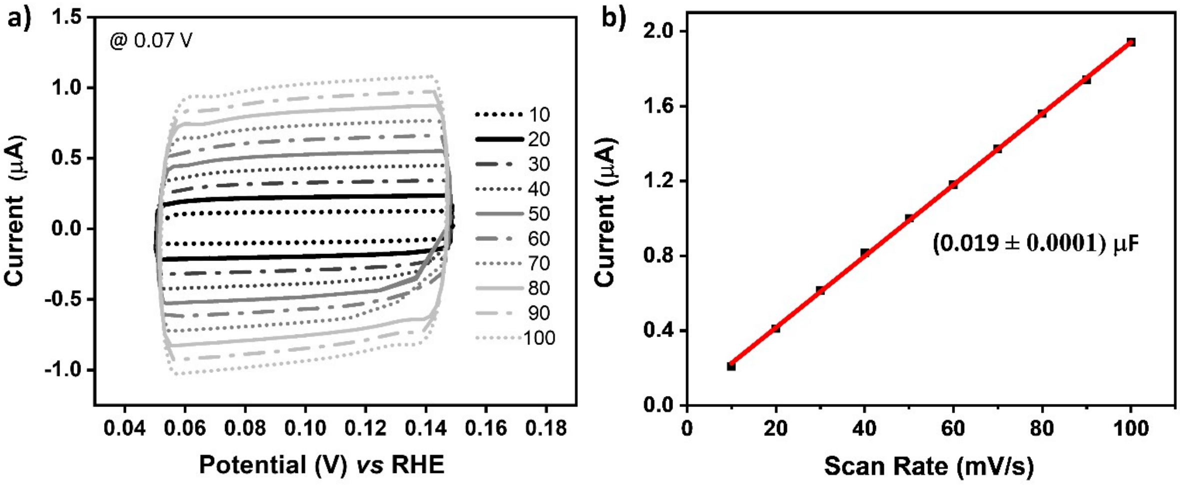


Figure S6 (a) CV plots and (b) measured current @ 0.07 V *vs* RHE at scan rates 10-100 mV/s in 1M $KHCO_3$ for FTO anode.

All measured currents (I_{oxd} -I_{red})in this region are assumed to be twice of double-layer charging current (i) which can be equated as the product of the electrochemical capacitance (CE), and the scan rate (ν), i =ν (2CE). The electrochemical surface area was found to be 0.31 cm^2 which was evaluated by dividing CE with specific capacitance (Cs): 30 mF/cm^2 for metal oxides.

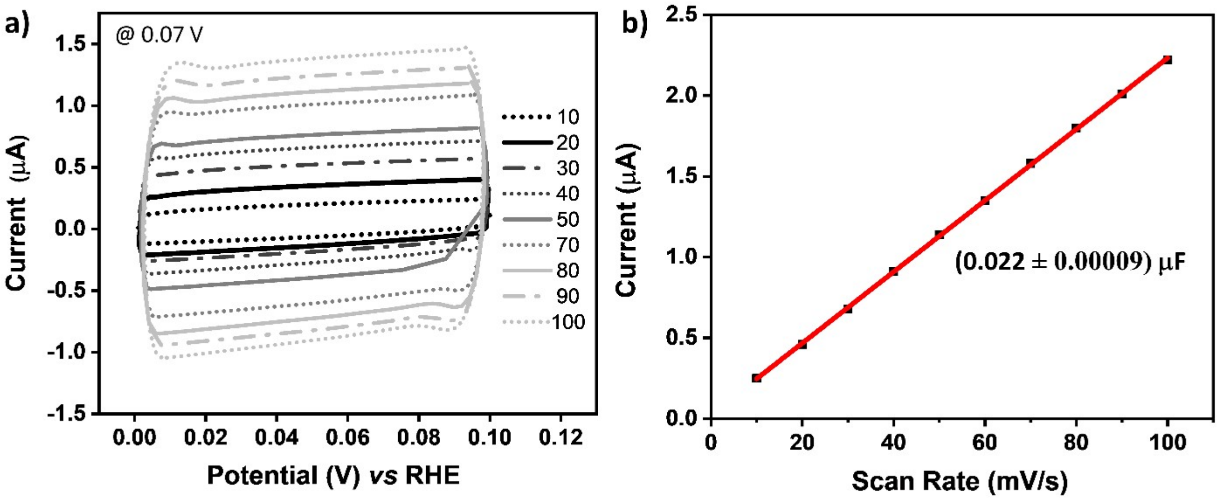
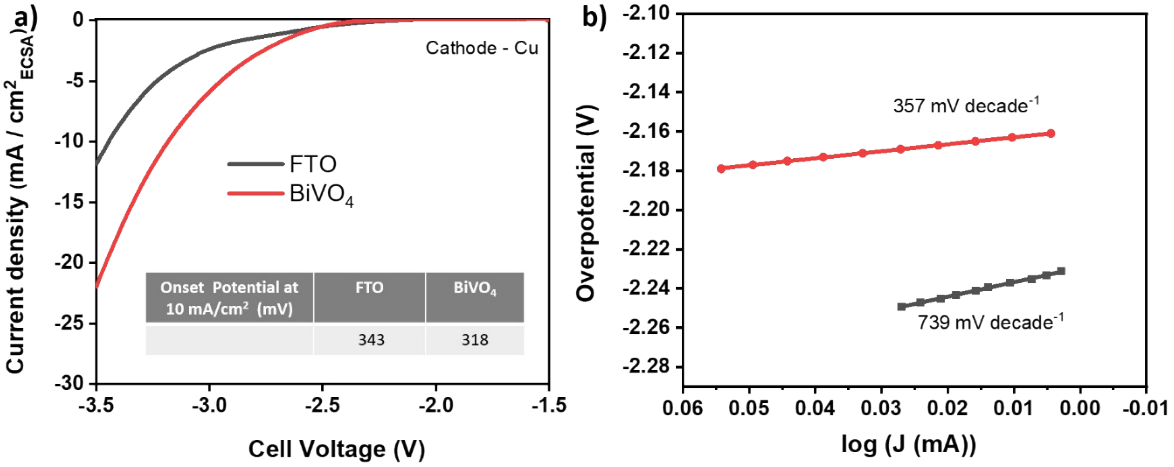


Figure S7 a) CV plots and measured current @ 0.07 V *vs* RHE at scan rates 10-100 mV/s in 1M $KHCO_3$ for $BiVO_4$ anode.

All measured currents (I_{oxd} -I_{red})in this region are assumed to be twice of double-layer charging current (i) which can be equated as the product of the electrochemical capacitance (CE), and the scan rate (ν), i =ν (2CE). The electrochemical surface area was found to be 0.36 cm^2 which was evaluated by dividing CE with specific capacitance (Cs): 30 mF/cm^2 for metal oxides.



Onset Potential at 10 mA/cm² (mV)	FTO	BiVO$_4$
	343	318

Figure S8 (a) LSV curves, and **(b)** Tafel plot comparison in the case of two Electrolyzers with Copper as cathode coupled to different anodes i.e. FTO and BiVO$_4$.

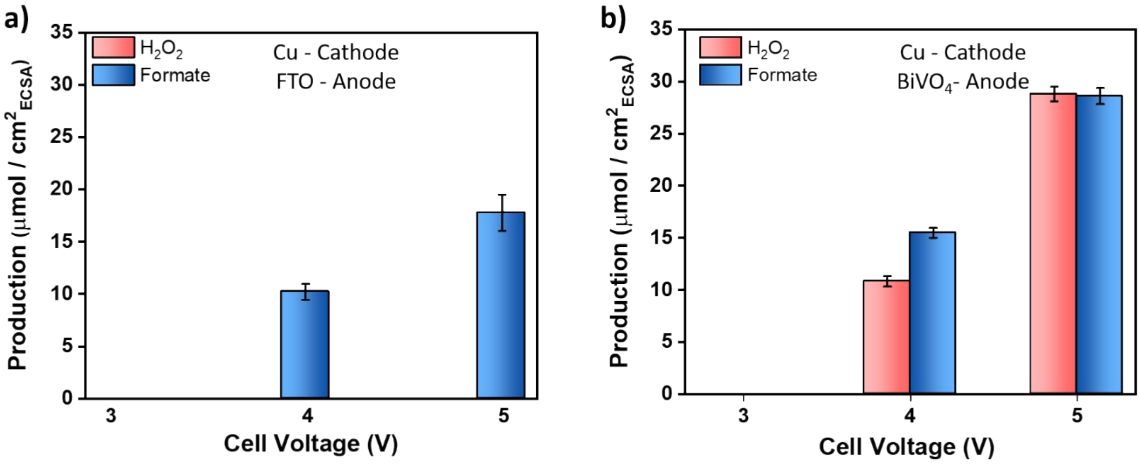


Figure S9 Production of formate and H_2O_2 obtained in the case of two Electrolyzers with Copper as cathode coupled to different anodes *i.e.* **(a)** FTO and **(b)** BiVO$_4$ at 3 V, 4 V and 5 V *vs* RHE, Electrolyte: 1 M $KHCO_3$.

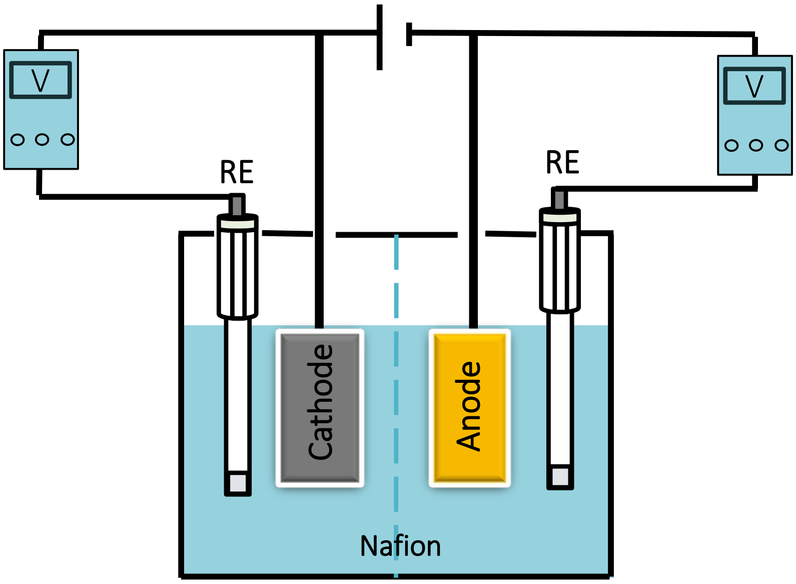


Figure S10. Schematic to obtain the absolute potential at each electrode in the electrolyzer. RE=Reference electrode.

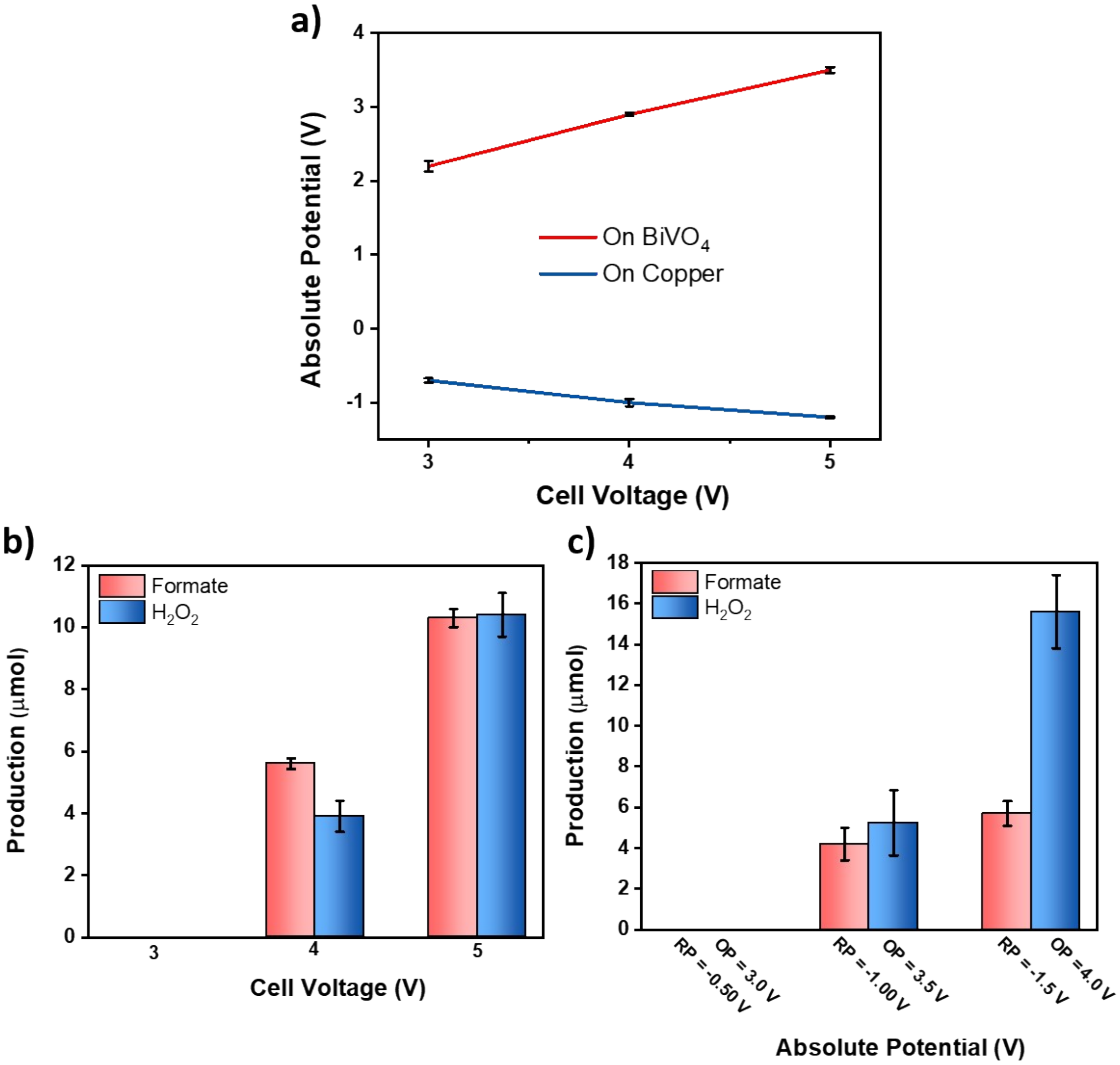


Figure S11 (a) Absolute potential values on cathode and anode, **(b)** Production of formate and H_2O_2 at a cell voltage of 3 V, 4 V, and 5 V in Electrolyzer employing $BiVO_4$ anode and Cu cathode. **(c)** Production of formate at -0.50 V, -1.0 V, and -1.5 V *vs* RHE in case of Cu and H_2O_2 at 3 V, 3.5 V, and 4 V in case of $BiVO_4$ in three-electrode setup, Counter Electrode - Platinum, Electrolyte: 1 M $KHCO_3$

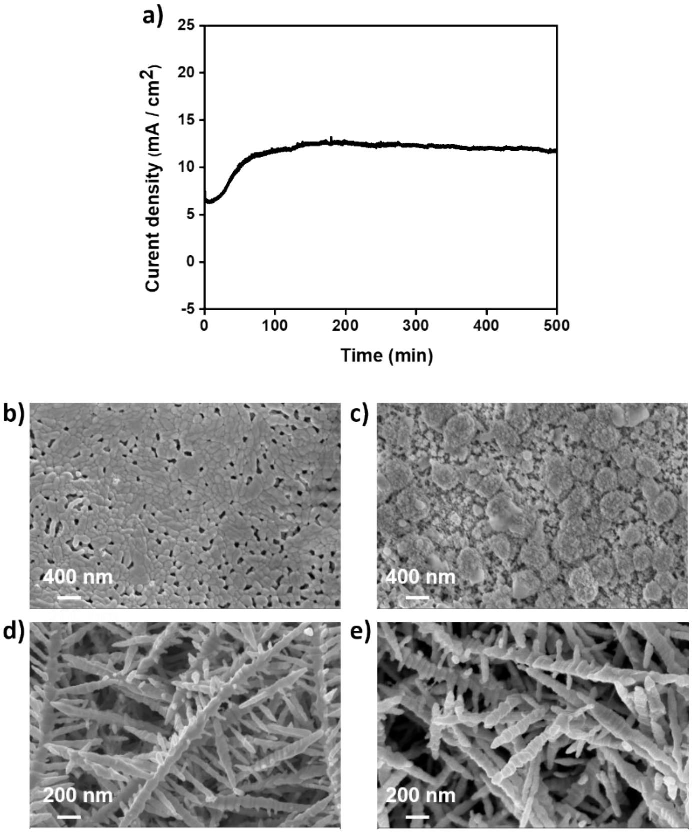


Figure S12. (a) Long-term stability (chronoamperometry experiment) for Electrolyzer (A) employing $BiVO_4$ anode and Bi cathode at a cell voltage of 4 V. SEM images of the top view of Bi **(b)** before and **(c)** after electrochemical measurement. SEM images of the top view of $BiVO_4$ **(d)** before and **(e)** after electrochemical measurement.

Table S1. Comparison of CO_2RR electrolyzers coupled to $2e^-$ water oxidation

Cathode	**Anode**	**Feed (C/#A)**	**Production (C, A) μmol/cm$^2_{ECSA}$**	**Faradic Efficiency**	**Cell voltage (V)**	**Toxic product produced**	**References**
(CoPc)/(CN) (CO_2RR)	FTO	$KHCO_3$ (0.5 M)/ K_2CO_3 (5 M)/	-	~60 % (H_2O_2 production) ~90% (CO production)	6.8	Yes (toxic CO is produced)	1
Bi dendrites (CO_2RR)	$BiVO_4$ (2e- water oxidation)	$KHCO_3$ (1 M)/ $KHCO_3$ (1 M)/	Formate (50) H_2O_2 (6)	~30% (H_2O_2 production) ~50% (Formate production)	4	No	**This work**

Table S2. Comparison of CO_2RR electrolyzers producing formate, which have replaced OER, with other oxidation reactions.

Cathode	**Anode**	**Feed (C/#A)**	**Production (C, A) μmol/cm$^2_{ECSA}$**	**Faradic Efficiency**	**Cell voltage (V)**	**Organic anodic consumables required /Pre-processing required**	**References**
mSnO_2/C C (CO_2RR)	CuONS/CF (Methanol oxidation)	$KHCO_3$ (1 M)/ KOH (1 M)	-	91.3% (methanol oxidation) 80.5% (Formate production)	1.2	Yes (organic methanol)	2
BiOx (CO_2RR)	NiONPs (Biomass Oxidation)	$KHCO_3$ (0.5 M)/ $KHCO_3$ (0.5 M)/	-	36% (Biomass oxidation) 81% (Formate production)	2.5	Yes (Biomass to HMF, pre-processing)	3
Bi dendrites (CO_2RR)	$BiVO_4$ (2e- water oxidation)	$KHCO_3$ (1 M)/ $KHCO_3$ (1 M)/	Formate (50) H_2O_2 (6)	~30% (H_2O_2 production) ~50% (Formate production)	4	No (Water (green solvent) pathway is steered, no pre-processing required)	**This work**

1. J. H. Wu, R. J. Guo, J. W. Wang, F. J. Niu, L. J. Guo and G. Ouyang, *Chem. Commun*., **2024**, 60, 12718
2. X. Wei, Y. Li, L. Chen and J. Shi, *Angew. Chem. – Int. Ed.*, 2021, **60**, 3148–3155
3. S. Choi, M. Balamurugan, K. G. Lee, K. H. Cho, S. Park, H. Seo and K. T. Nam, *J. Phys. Chem.*, 2020, **11**, 2941–2948.