Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Improved Charge Separation via Fe-doping of Copper Tungstate Photoanodes

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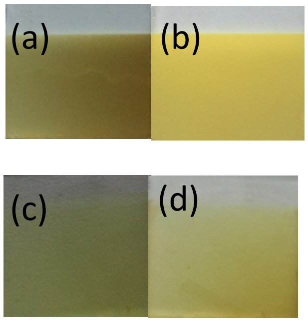

Figure S 1. Typical films spray deposited at different conditions; (a) 350°C with a basic solution (pH=12.1), (b) 350°C with a basic solution (pH = 12.1) and annealed at 500°C for 2 hours (c) 350°C with an acidic solution (pH=1.6) and (d) 350°C with a acidic solution (pH=1.6) and annealed at 500°C for 2 hours respectively.

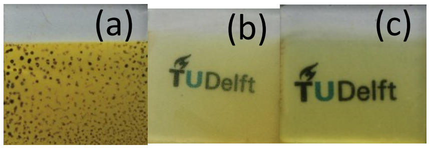

Figure S2. Visual comparison of films deposited at different substrate temperatures; (a) 250°C, (b) 350°C and (c) 450°C. The films have been annealed in air at 500°C for 2 h. Number of spray cycles is same for all the films.

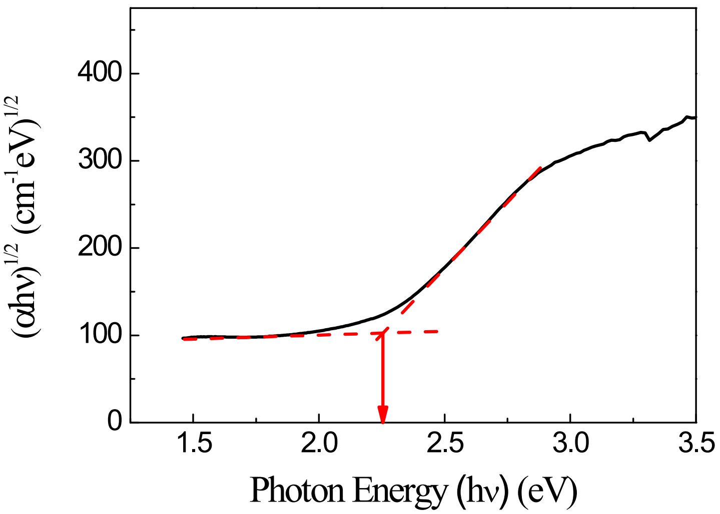

Figure S3. Tauc plot for $CuWO_4$ films deposited at 350°C and annealed in O_2 at 500°C for 2 h using acidic precursor solution (pH=1.6). The red dashed lines demonstrate a band gap of 2.25 eV for film 1.5-2 μm thick.

The inverse of the absorption coefficient gives the penetration depth of light in a material. The lesser the penetration depth, the earlier the incident light is attenuated or absorbed in the material with respect to the thickness of the film.

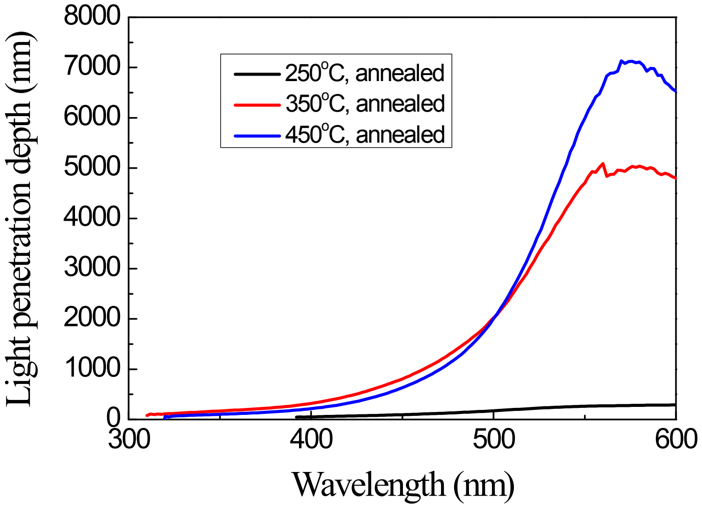

Figure S4: Comparison of light penetration depth for samples deposited using acidic precursor solution (pH=1.6) at different temperatures annealed for 2 h in O2 atmosphere at 500°C

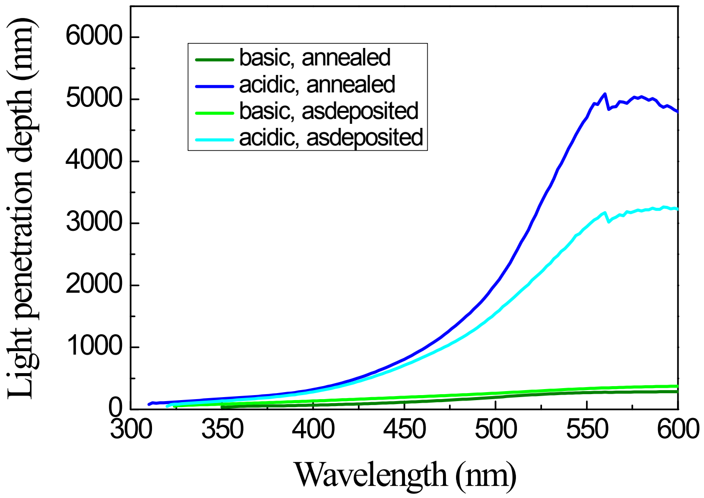

Figure S5: Comparison of light penetration depth for films deposited using acidic (pH=1.6) and basic (pH=12.1) solutions at 350°C and annealed for 2 h in O_2 atmosphere at 500°C

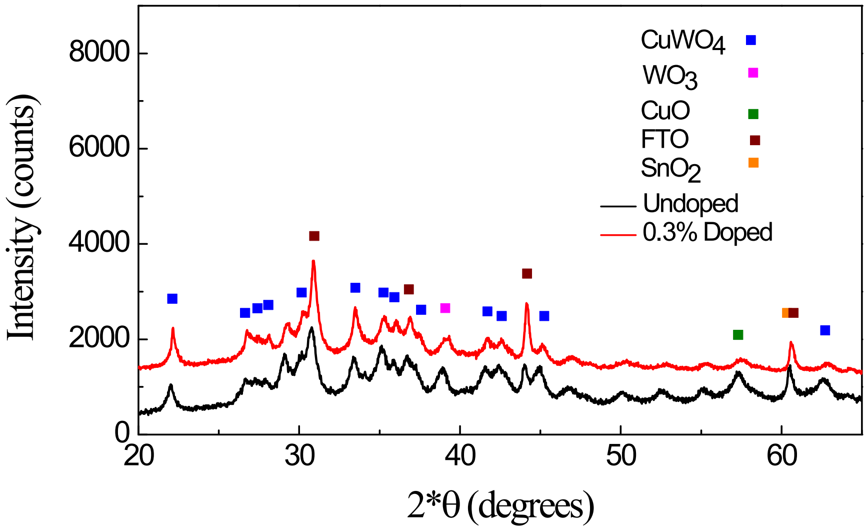

Figure S6: XRD plot with identified peaks for asdeposited 0.3% Fe doped and undoped $CuWO_4$ films deposited using 300 spray cycles of acidic precursor solution at 350°C substrate temperature.

J_{abs} can be estimated by integrating the absorptance of the film over the solar spectrum in the wavelength range of 320 nm to 600 nm as shown in Figure S7.

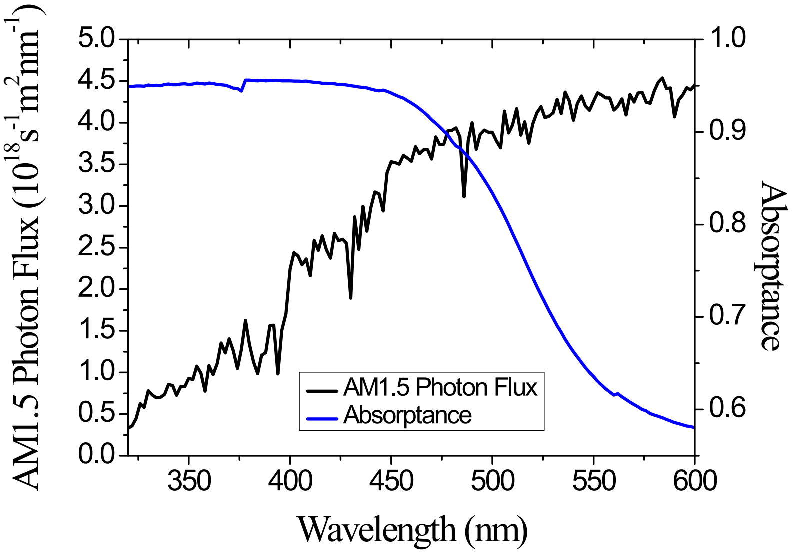

Figure S7: The absorptance of CuWO4 film and the AM1.5 solar simulator photon flux as a function of the wavelength of light.

With an aim to optimize the thickness, films were deposited using different number of spray cycles with all other deposition parameters alike. The photocurrent was then measured for front and back illumination as well as in dark at 1.23 V vs. RHE. The result of this study is shown in Figure S8. It was found that the films deposited using 300 cycles (1.5-2 µm thick) show the best performance in terms of both the front and the back illumination. Clearly, in the thickness range explored for this analysis, the film thickness is already larger than the length the electrons can diffuse, as the current for front illumination is always lower than the back illumination. The rise in both front and back illumination current values shows the steepest rise at the lower thickness value and the trend is relatively flat for thicker films. We also observed that thicker films showed higher surface porosity and a lower band gap than their thinner counterparts. These might be some of the few other factors contributing to this trend in photocurrent with thickness. The observed photocurrent has contributions from three efficiencies: light absorption, charge separation and catalytic efficiency at the semiconductor-electrolyte interphase. The effect of film thickness on each of these aspects of observed photocurrent need to be investigated further using optical and PEC measurements. Yourey and Bartlett have suggested earlier [3] that a reduction in photocurrent was only observed by them after a thickness of 4 µm. This is almost double the thickness of our film deposited using 300 cycles.

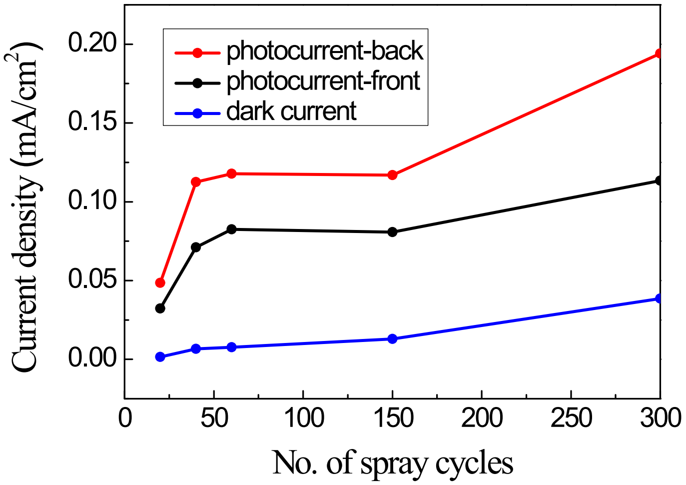

Figure S8: Current density obtained for front illumination, back illumination and dark at 1.23 V vs. RHE for films deposited using different number of spray cycles.

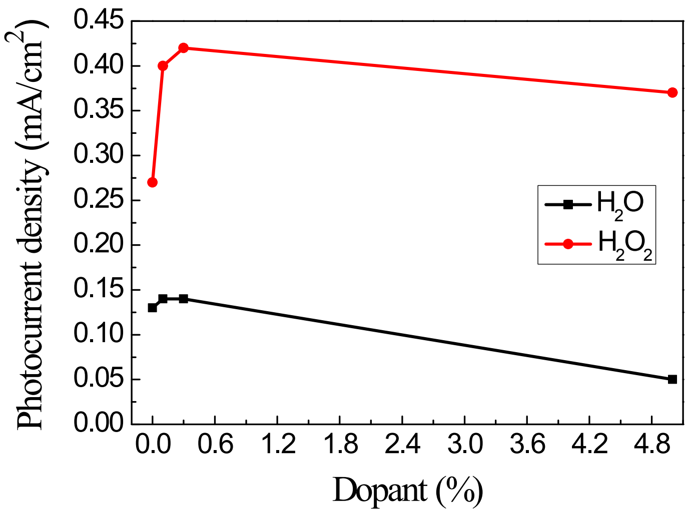

Figure S9: Photocurrent density measured at 1.23 V vs. RHE plotted against Fe dopant concentration in the $CuWO_4$ films

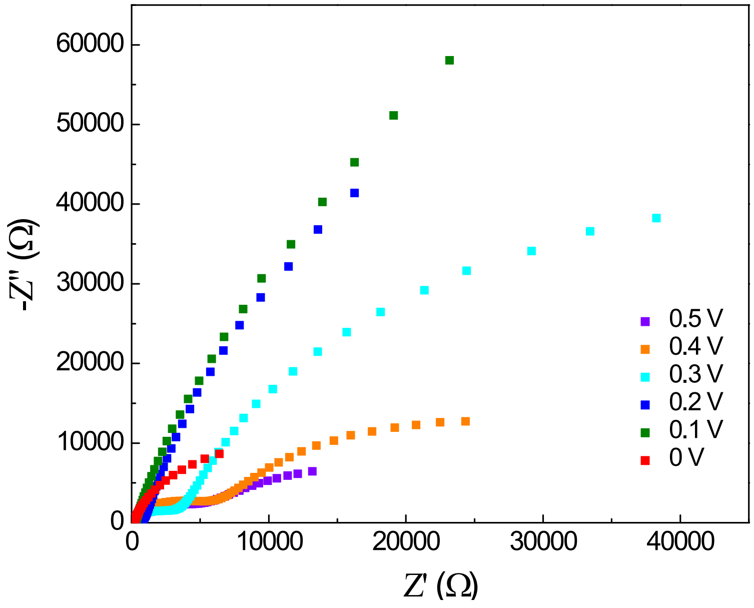

Figure S10. Nyquist plot of the impedance spectra measured for $CuWO_4$ films for different bias potentials vs. Ag/AgCl under 1 sun illumination. The amplitude of perturbation is 10 mV and the frequency range of each sweep is from 0.01 Hz to 100 kHz.

a)

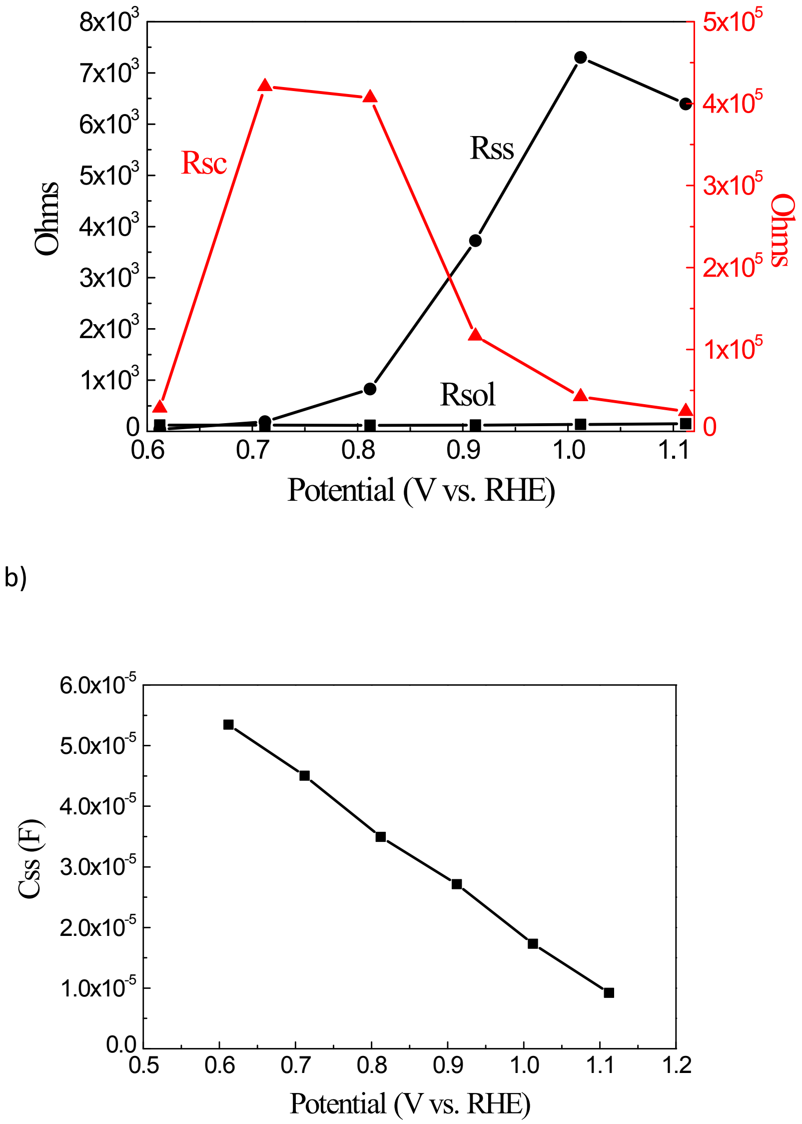

Figure S11. a) Rsol, Rsc and Rss plotted against applied bias voltage. b) Css plotted against the applied bias voltage.

Table S1: EIS model fitting: Parameter values

Voltage (V) vs. Ag/AgCl	**0.50**	**Error%**	**0.40**	**Error%**	**0.30**	**Error%**	**0.20**	**Error%**	**0.10**	**Error%**	**0.00**	**Error%**
Voltage (V) vs. RHE	1.11	1.11	1.01	1.01	0.91	0.91	0.81	0.81	0.71	0.71	0.61	0.61
Rsol (Ω)	149.03	0.21	136.83	0.22	123.20	0.32	119.20	0.46	120.40	0.50	123.50	0.45
Rsc (Ω)	24372.00	3.41	42243.00	1.52	116400.00	2.32	407190.00	11.40	420740.00	9.24	28408.00	2.90
Rss (Ω)	6392.80	2.05	7300.10	0.86	3722.00	0.75	826.30	1.26	189.70	2.41	38.77	5.75
CPEss-T	0.00	3.64	0.00	1.02	0.00	0.50	0.00	0.76	0.00	2.39	0.00	4.97
CPEss-P	0.69	1.65	0.76	0.71	0.83	0.42	0.87	0.37	0.90	0.57	0.87	0.82
Wmax-ss	94.83	-	74.21	-	125.17	-	510.27	-	3353.80	-	17469.00	-
Css* (F)	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-
CPEsc-T	0.00	1.43	0.00	0.98	0.00	1.59	0.00	4.30	0.00	10.30	0.00	34.80
CPEsc-P	0.89	0.21	0.90	0.15	0.87	0.25	0.79	0.69	0.73	1.64	0.79	4.82
Wmax-sc	0.57	-	0.32	-	0.10	-	NA**	-	NA**	-	NA**	-
Csc* (F)	0.00	-	0.00	-	0.00	-	-	-	-	-	-	-
RMS Error %	2.20	-	0.90	-	1.14	-	4.65	-	5.43	-	13.60	-

Voltage (V) vs. Ag/AgCl	0.4-dark	Error%	0.4-light	Error%	0.4-light+H_2O_2	Error%
Rsol (Ω)	127.90	0.32	137.00	0.22	144.10	0.26
Rsc (Ω)	63199.00	6.95	42200.00	1.52	13470.00	1.34
Rss (Ω)	14814.00	2.41	7300.00	0.86	9603.00	2.98
CPEss-T	0.00	4.88	0.00	1.02	0.00	5.97
CPEss-P	0.85	1.90	0.76	0.71	0.84	2.00
Wmax-ss	40.47	-	74.21	-	68.90	-
Css* (F)	0.00	-	0.00	-	0.00	-
CPEsc-T	0.00	1.13	0.00	0.98	0.00	1.52
CPEsc-P	0.91	0.18	0.90	0.15	0.88	0.23
Wmax-sc	NA**	-	0.32	-	6.41	-
Csc* (F)	-	-	0.00	-	0.00	-
RMS Error %	3.44	-	0.90	-	2.74	-

* these values have been calculated using the equation for equivalent capacitance of a constant phase element:

$$C_{CPE} = CPE_T(\omega_{max})^{n-1}$$

where CPE_T is the so-called numerical value of the capacitance of the element such that for n=0 the CPE behaves like a pure resistance and for n=1 it behaves purely capacitive. ω_{max} is the frequency at which the imaginary value of the impedance has a maximum as seen in the Nyquist plot.

** these values could not be estimated due to lack of information in the data