Supporting Information for:

Solar-Driven Water Oxidation and Decoupled Hydrogen Production Mediated by an Electron-Coupled-Proton Buffer

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SI-1: General Experimental Remarks: All chemical reagents and solvents were purchased from Sigma Aldrich, except for phosphomolybdic acid ($H_3PMo_{12}O_{40}$), 0.180 mm-thick Nafion N-117 membrane, Pt mesh and carbon felt, which were purchased from Alfa Aesar. All chemical reagents and solvents were used as purchased. All electrolyte solutions were prepared with reagent grade water (18 MΩ-cm resistivity). pH determinations were made with a Hanna HI 9124 waterproof pH meter. Fluorine-doped tin oxide on glass (FTO) coated plain float electrodes (7 Ohm per sheet) were purchased from Hartford Glass Co., Inc. All other materials were obtained as stated in the text. Experiments performed at "room temperature" were carried out at 20 °C. Specialist glassware was purchased from Adams & Chittenden. An AM 1.5 solar filter (Ocean Optics) was used as the light source at a fixed distance of 1 cm.

SI-2: Electrochemical Methods and Cell Set-up: In the cathodic side of the cell, 25 mL of oxidised 0.5 M phosphomolybdic acid in water was stirred in a sealed, oxygen-free and dark environment in contact with a large surface area carbon felt cathode. In the anodic compartment, 25 mL of 1 M methanesulfonic was stirred in a sealed, oxygen-free environment with a WO_3 on FTO anode (of area = 1 cm^2 and prepared by literature methods[S1]) suspended in solution by a crocodile clip. Solutions are degassed with argon for 20 minutes prior to use. An electrical connection was established between the WO_3 photoanode and carbon felt cathode through a Uniscan PG580RM potentiostat. The reference and counter electrode leads of this potentiostat were both connected to the cathode to give a floating reference (or two-electrode) configuration, across which fixed bias voltages could be applied in a controlled fashion. The two chambers of the electrolysis cell were separated by a Nafion 117 membrane. The resistance of this cell was found to be on the order of 14 Ohm, but all data reported in this manuscript are reported without correction for this resistance. Irradiation was conducted using an Oriel 150 W solar simulator equipped with AM 1.5 G filter, with an anode-light source distance that gave an irradiation intensity on the photoanode of 100 mW cm^{-2} (as gauged by a light meter). In a two-electrode, chopped light experiment such as that shown in Figure 3a, a bias of 0 V was set across the cell. The anode was kept in dark conditions for 30 s followed by irradiation with AM 1.5 light for 30 s. This process was repeated 10 times and the current recorded. Repeat experiments with both the same anode and different WO_3-FTO anodes made by the same procedure gave very similar results. A schematic of this general cell set-up is shown in Figure S1.

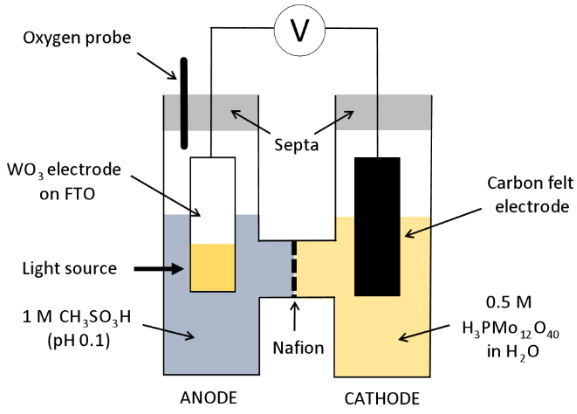

Figure S1. The general cell set-up used in this work. In most cases, no bias voltage was applied between the electrodes and therefore V = 0.

In a two-electrode, chopped light experiment such as that shown in Figure 3a in the main text, a bias of 0 V was set across the cell. The anode was kept in dark conditions for 30 s followed by irradiation with AM 1.5 light for 30 s with stirring. This process was repeated 10 times and the current recorded. Repeat experiments with both the same anode and different WO_3-FTO anodes made by the same procedure gave very similar results. Alternatively, linear sweep voltammetry was employed in this two-electrode configuration between 0 V (no bias) and a defined positive bias on the WO_3-FTO electrode (which was therefore acting as the anode). The positive biases reached and the scan rates are specified where this data is reported. As the voltage was swept, irradiation of the WO_3-FTO electrode was again performed according to the pattern: 10 s dark, then 10 s irradiation at 1 Sun, then repeated with stirring.

SI-3: Headspace Oxygen Determination: The WO_3 films were tested for their photoelectrochemical activity towards oxygen evolution in a two chamber Teflon cell equipped with a quartz window in anodic compartment (to allow illumination). A two electrode set-up was used, with a Pt mesh as the counter electrode and 1 cm^2 WO_3-FTO films as the working electrode (anode). After several minutes without electrolysis (to ascertain if the cell was leaking), the WO_3-FTO anode was irradiated with simulated solar light (1 Sun intensity, provided by an Oriel 150 W solar simulator equipped with AM 1.5 G filter) with 0

V bias across the cell (two-electrode configuration). Light intensity was measured with a calibrated reference cell (Oriel, 91150V) and adjusted to 100 mW cm^2. The illuminated surface area of the WO_3 electrode was 1 cm^2. Oxygen was detected quantitatively using a PyroScience fluorescence based oxygen sensor (OXROB10). The photoanodic compartment was filled with 25 mL 1 M CH_3SO_3H and degassed with argon prior to the measurements. The cathodic compartment contained 25 mL 0.5 M phosphomolybdic acid. The oxygen probe was inserted through a rubber septum and continuous O_2 readings were conducted at 1 s intervals throughout the experiment. The probe was calibrated using a 2-point method (argon: 0% O_2 and air: 20.9% O_2) with an error of 5% on the reading. Prior to the experiment, the baseline was measured for 60 minutes, in the dark, followed by 1 hour illumination at 1 Sun. The total system headspace was determined to be 12 mL. Charges passed during irradiation (at 0 V bias) and measured by the potentiostat were converted into expected volume percentages of oxygen in the headspace by converting charges to an expected number of moles of gas (by dividing 4*F* for O_2, where *F* is the Faraday constant), and then taking the volume of 1 mole of an ideal gas at room temperature and pressure to be 24 L. Faradaic efficiencies were then calculated by taking the ratio of gas volume % based on the charge passed to the gas volume % measured in the cell headspace by the O_2-sensing probe. Faradaic efficiencies were based on the total amount of charge passed. All gas determinations were performed at least twice. A Faradaic yield of 84% (±6%) was obtained for O_2 production by this method.

SI-4: Headspace Hydrogen Determination: Gas chromatography was conducted using an Agilent Technologies 7890A GC system. For determining hydrogen evolution during irradiation (V = 0 V), an airtight two-chamber cell (as in Figure S1) was used. The solution was stirred and the headspace was sampled by gas-tight syringe (volume taken per sampling event = 50 µL) and introduced onto the GC column by direct injection at various intervals. The column used was a 30 metre-long 0.320 mm widebore HP-molesieve column (Agilent). The GC oven temperature was set to 27 ºC and the carrier gas was Ar. The front inlet was set to 100 °C. The GC system was calibrated for H_2 using certified standards of hydrogen at a range of volume % in argon supplied by CK Gas Products Limited (UK). Linear fits of volume % *vs.* peak area were obtained, which allowed peak areas to be converted into volume % of H_2 in the cell headspace. Total system headspaces were calculated by filling the cells with water at room temperature. Typical headspaces were on the order of 12 mL. During irradiation, no hydrogen was detected in either the anode or cathode headspace, with the lower limit of detection of H_2 in the headspace being 0.04%. Charges passed were converted into expected volume percentages of hydrogen in the headspace by converting charges to an expected number of moles of gas (by dividing $2F$ for H_2, where F is the Faraday constant), and then taking the volume of 1 mole of an ideal gas at room temperature and pressure to be 24 L.

SI-5: Calculation of array size necessary to produce 500 g H_2 in 8 hours: The following calculation assumes that a solar-to-hydrogen array operates under a regime where the rate of hydrogen production and the rate of solar-driven water oxidation are equivalent, as is the case when the two half-reactions of water splitting are not decoupled:

500 g H_2 = 250 moles H_2

This requires the passage of 250 × 2 × 96485 Coulomb = 48242500 C

An array running at 0.01 A cm^{-2} will pass 0.01 × 8 × 3600 Coulomb per centimetre in 8 hours = 288 C cm^{-2}

Hence an area of 48242500/288 = 167508 cm^2 is required, or 16.8 m^2.

This is a minimum size of array. In reality, larger arrays would be needed as constant irradiation for 8 hours at the necessary intensity would be subject to the prevailing conditions (*e.g.* cloud cover).

SI-6: Electrochemical re-oxidation of the reduced Electron-Coupled-Proton Buffer and H_2 generation: The Electron-Coupled-Proton Buffer was first reduced whilst water was photo-oxidised in a cell set-up as shown in Figure S1. Hence a 1 cm^2 WO_3 photoanode in 25 mL 1 M CH_3SO_3H was irradiated with simulated sunlight overnight at 0 V bias. This caused the Electron-Coupled-Proton Buffer (0.5 M phosphomolybdic acid in H_2O, 25 mL) to become reduced at the carbon electrode in the counter electrode compartment. A total charge of 47 C was passed.

Electrochemical re-oxidation of this reduced Electron-Coupled-Proton Buffer was then performed in an airtight two-compartment cell with a three-electrode configuration at 25 °C.

The compartments were separated by a Nafion membrane and the cell was fully degassed with argon before electrolysis was started. The working electrode compartment was charged with the same 25 mL of phosphomolybdic acid (0.5 M in H_2O), which had previously been reduced by 47 C during the photo-driven oxidation of water (see above). A carbon felt working electrode was used, along with an Ag/AgCl reference electrode. In the counter electrode compartment, a platinum mesh counter electrode was used in 25 mL 1 M CH_3SO_3H. This counter electrode chamber was further equipped with a gas burette. The Electron-Coupled-Proton Buffer was then oxidised at a potential of +0.75 V (*vs.* reference) and the volume of gas evolved at the counter electrode was measured using the gas burette. 47 C of charge were thus passed before the Electron-Coupled-Proton Buffer returned to its original yellow colour (indicative of full re-oxidation) and the current fell away to negligible background levels. 6.0 mL of gas were collected in the burette, and gas chromatography confirmed that this was hydrogen. This equates to 2.5×10^{-4} moles of hydrogen produced, which agrees well with the theoretical maximum amount of hydrogen that could be produced based on the charge passed ($47/2F = 2.44 \times 10^{-4}$ moles of hydrogen). The Faradaic efficiency of the system is thus unity to within the error of this technique ($\pm\ 0.1 \times 10^{-4}$ moles of hydrogen based on an error of ± 0.2 mL in the burette readings).

SI-7: Estimation of overall system efficiency: A very rough estimate of the overall efficiency of the system can be gauged by considering the solar and electrical energy inputs on one hand and the total energy that could be released by burning the hydrogen that is produced by the system on the other. As we show below, the efficiency is dominated by the solar-driven step and is limited by the solar-derived current densities that can be achieved.

A solar input at 1 Sun intensity has a power rating of 0.1 W cm^{-2}. Taking the average current density achieved at this intensity at 0 V electrical bias to be 1 mA cm^{-2} (Figure 3 in the main text), 100 C of charge for water oxidation coupled to ECPB reduction would be passed in 100,000 seconds (assuming an electrode size of 1 cm^2). At a power density of 0.1 W cm^{-2}, this means that 10 kJ of solar energy would be required in order to pass this much charge.

Compared to the above figure, the electrical energy required to re-oxidize the ECPB and generate H_2 is small. If we assume that a fixed voltage of 1.5 V across the cell is sufficient for this process,[S2] then passing 100 C at this voltage requires only 150 J.

As the results presented here show, all this charge can be extracted as hydrogen. Hence 100 C of electrical charge equates to 5.18×10^{-4} moles of hydrogen. Taking the higher heating value of hydrogen oxidation to be 286 kJ mol^{-1}, this amount of hydrogen would liberate 148 J upon complete combustion. Compared to the energy input (~10150 J), this gives an overall efficiency in the region of 1.5%. We note that this does not include any balance of plant energy requirements, for items such as pumps, compressors and so-forth.

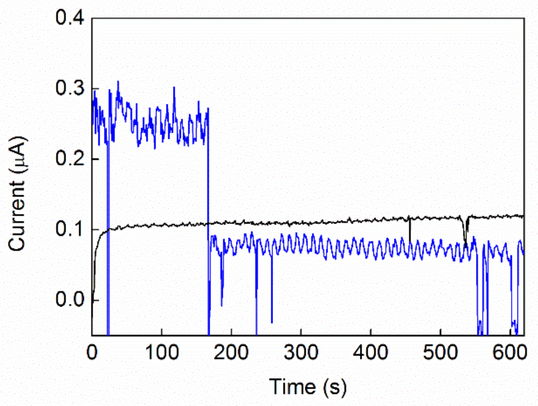

Figure S2. Expansion of the data given in Figure 3A in the main text. Black line: with $H_3PMo_{12}O_{40}$ but using only FTO as the anode. Blue line: with a WO_3-FTO anode, but using no Electron-Coupled-Proton Buffer.

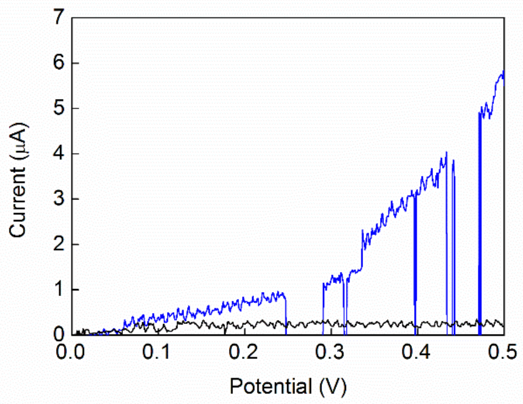

Figure S3. Expansion of the data given in Figure 3B in the main text. Black line: with $H_3PMo_{12}O_{40}$ but using only FTO as the anode. Blue line: with a WO_3-FTO anode, but using no Electron-Coupled-Proton Buffer.

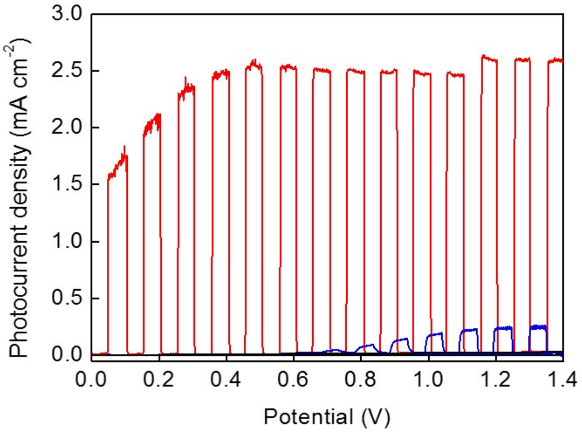

Figure S4. Chopped light experiment in a two-electrode configuration according to the cell set-up shown in Figure S1. The bias potential was varied from 0 to +1.5 V (WO_3 anode positive) at a rate of 5 mv/s. Red line: cell set up as Figure S1, with FTO-WO_3 photoanode in 1 M methanesulfonic acid and 0.5 M $H_3PMo_{12}O_{40}$ in the cathode compartment. Black line: with $H_3PMo_{12}O_{40}$ in the cathode compartment but using only FTO as the anode. Blue line: with a WO_3-FTO anode, but using 1 M methanesulfonic acid in both compartments.

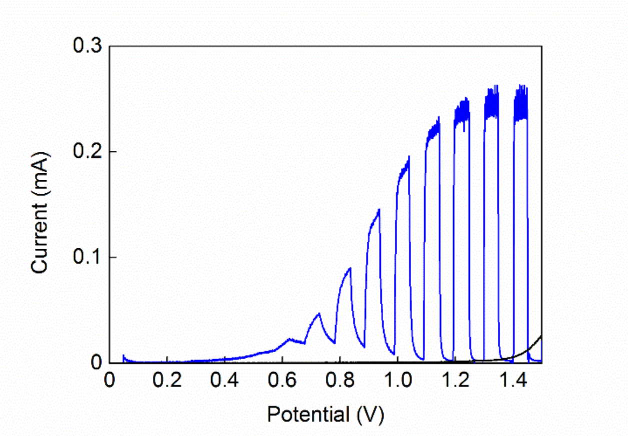

Figure S5. Expansion of the data given in Figure S4. Black line: with $H_3PMo_{12}O_{40}$ in the cathode compartment but using only FTO as the anode. Blue line: with a WO_3-FTO anode, but using 1 M methanesulfonic acid in both compartments.

References

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