Electronic Supplementary Material (ESI) for Faraday Discussions.

Light induced formation of a surface hetero-junction in photocharged $CuWO_4$ photoanodes

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Supporting information

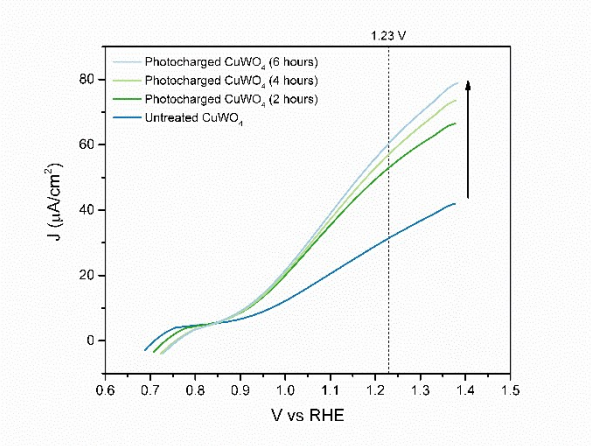

Figure S1 : Photocharging time dependent evolution of performance

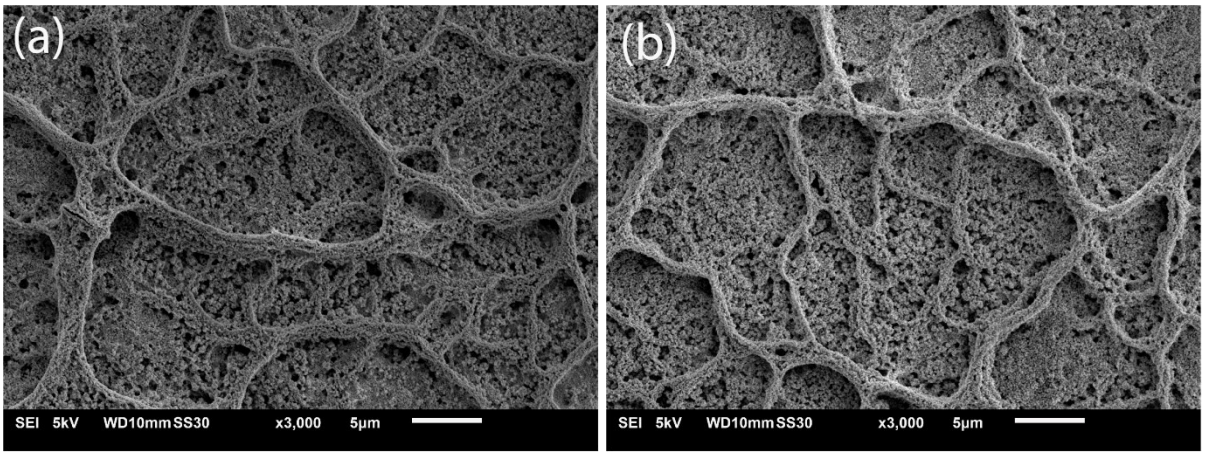

Figure S2 : (a) SEM images of UT – $CuWO_4$ and (b) PC – $CuWO_4$

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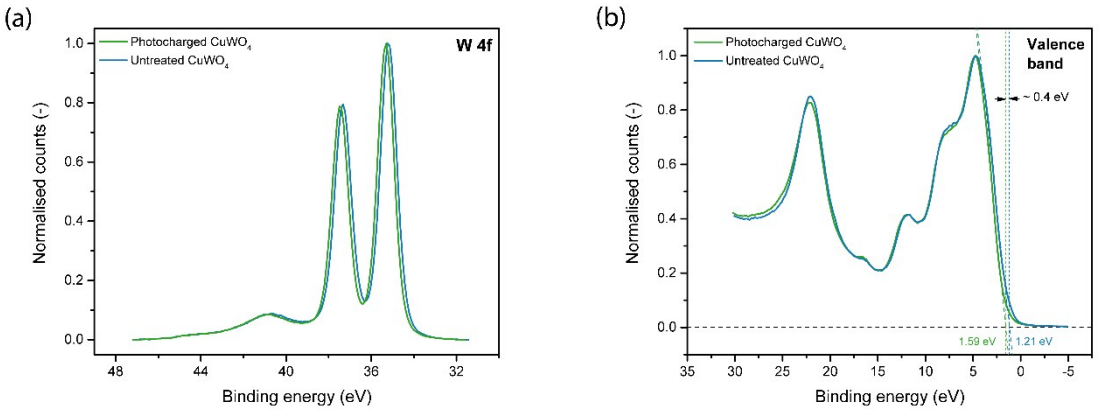

Figure S3 : (a) XPS spectra for W 4f for UT and PC – $CuWO_4$ (b) Valence band spectra for UT and PC – $CuWO_4$ sample

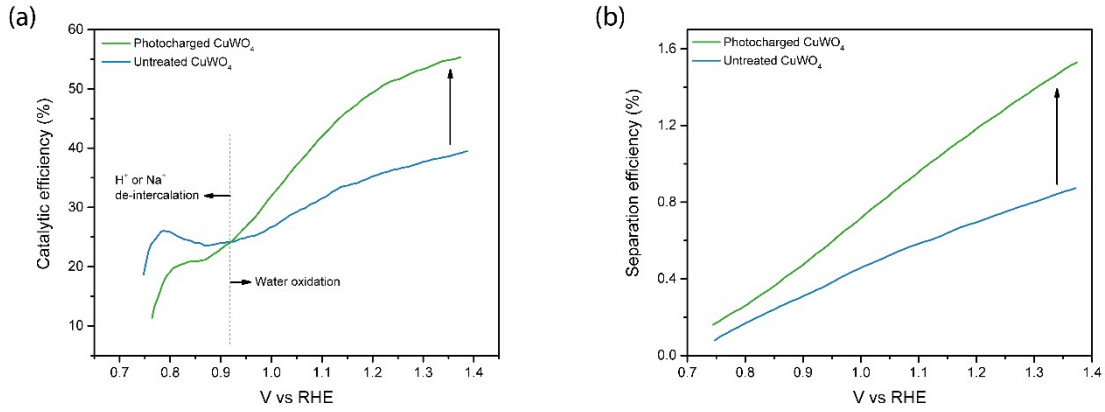

Figure S4 : (a) Catalytic efficiency of UT and PC – $CuWO_4$ (b) Separation efficiency of UT and PC – $CuWO_4$

The catalytic and separation efficiencies, as in figure S4 (a-b), were calculated as per the method recommended by Dotan et al. (1),

$$\eta_{cat} = \frac{J_{H_2O}}{J_{hole\ scavenger}} \times 100\ \% \qquad \eta_{sep} = \frac{J_{hole\ scavenger}}{J_{abs}} \times 100\ \%$$

Where, J_{H_2O} is the photocurrent in the absence of a hole scavenger, $J_{hole\ scavenger}$ is the photocurrent in the presence of a hole scavenger and J_{abs} (10.43 mA/cm²) (2) is the theoretical absorption current density.

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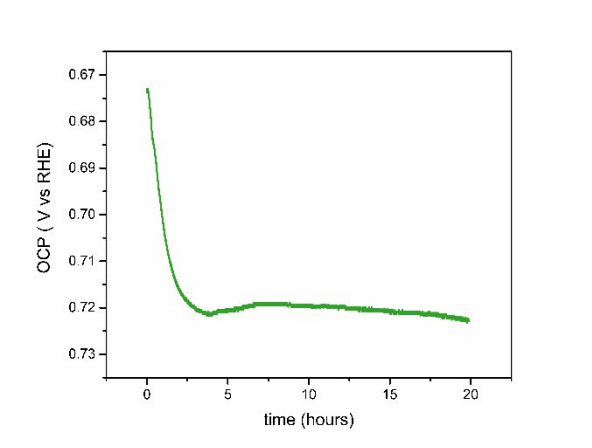

Figure S5 : Open circuit potential (OCP) vs time plot measured during the photocharging process

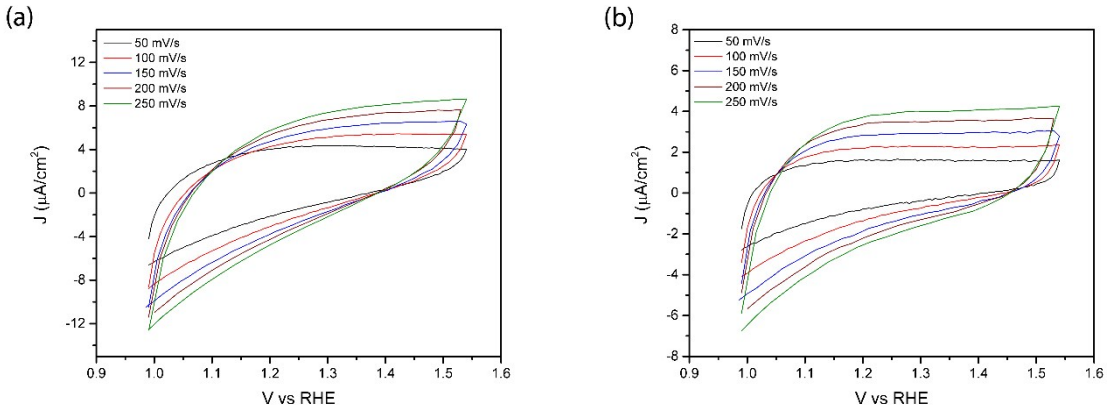

Figure S6 : Cyclic voltammetry scans performed at different scan rates, in the dark, for the ECSA calculation for (a) Untreated $CuWO_4$ (b) Photocharged $CuWO_4$

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) was used to analyse the electrolyte solution after the photocharging treatment of the CuWO4 samples, to see if the copper or tungsten has leached into the solution during the photocharging treatment. A PerkinElmer Optima 5300 DV ICP-OES system was used for these measurements. Reference solutions were made with known concentrations of copper and tungsten in the electrolyte solution used for this study to make a trend line for calibration.

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Table S1 : ICP-OES measurement data

Sample	Measured Cu [mg/l]	Measured W [mg/l]
Reference 1 (0 mg/L Cu + 0 mg/L W)	0,005	0,00
Reference 2 (0.26 mg/L Cu + 0.74 mg/L W)	0,055	0,66
Reference 3 (0.51 mg/L Cu + 1.47 mg/L W)	0,085	1,35
Reference 4 (1.02 mg/L Cu + 2.94 mg/L W)	0,159	2,58
10 hour photocharging	<0.05	<0.05
16 hour photocharging	<0.05	<0.05
20 hour photocharging	<0.05	<0.05

References

1. Dotan H, Sivula K, Grätzel M, Rothschild A, Warren SC. Probing the photoelectrochemical properties of hematite (α-Fe2O3) electrodes using hydrogen peroxide as a hole scavenger. Energy Environ Sci. 2011;4(3):958-64
2. Bohra D, Smith WA. Improved charge separation via Fe-doping of copper tungstate photoanodes. Phys Chem Chem Phys. 2015;17(15):9857-66

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