Electronic Supplementary Material (ESI) for Dalton Transactions.
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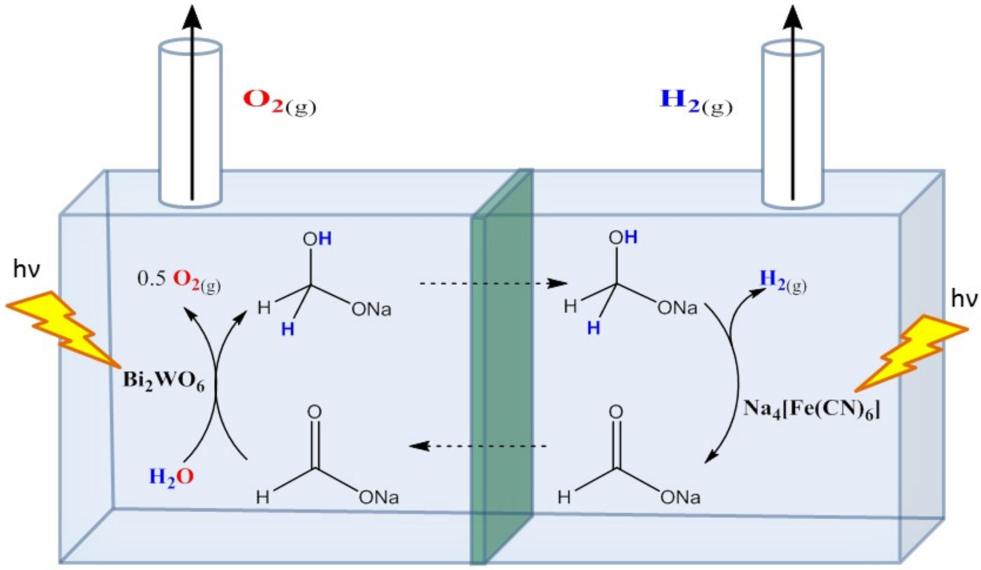
Supplementary Materials

GRAPHICAL ABSTRACT



Proposed schematic of an industrial set-up for our water splitting cycle with separate emission of oxygen and hydrogen gasses using photosemiconductors and a carbon shuttle.

EXPERIMENTAL

Paraformaldehyde, 37% formaldehyde solution, and sodium ferrocyanide decahydrate, were purchased from Sigma Aldrich. Formic acid was purchased from Acros Organics. Sodium thiosulfate was purchased from Oakwood Chemicals. Iodine was purchased from Strem. Acetamide was purchased from Fluka. Citric acid was purchased from Fisher Scientific. Acetic anhydride was purchased from VWR. Chemicals were used without further purification. H_2O^{18} was purchased from Huayi Isoptopes Company. If not specifically mentioned, all reactions were carried out in distilled water without degassing or other modifications.

Analytical Equipment. pH measurements were taken with a Hanna HI 2210 benchtop pH meter with a general purpose combination pH electrode.

Powder XRD diffractograms were obtained on a Rigaku Ultima IV diffractometer set to 2 2θ°/min from 10-70 2θ°. UV-Vis spectra were obtained on a Specmate UV-1100 spectrometer.

EDS data was obtained on a JEOL JSM-7500F SEM

EI-MS for isotopic labelling experiments was performed on a Kratos Analytical Concept 1S Magnetic Sector Mass Spectrometer.

Product analysis. H_2, CO_2, CO and O_2 gas identification and detection was carried out with an Agilent 7820A GC equipped with a thermal conductivity detector (TCD), using an Agilent GS-CarbonPlot column (for CO_2) or Agilent HP-Molesieve column (for all other gasses).

Dehydrogenation of *p*-FA. In a typical experiment, 50 mmol of *p*-FA were added to 250 mmol of NaOH in H_2O, in a round bottomed flask connected to the volumetric apparatus. The reaction mixture was illuminated with a 300 W Mercury or Xe arc-lamp. $[Na_4\ Fe(CN)_6]\ .10H_2O$ (500 μmol, 1 mol%) was added to the solution to yield 825 mL of H_2 in 300 min. This protocol was repeated for use with commercial 37% FA solutions. This protocol was repeated for further additions of substrate when appropriate.

Determination of reaction kinetics. In a typical experiment, 50 mmol of *p*-FA were added to 250 mmol of NaOH in H_2O, in a round bottomed flask connected to the volumetric apparatus. The reaction mixture was opened to light from a 300 W Xe lamp. 500 μmol (1 mol%) of $[Na_4\ Fe(CN)_6]\ .10H_2O$ was added to the solution and the gaseous outflow of the solution was measured by a Restek ProFLOW 6000 Electronic Flowmeter connected to a computer.

Determination of pH. Two identical solutions of 66.6 mmol of pFA and 375 mmol of NaOH were prepared simultaneously and were measured to have identical pH values. Both solutions were then illuminated and to one solution, 2 mmol of $[(CN)_6Fe]\ Na_4(H_2O)_{10}$ was added. pH values were measured at regular intervals for 300 minutes.

Determination of formate concentration. Concentration of dissolved formate was determined according to a modified colorimetric procedure by Sleat and Mah.[39] An aliquot of 0.5 mL of the reaction mixture was added to 2 mL of 10% acetamide and 0.05% citric acid dissolved in a 1:1 mixture of isopropanol and water. To the test mixture, 0.1 mL of 30% sodium acetate and 7 mL of acetic anhydride were added. The test mixture was shaken and incubated at room temperature for 60 minutes and measured spectrophotometrically at 510 nm. The concentration was determined by comparison against a standard curve.

Determination of formaldehyde concentration. Formaldehyde concentrations for concentrated samples (dehydrogenation of formaldehyde experiments) were determined through iodine / sodium thiosulphate titrations.[40] To a 10 mL sample of the reaction mixture, de-ionised water (20 mL), iodine (25 mL, 0.05M/L in methanol) and sodium hydroxide (10 mL, 1.0M) were added and stirred for 10 minutes followed by the addition of sulphuric acid (15 mL, 1.0M). The sample solution was then titrated with sodium thiosulphate, with addition of a 1% starch solution as an indicator once the solution turned light yellow. The concentration of formaldehyde was then calculated by a standard curve.

Formaldehyde concentrations for dilute samples (reduction of formate experiments) were determined through a colormetric reaction with acetyl acetone. To a solution of ammonium acetate (15.4 g) in water (50 mL), acetyl acetone (0.2 mL) and glacial acetic acid (0.3 mL) were added whilst stirring. This was further diluted with water (49.5 mL) and stored in the fridge for up to 3 days. To determine the formaldehyde concentration, 2 mL of the sample were mixed with 2 mL of the acetyl acetone solution and heated to 60°C for 10 minutes. After cooling for 10 minutes, the absorbance of the solution was measured at 412 nm and compared to a calibration curve.

Isolation of iron oxide. Iron oxide was collected after allowing a standard reaction to continue for 5 days with a continuous addition of pFA and NaOH. A brown-red precipitate slowly formed which was centrifuged, washed and dried and identified by its XRD pattern.

Computational details. Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the B3LYP[41] functional and TZVP[42] basis set for all atoms. Frequency calculations at the same level of theory have also been performed to confirm all of possible intermediate states (one imaginary frequency), and to provide free energies at 298.15 K, which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Intermediate states were located using the Berny algorithm. The Polarizable Continuum Model (PCM) was used to correct the energies taking into account the reaction occurs in water. All calculations were performed with the Gaussian 09[43] software package.

Isotopic Experiments. H_2O^{18} (0.5 mL) was placed in a closed quartz cuvette with sodium formate (4.4 mmoles) and Bi_2WO_6 (140 µmoles). This was illuminated for 12 hours by 300W mercury arc lamp, after which the gasses were injected into the EI-MS.

FIGURES

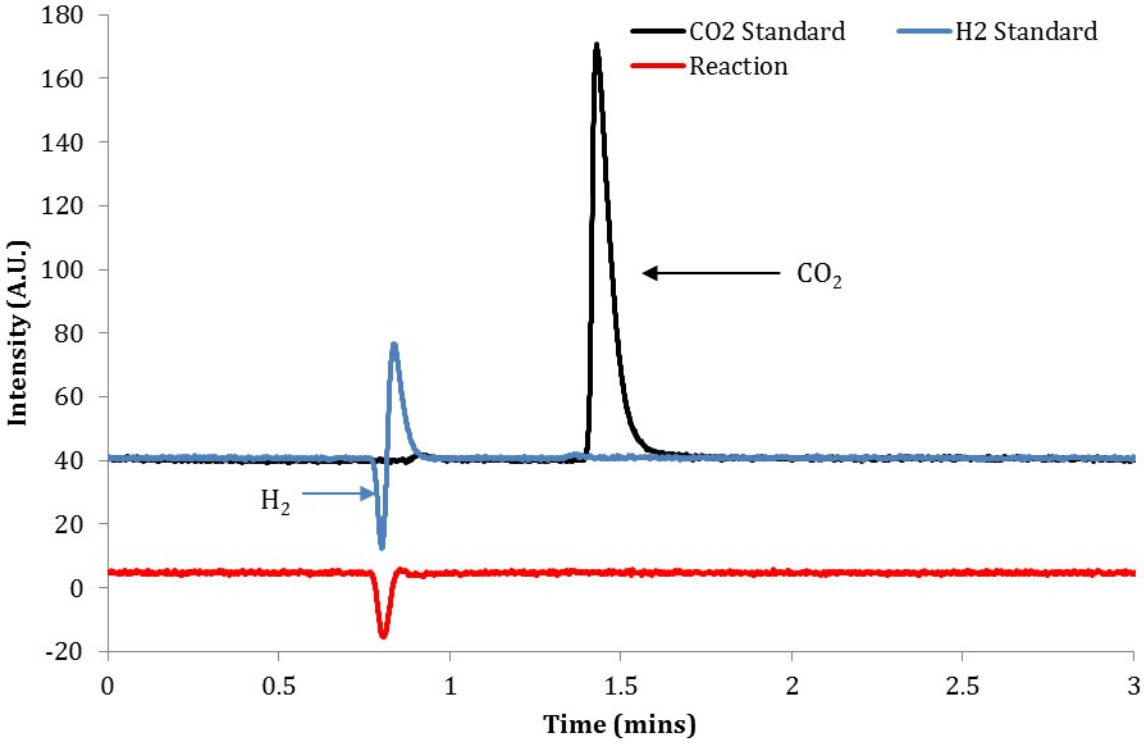


Figure S1. Gas chromatograph of evolved gas using a GS-CarbonPlot column for the detection of H_2 and CO_2.

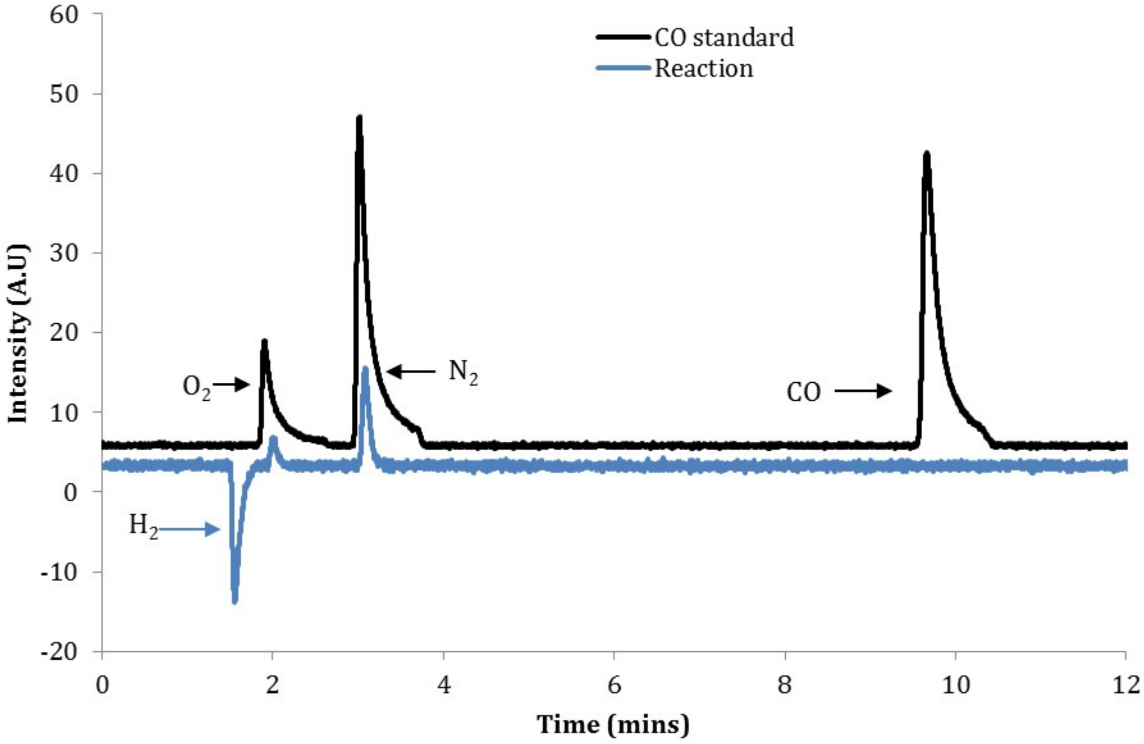


Figure S2. Gas chromatograph of evolved gas using a HP-Molesieve column for the detection of H_2, O_2, N_2 and CO.

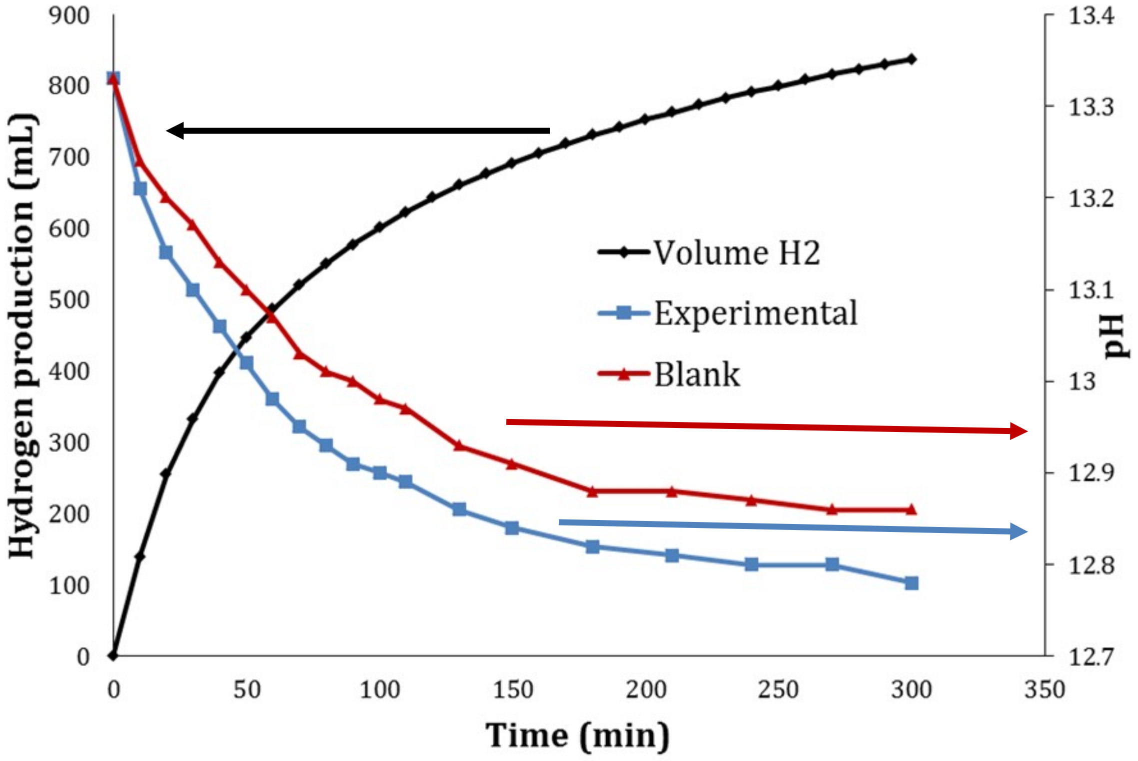


Figure S3. Change of pH of blank and catalytic solution over time. Catalytic runs were carried out with a single addition of 67 mmol of *p*-FA, 375 mmol of NaOH and 2 mmol [Na_4 $Fe(CN)_6$] .$10H_2O$ to a total volume of 300 mL. No hydrogen evolution was observed in the blank.

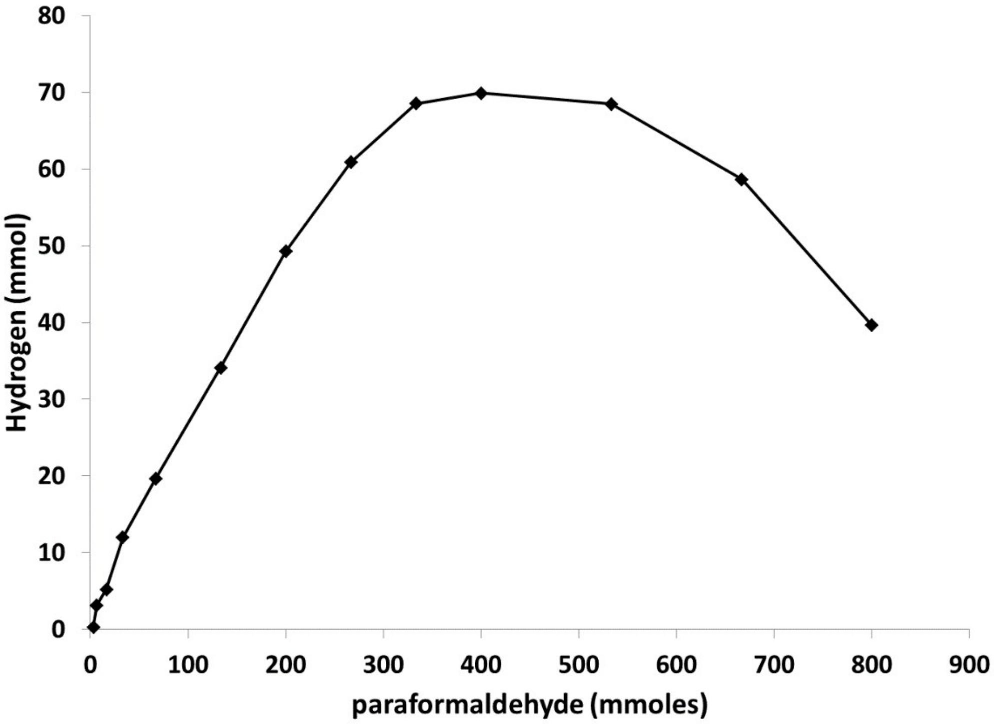


Figure S4. Total volume of hydrogen evolved with variable initial concentration of p-FA. All reactions were carried out with 325 mmoles of NaOH and 0.5 mmoles of $Na_4[Fe(CN)_6].10H_2O$ in 250 mL of water.

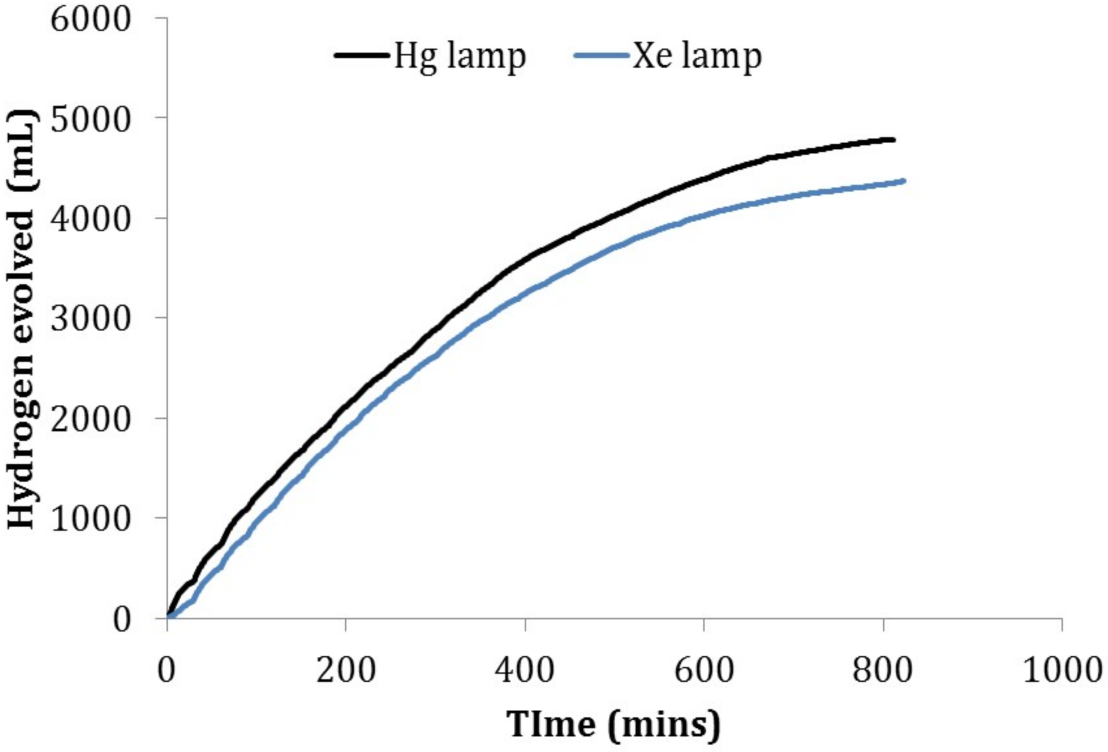


Figure S5. Long range catalytic runs showing catalyst deactivation. Addition of 0.05 moles of both p-FA and NaOH were carried out every 30 minutes to an initial solution containing 250 µmoles of catalyst, 0.05 moles of p-FA and 0.25 moles of NaOH.

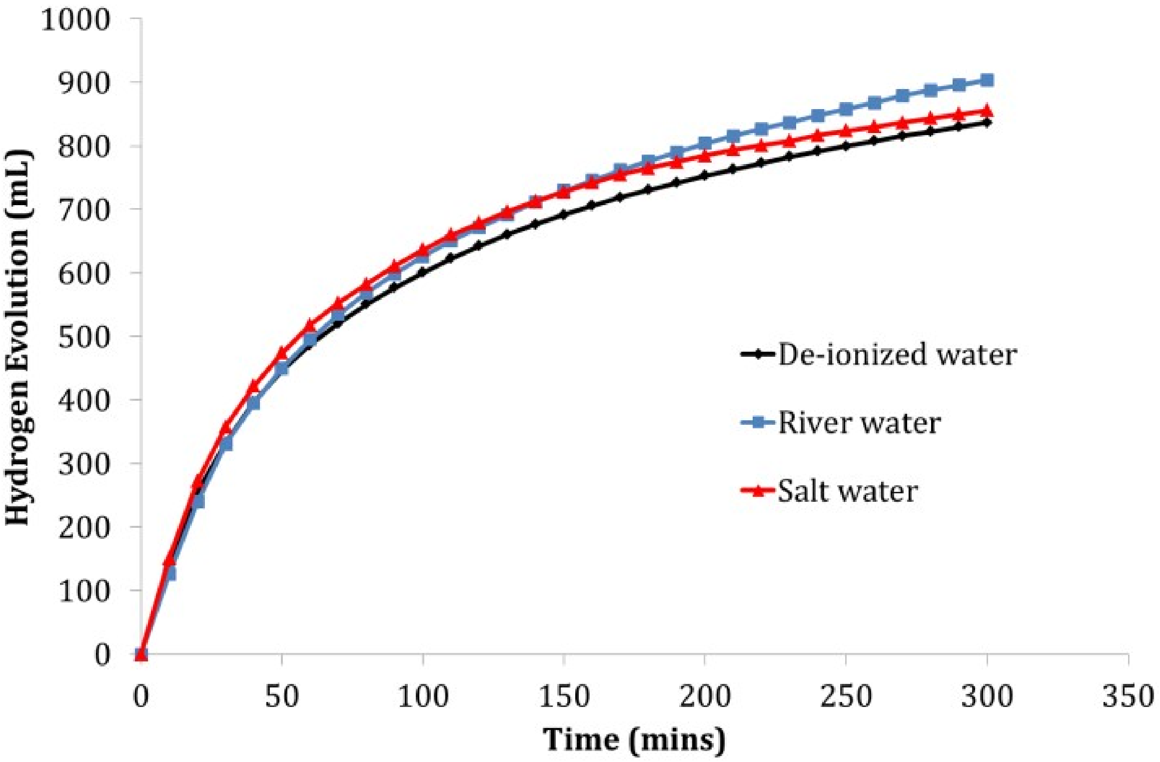


Figure S6. Volume of hydrogen evolution in various water sources during photocatalysis over time. Experiments were performed with a single addition of 67 mmol of *p*-FA, 375 mmol of NaOH and 2 mmol of $[(CN)_6Fe]\ Na_4(H_2O)_{10}$ in 300 mL of water

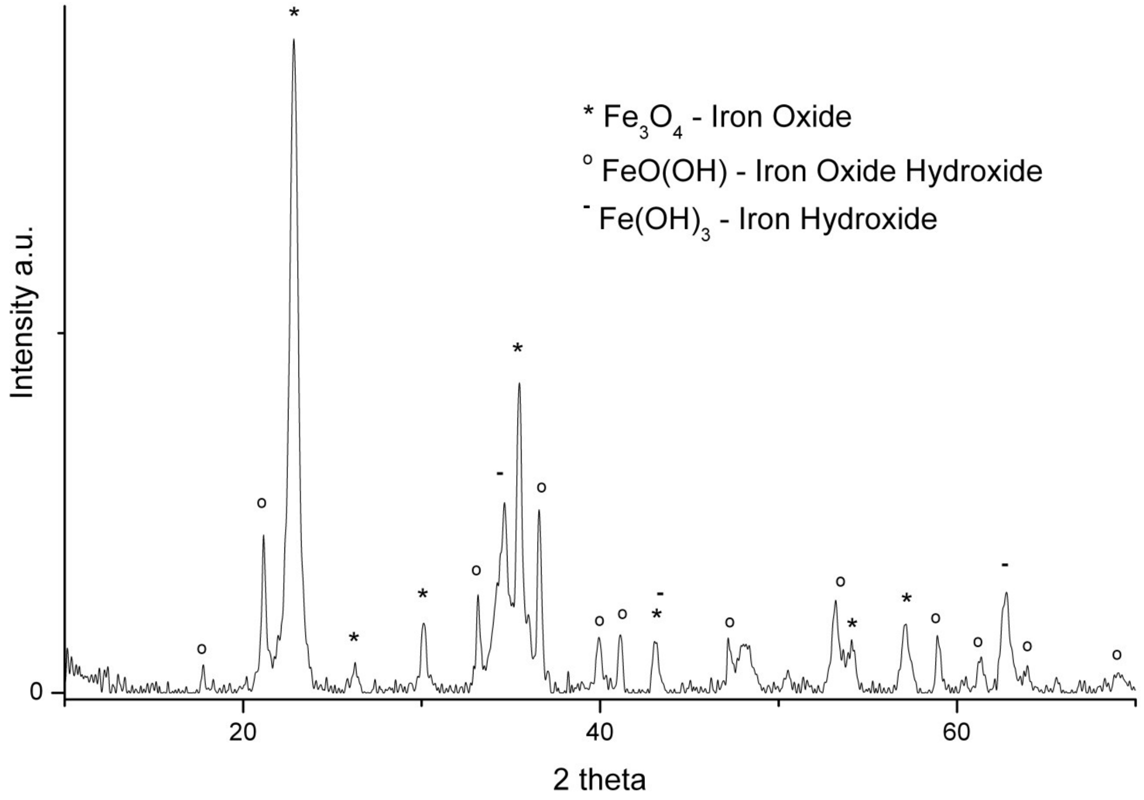


Figure S7. Powder X-ray diffraction (XRD) data for deactivated catalyst. Isolated brown heterogeneous crystalline material showing a mixture of at least three separate iron oxides.

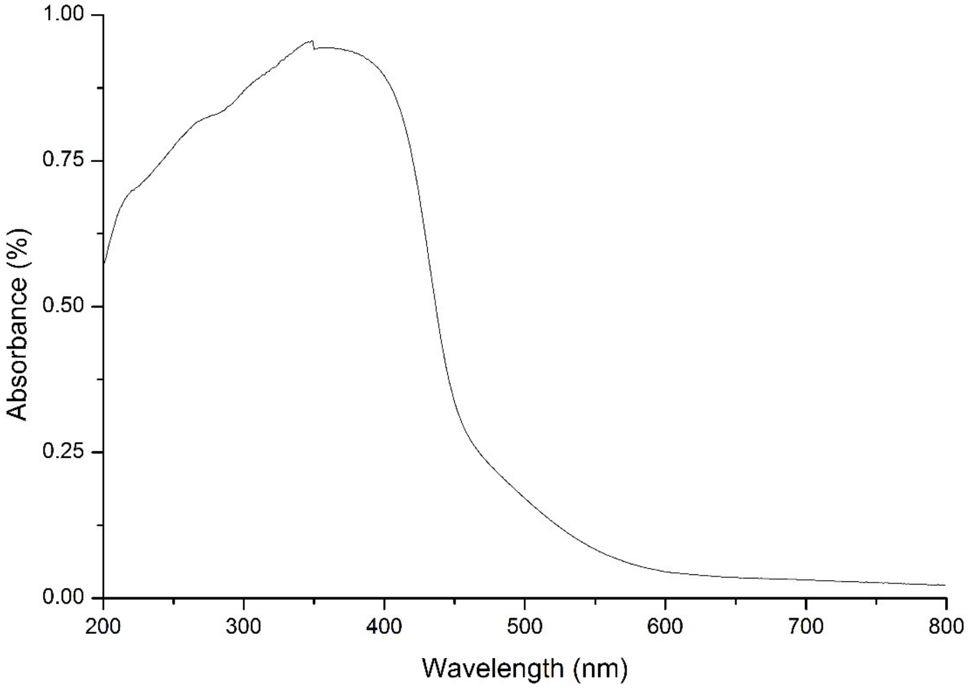


Figure S8. UV-Vis spectrum of Bi_2WO_6. Bandgap was determined to be 470 nm.

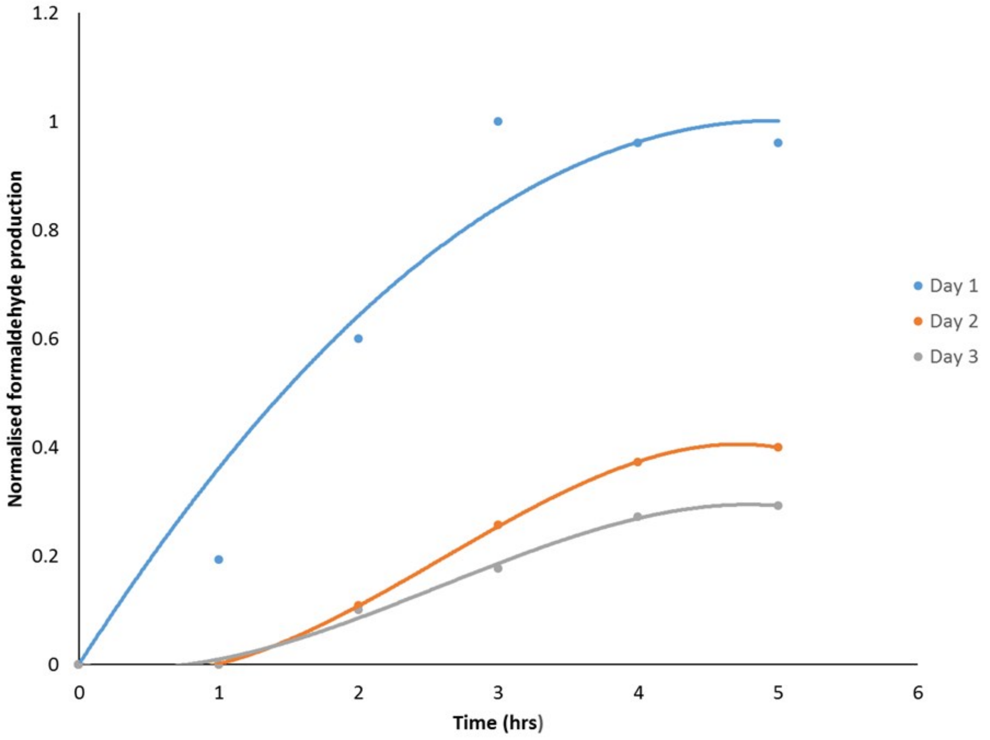


Figure S9. Attempted reactivation of Bi_2WO_6 by heating to 300°C for 14 hours in air.

Regeneration	Formaldehyde	W atomic %	Bi atomic %	W/Bi ratio

number	production (umoles)			
Fresh	8.2	11.21	21.48	0.52
1	4.0	11.13	22.26	0.50
2	3.2	11.16	22.15	0.50

Figure S10. Composition of the Bi_2WO_6 during each regeneration step as measured by EDS

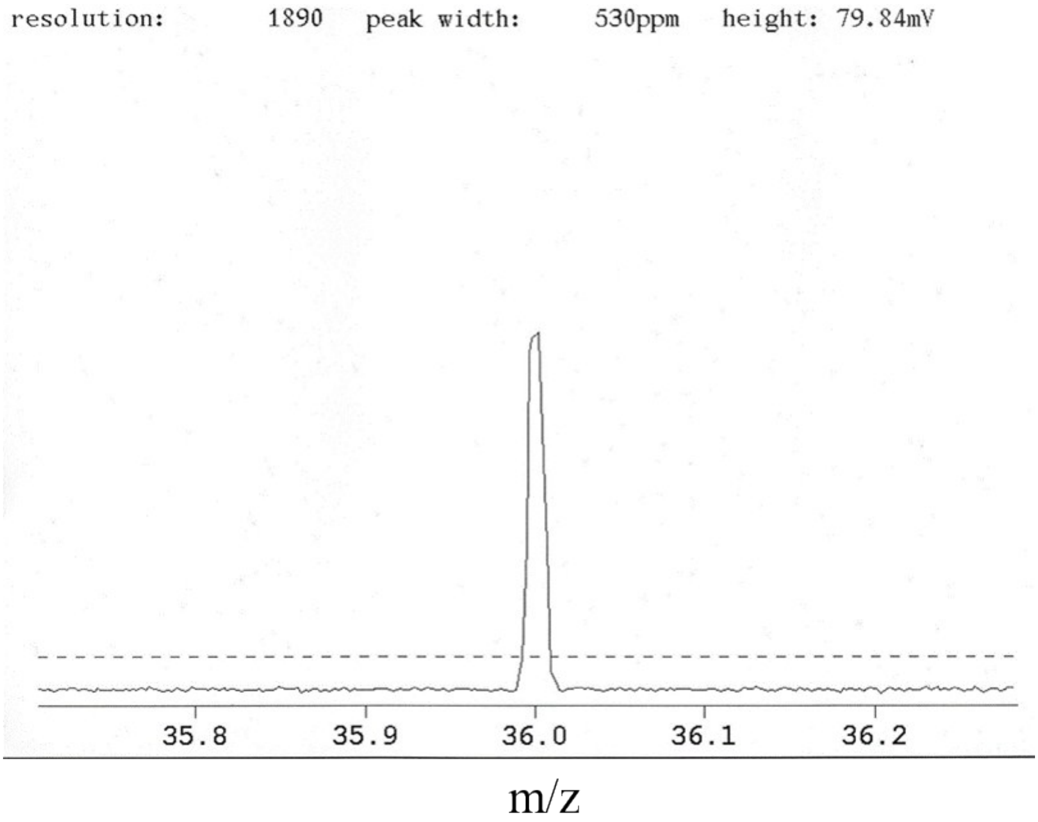


Figure S11. Isotopic experiment using H_2O^{18} in the reduction of sodium formate to formaldehyde showing the $^{18}O_2$ peak

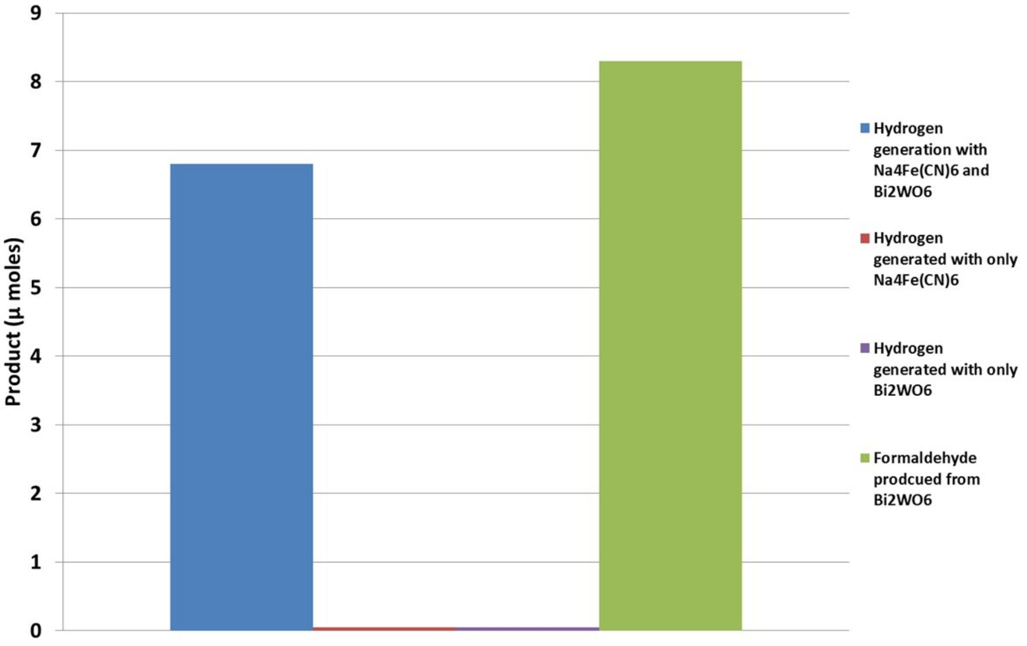


Figure S12– The hydrogen generation from sodium formate and water with both Bi_2WO_6 and $Na_4Fe(CN)_6$, only Bi_2WO_6 and with only $Na_4Fe(CN)_6$ as well as the formaldehyde generated by Bi_2WO_6