Electronic Supplementary Material (ESI) for ChemComm.

Quantitative Hole Collection for Photoelectrochemical Water Oxidation with $CuWO_4$

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Electronic Supplementary Information

Experimental

Film Preparation and Characterization

Copper tungstate ($CuWO_4$) thin films were deposited on fluorine-doped tin oxide (FTO) coated glass (Hartford Glass, 12 Ω cm^{-2}) and Si wafer (University Wafer) by an atomic layer stack deposition-annealing (SDA) method via atomic layer deposition (ALD) (Savannah 100, Cambridge Nanotech Inc.) using a procedure described previously.[1] Briefly, the substrates were sonicated in soap water, distilled water and isopropanol, and blown dry with nitrogen prior to deposition. The precursors for the deposition of WO_3 and CuO were bis(*tert*-butylimido)bis(dimethylamido)tungsten (VI) (Strem Chemicals Inc., >97%) and *N,N'*-di-*sec*-butylacetamidinate (Dow Chemical Co., >99.0%), respectively. The nitrogen carrier gas was kept at 5 sccm. 1000 ALD cycles of WO_3 was deposited using a modified version of a reported procedure.[2] The tungsten precursor was heated up to 75 °C but the vapor pressure was too small to be detected by our pressure gauge. In each ALD cycle, the tungsten precursor was pulsed for 2 s, followed by 10 s under exposure mode and 6 s nitrogen purge. De-ionized water (millipore, 18 MΩm) was used as the oxidant and was pulsed for 0.5 s followed by 15 s of exposure mode and 6 s of purge. ~170 ALD cycles of CuO was deposited on 1000 cycles of WO_3 according to calculations described in our previous work[1] to match 1:1 ratio between the two metals. The copper precursor was heated to 150 °C but the vapor pressure was not detectable by the pressure gauge. The copper precursor was pulsed for 3 s in each ALD cycle. After purging for 6 s, the oxidation was performed. The oxidation was a 2 s ozone (~10% by weight O_3 in ultrahigh purity O_2 produced by Yanco Industries ozone generator) pulse, followed by a 3 s purge to allow for enough generation of ozone, and performed for 10 times. After deposition, the stack of binary oxides was annealed at 550 °C in air for 30 min with a ramping rate of 2 °C / min. The slight adjustment of annealing temperature is explained in the following text in this electronic supplementary information (ESI). The thickness of as-deposited WO_3 films were measured to be ~65 nm thick on Si by ellipsometry measurements (Horiba Jobin Yvon, Smart-SE). The thickness of the $CuWO_4$ thin film was calculated to be ~80 nm using the method described in our previous publication,[1] which agrees with the measured growth rate and previous measurement using AFM and SEM.[1] The annealed films were characterized by X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM) (Carl Zeiss Microscopy).

Photoelectrochemical Measurements

$CuWO_4$ electrodes were masked with a 60 μm Surlyn film (Solaronix) with a 0.28 cm^2 hole to define the active area and to prevent scratching of the thin films. The electrodes were clamped to a custom-made glass electrochemical cell with a quartz window to allow illumination from the electrolyte-electrode (front) side. Surlyn films were adhered to the electrodes by heating to 120 °C. A home-made "no leak" saturated Ag/AgCl electrode was used as a reference electrode, and high surface area platinum mesh was used as the counter electrode. The $CuWO_4$ electrodes were examined in contact with aqueous pH9.0 1 M KB_i buffer with or without 0.5 M Na_2SO_3 or H_2O_2. The 1 M KB_i buffer was prepared by adding an appropriate amount of KOH pellets into 1 M H_3BO_3 to adjust the pH. The pH was determined using a Fisher Scientific Accumet pH meter. All potentials measured in aqueous solutions were converted to the reversible hydrogen electrode (RHE) scaled by the equation $V_{RHE} = V_{Ag/AgCl} + 0.197 + pH(0.059)$. All photoelectrochemical measurements were made with an Eco Chemie Autolab potentiostat coupled with Nova electrochemical software. Current density-voltage (*J*-*V*) curves were measured using a scan rate of 20 mV s^{-1}. The white light source was a 450 W Xe arc lamp (Horiba Jobin Yvon). An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm^{-2}. All photoelectrochemical measurements were performed by shining light on the $CuWO_4$ electrode through the electrolyte. Photocurrent densities (J_{photo}) are obtained by subtracting the dark current density from the current density under illumination. Intensity modulated photocurrent spectroscopy (IMPS) was gathered using 10% of the fixed LED driving current as the ac perturbation of the incident light intensity from 10000 to 0.1 Hz. The incident light of IMPS measurements was provided by a 470 nm LED with an LED driver from Metrohm, and the light intensity was calibrated using the current measured with a photodiode from the same manufacturer. The constant light intensity was adjusted to 116 mW cm^{-2} so that the *J*-*V* curve is close to that under 1 sun illumination. This ensures that the flux of holes reaching the surface is about the same as 1 sun condition, so that the surface dynamics (rate of hole collection and recombination) is comparable.

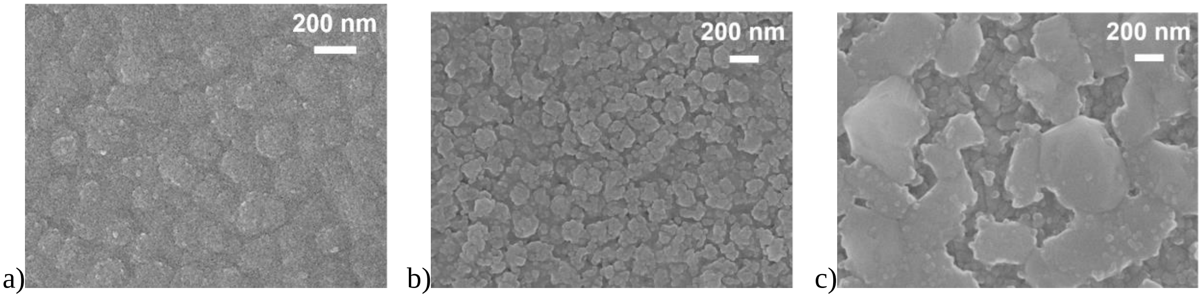

Figure S1 SEM images of a) as-deposited CuO on WO_3, and $CuWO_4$ annealed at b) 550 °C and c) 600 °C.

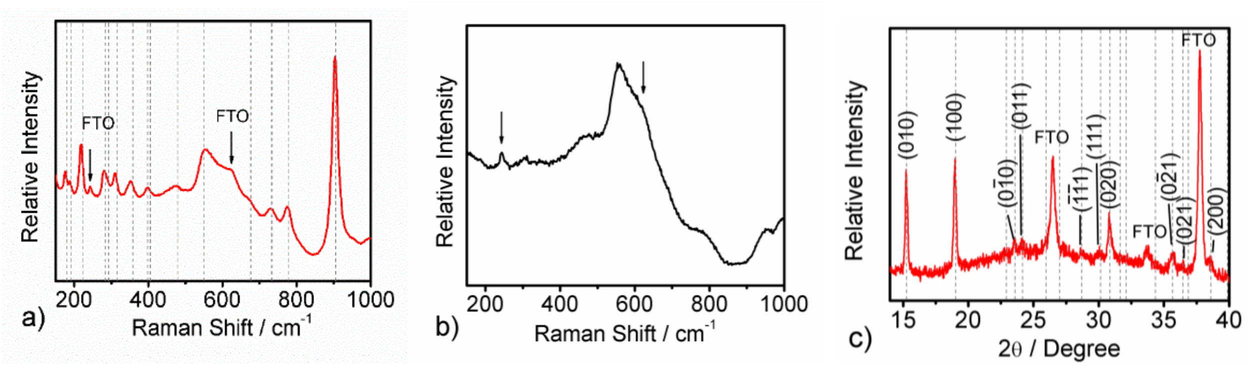

Figure S2 Raman spectra of a) $CuWO_4$ annealed at 550 °C and b) FTO. c) X-ray diffraction pattern of $CuWO_4$ annealed at 550 °C. Vertical gray dashed lines represent the peak positions of $CuWO_4$ recorded in literature[3–5].

The SEM images in Figure S1 show that the as-deposited CuO on WO_3 makes a uniform film. After annealing at 550 °C, the grains are sharpened but the film is still uniform. However, after annealing at 600 °C, although Raman and XRD show a pure composition of $CuWO_4$[1], severe aggregation occurs at the surface of the film, while underneath the top aggregated layer there are smaller grains. We adjusted the annealing temperature to 550 °C for the ease of fundamental investigations especially on-going charge carrier collection length studies in our laboratory. Raman and XRD spectra in Figure S2 show that the peaks of the resulted film match with $CuWO_4$ peaks in literature[3–5], except for those from the underlying FTO substrate. The XRD pattern of FTO can be found in our previous publication[1]. Complementary X-ray photoelectron spectroscopy (XPS) measurements of comparable $CuWO_4$ electrodes were reported by us previously.[1]

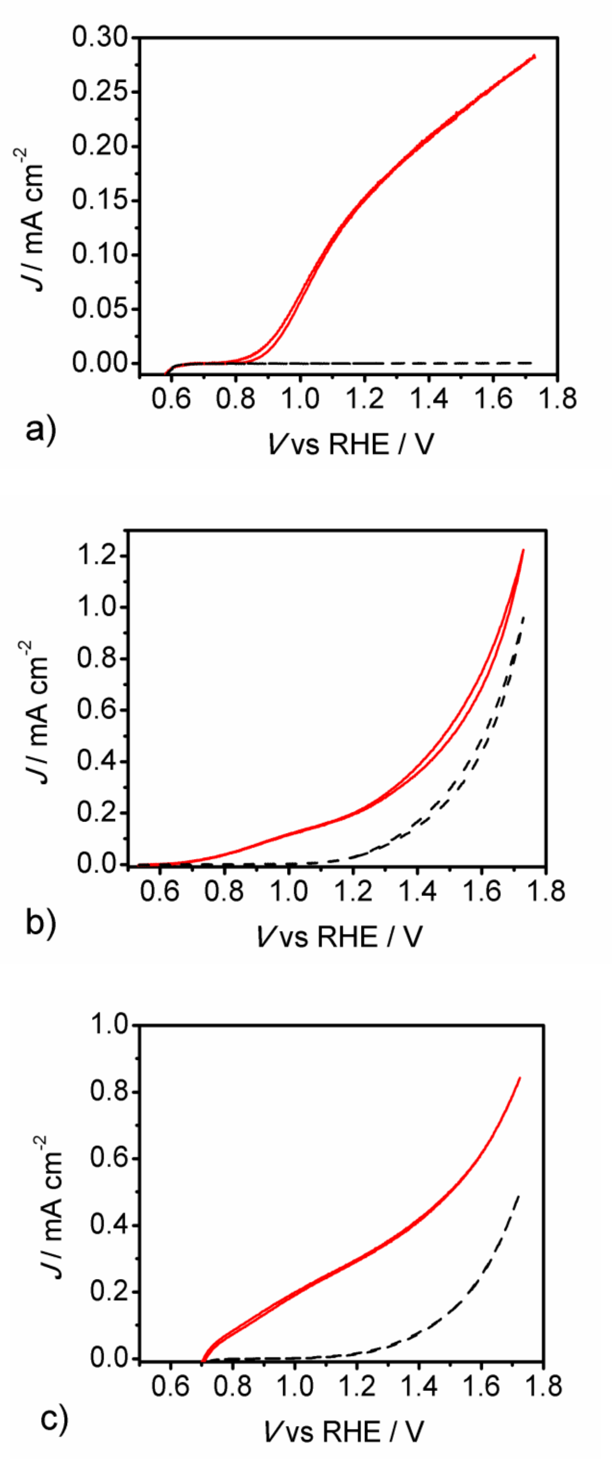

Figure S3 J_{dark}-V (black dash) and J_{total}-V (red solid) curves of $CuWO_4$ electrode measured in a) H_2O, b) 0.5 M Na_2SO_3 and c) 0.5 M H_2O_2 electrolytes in the dark and under 1 sun illumination.

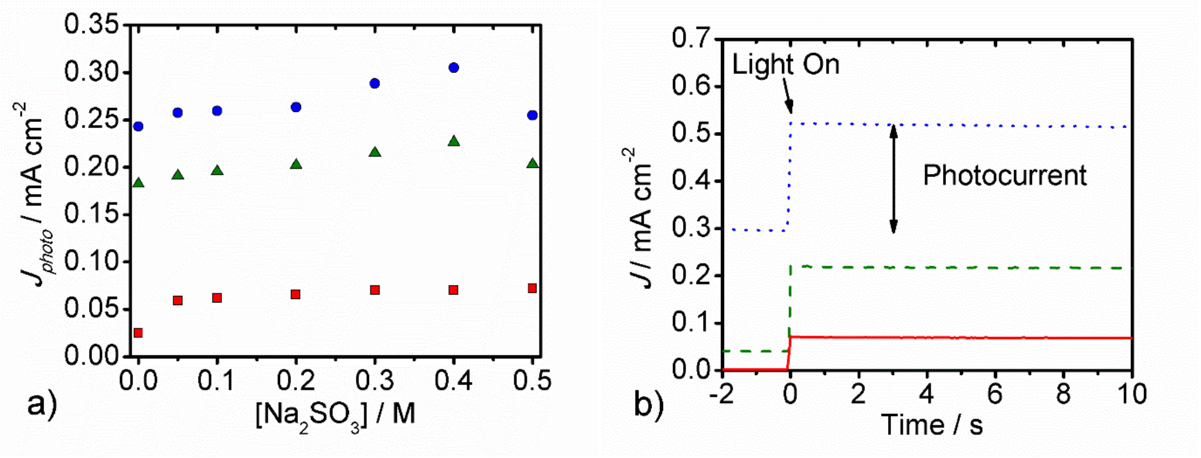

Figure S4 a) Photocurrent densities measured with a $CuWO_4$ electrode in an aqueous electrolyte containing Na_2SO_3 with various concentrations at 0.88 (red squares), 1.23 (green triangles) and 1.53 (blue circles) V vs RHE under 1 sun illumination. b) Current transients measured under 1 sun illumination in 0.5 M Na_2SO_3 electrolyte at 0.88 (red solid), 1.23 (green dash) and 1.53 (blue dots) V vs RHE.

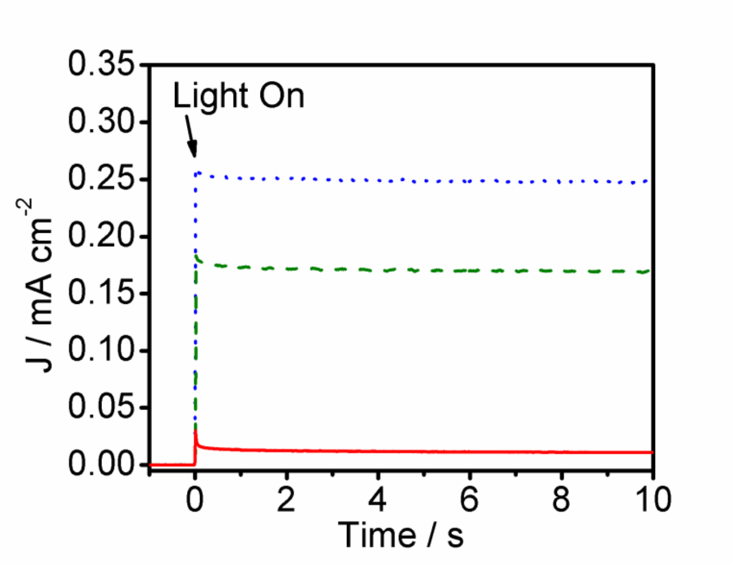

Figure S5 Current transients measured with $CuWO_4$ in an aqueous electrolyte (H_2O) under 1 sun illumination at 0.88 (red solid), 1.23 (green dash) and 1.53 (blue dots) V vs RHE.

Current multiplication mechanism of H_2O_2 in the anodic region proposed by previous studies[6] (the reaction is considered in a basic electrolyte):

$$H_2O_2 + h^+ + OH^- \rightarrow HO_2^\bullet + H_2O \tag{S1}$$

$$HO_2^\bullet + h^+ + OH^- \rightarrow O_2 + H_2O \tag{S2}$$

$$HO_2^\bullet + OH^- \rightarrow O_2 + H_2O + e^- \tag{S3}$$

H_2O_2 captures a hole from the valence band (VB) of the n-type semiconductor to form a radical intermediate (equation S1). The radical either captures another hole from VB, which is the route of normal photoelectrochemical oxidation of H_2O_2 (equation S2), or inject an electron to the conduction band (CB) of the semiconductor (equation S3). The second pathway contributes to the current doubling effect, since the original two-hole process becomes a one-hole process.

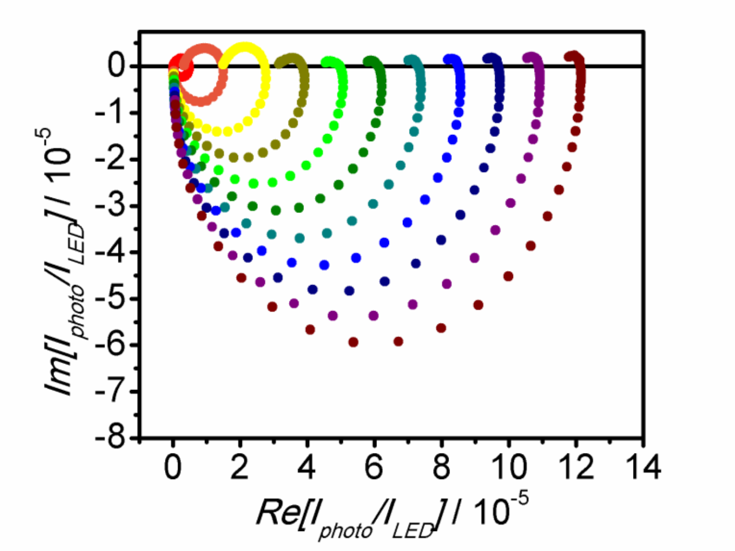

Figure S6 Nyquist plots of IMPS measured with $CuWO_4$ in H_2O under 470 nm monochromatic light with intensity of 116 mW cm^{-2}. Potential ranges from 0.73 to 1.73 V vs RHE with an interval of 0.1 V corresponding to the red, orange, yellow, dark yellow, green, dark green, dark cyan, blue, navy, purple and wine colored circles.

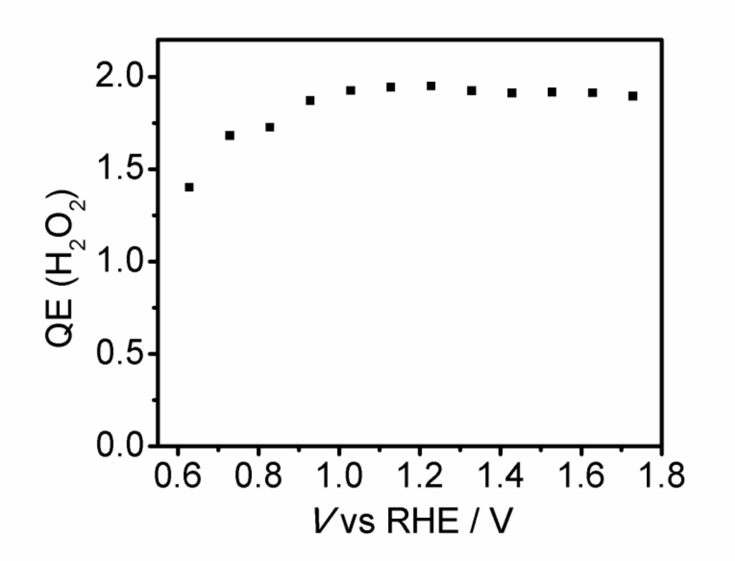

Figure S7 Current multiplication factor of $CuWO_4$ in contact with H_2O_2 represented as quantum efficiency (QE) extracted from IMPS data.

References

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