# **Supplementary Information**

# **Upconversion-Powered Photoelectrochemistry**

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**Materials.** Tungsten(VI) oxide (WO<sub>3</sub>) nanopowder (<100 nm particle size (TEM)), hydroxypropylcellulose, hexacholoroplatinic acid hexahydrate, anhydrous isopropanol and glacial acetic acid were purchased from Aldrich and used without further purification. Concentrated sulfuric acid was purchased from EMD. Water was deionized using a Barnstead nanopure system. Fluorine doped tin oxide (FTO) conductive glass substrates (TEC 15) were purchased from Hartford Glass. Pd(II) octaethylporphyrin (PdOEP) was purchased from Frontier Scientific and used without further purification. 9, 10-Diphenylanthracene (DPA) was purchased from Aldrich.

WO<sub>3</sub> film formation. FTO conducting glass substrates were cleaned by sonication using a solution of HCl in isopropanol, a solution of laboratory soap in water, then finally acetone. The FTO glass was then dried in an oven. A mixture of 3:1 by volume H<sub>2</sub>O:CH<sub>3</sub>COOH (glacial acetic acid) was mixed slowly with the WO<sub>3</sub> solid (12 wt.%) and hydroxypropylcellulose (6 wt.%). This mixture was sonicated and stirred vigorously overnight. The resultant paste was doctor bladed on FTO glass between 3 Scotch tape layers and the final WO<sub>3</sub> electrode area was adjusted to 1 cm<sup>2</sup> after the electrode was sintered at 500 °C for 30 minutes at a heating rate of 5 °C per min. The sintering resulted in a material with 10 µm average thickness as measured using a KLA-Tencor Alpha-Step IQ surface profiler.

**Photoelectrochemical (PEC) characterization.** Electrochemical measurements were performed using a BAS Epsilon electrochemistry workstation using a standard three-electrode arrangement and corrected for the dark current which was allowed to stabilize for several minutes before initiating the measurements. The PEC cell consisted of fused optically flat silica possessing a cubic shape equipped with a Teflon cap where all the electrodes were inserted. All solutions were degassed for 30 minutes before each experiment and maintained under an Ar atmosphere blanket. Current/time measurements (Figure 2) were performed using controlled potential electrolysis (CPE) at a positive overpotential to assist water oxidation. The potential for CPE was chosen in order to achieve a stable current after few minutes of electrolysis while simultaneously producing detectable photocurrents. PEC linear sweep voltammetry (LSV) experiments were also performed to obtain photocurrent response as a function of applied potential. LSV was performed at a scan rate of 1 mV/s and 0.033 Hz light chopping frequency. The electrolyte in all these experiments was 1.0 M H<sub>2</sub>SO<sub>4</sub> solution owing to the stability of WO<sub>3</sub> in acidic media. The

light source in these experiments was a 300 W Xe lamp equipped with a water filter to remove IR irradiation (heat) and two 500 nm long pass filters. The output of this apparatus was passed through a bifurcated fiber optic bundle to give 32 mW/cm<sup>2</sup> optical power density at the two outputs (25 mW,  $0.79 \text{ cm}^2$  beam size). The upconversion cuvette was placed as close as possible to the WO<sub>3</sub> photoanode affording backside illumination of the electrode. The irradiation of the upconversion mixture was achieved by simultaneously exciting two sides of the optical cell using the bifurcated fiber optic, as photographed in Figure 1.

**Upconversion Photoaction Spectra.** The photoaction curve presented in Figure 3 was calculated from the measured photocurrent (BAS Epsilon instrument) at different wavelengths using the identical PEC setup as described immediately above. Photocurrents were allowed to stabilize for 2-3 minutes and were corrected for dark current background. The light source in this experiment was a 450 W xenon arc lamp coupled to a monochromator installed in an Edinburgh Instruments fluorimeter (FS920) in tandem with a 455 nm long pass filter. The light power at different wavelengths was measured using a Nova II/PD300-UV power meter/detector head from Ophir. The following formula was used to calculate the photoaction as a function of excitation wavelength:

Photoaction (
$$\lambda$$
) = h × c ×  $\lambda^{-1}$  × Photocurrent × Incident Optical Power<sup>-1</sup> [1]

where, h = Planck's constant =  $6.626 \times 10^{-34}$  (J × s<sup>-1</sup>), c = speed of light = 299,792,458 (m × s<sup>-1</sup>),  $\lambda$  = wavelength in meters (m), photocurrent was measured in amps (A), and incident optical power was measured in watts (W).

Linear Sweep Voltammetry (LSV) of bare WO<sub>3</sub>. PEC measurements resulting from direct bandgap illumination of the WO<sub>3</sub> photoanode were performed using LSV to obtain the photocurrent achieved as a function of applied potential. Using the same three electrode configuration as described in the text, WO<sub>3</sub> was illuminated with a xenon lamp whose output is water filtered then sent directly through a fiber optic bundle to give 200 mW/cm<sup>2</sup> broadband illumination (200 mW, 1 cm<sup>2</sup> beam size). The LSV was performed at a 5 mV/s scan.



**Figure S1.** Linear sweep voltammetry at 5 mV/s scan rate of a WO<sub>3</sub> electrode in 1.0 M  $H_2SO_4$  solution subject to modulated backside illumination from a 300 W Xe lamp whose output is water filtered and sent through a fiber optic bundle to give 200 mW/cm<sup>2</sup> broadband power density.

## **Direct Bandgap WO3 Photoaction Spectrum.**

- a. Preparation of the Platinum Cathode. 5 mM  $K_2PtCl_6$  in anhydrous isopropanol was added dropwise on FTO glass surface and allowed to air dry. The platinized slides were then heated in a tube furnace at 380°C for 30 min and then cooled to RT.
- **b.** Fabrication of the WO<sub>3</sub> Sandwich Device. The area of WO<sub>3</sub> active area was adjusted to  $0.25 \text{ cm}^2$  by removing the excess material. Stretched Parafilm-M was used as spacer (20-30 µm) between WO<sub>3</sub> and platinum counter electrode, the part covering the WO<sub>3</sub> active surface was removed and 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte was added to fill the space. The device was then mounted by placing the Pt electrode on top of WO<sub>3</sub> photoanode and binder clips were used to hold them together.
- **c. Photoaction measurements**. Photoaction measurements of the WO<sub>3</sub> anode were carried out using a commercial system from PV Measurements, Inc.equipped with a 150 W xenon arc lamp and calibrated using a silicon reference photodiode.



**Figure S2.** Normalized photoaction of a WO<sub>3</sub> electrode sandwiched with platinum counter electrode in 1.0 M  $H_2SO_4$  electrolyte under +0.9 V applied bias measured in a two-electrode configuration.

**Spectroscopic measurements.** Static absorption spectra were measured with a Cary 50 Bio UV-Vis spectrophotometer from Varian. Steady-state luminescence spectra were obtained on a FL/FS920 from Edinburgh Instruments or with a PTI Instruments spectrofluorimeter, realizing excitation with a 450 W xenon arc lamp or a 75 W xenon arc lamp, respectively. In all cases, long pass sorting filters were utilized to remove unwanted higher energy light that passes through the excitation monochromator. Excitation power was measured using a Nova II/PD300-UV power meter/detector head from Ophir. Different incident excitation powers were realized by using a series of neutral density filters. Single wavelength emission intensity decays were acquired with a N<sub>2</sub> pumped dye laser (2-3 nm fwhm) from PTI (GL-3300 N<sub>2</sub> laser, GL-301 dye laser). Coumarin 500 (C500) was used to tune the unfocused pulsed excitation beam to selectively excite PdOEP. All luminescence samples were prepared either in 1 cm<sup>2</sup> anaerobic quartz cells purchased from Starna Cells or in a specially designed 1 cm<sup>2</sup> optical cell bearing a side arm round bottom flask and were either deoxygenated for at least 30 minutes with high purity argon or subjected to a minimum of three freeze-pump-thaw cycles prior to measurements.



Figure S3. Normalized absorption and photoluminescence spectra of PdOEP and DPA.

### PdOEP/DPA Upconversion Composition in Toluene.

Stern-Volmer Quenching. The Stern-Volmer ( $K_{SV}$ ) and the bimolecular quenching constants ( $k_q$ ) were obtained according to the dynamic Stern-Volmer relation,  $\tau_0/\tau = 1 + K_{SV}[Q]$ , where  $\tau_0$  and  $\tau$  are the PdOEP lifetimes in the absence or presence of the DPA quencher (Q), respectively.  $K_{SV}$  is the Stern-Volmer constant,  $K_{SV} = k_q \tau_0$ , and [Q] is the molar concentration of DPA. The Stern-Volmer slope was linear over the entire range of quencher concentrations utilized.



**Figure S4.** Luminescence decay profiles of PdOEP measured as a function of DPA concentration in deaerated toluene (C500 as laser dye, emission detected at 665 nm).



**Figure S5.** Stern-Volmer plot generated from lifetime quenching of PdOEP with DPA in deareated toluene, using the data from Figure S4.

Relative actinometry, quantum yield (QY) measurements.  $\Phi$ , A, I and  $\eta$  represents the quantum yield, absorbance at  $\lambda = 515$  nm (Figure S6, A<sub>515</sub> ~ 0.09), integrated photoluminescence intensity and refractive index respectively of the upconversion sample (UC) and the standard (std). UV-Vis absorption spectra were measured on a Cary 50 Bio spectrophotometer. Steady-state photoluminescence spectra were recorded using QM-4/2006SE fluorescence spectrometer obtained from Photon Technologies Incorporated coupled with an argon ion laser (Coherent Innova 300) excitation source, whose 515.5 nm line was isolated using a series of diffraction grating, band-pass filter, 500 nm long-pass filter and neutral density filters to obtain 350 mW/cm<sup>2</sup> beam power measured by a Molectron Power Max 5200 power meter (11 mW, 0.0314 cm<sup>2</sup> beam size). The QY standard was Ru(bpy)<sub>3</sub>Cl<sub>2</sub> in aerated water whose  $\Phi_{std}$ =0.04 ± 0.002.<sup>1</sup> The refractive index of the solvents used were  $\eta_{water}$  = 1.340 and  $\eta_{toluene}$ = 1.496 as obtained from Sigma-Aldrich solvent physical proprieties. The following formulas was used to calculate the quantum yield of upconversion:<sup>2</sup>

$$\Phi_{UC} = 2\Phi_{std} \left(\frac{A_{std}}{A_{UC}}\right) \left(\frac{I_{UC}}{I_{std}}\right) \left(\frac{\eta_{toluens}}{\eta_{water}}\right)^2 (1)$$
$$\Phi_{UC} = \Phi_q \ x \ \Phi_{TTA} \ x \ \Phi_f \qquad (2)$$

Where  $\Phi_{UC}$  is the upconversion QY,  $\Phi_q$  is the quenching QY,  $\Phi_{TTA}$  is the triplet-triplet annihilation QY and  $\Phi_f$  is the emitter's QY (DPA in this case).

The upconversion mixture in toluene contained [PdOEP] = 5µM and [DPA] = 0.1 mM; a condition allowing the  $\Phi_q$  close to unity ( $\Phi_q = 0.93$ ). The factor 2 comes from the fact that for each upconverted photon, two triplet excited states should be consumed in the TTA process. If the quantum yield was calculated using the as recorded spectra (Figure S7), the emission of the Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was integrated over 550–850 nm and the upconversion emission was integrated over 400-500 nm (Figure S10), the value would be  $\Phi_{UC} = 0.32 \pm 0.01$ . But the emission spectra of DPA in the upconversion mixture suffers from re-absorption coming from the Soret band of PdOEP at  $\lambda < 430$  nm. To mitigate this problem, a simulated DPA emission spectra based on  $\lambda_{em} = 432$  nm (Figure S8) was used to calculate the QY. The emission of the Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was integrated over 550–850 nm and the simulated upconversion emission was integrated over 375-550 nm (Figure S8). The value of the upconversion QY was:  $\Phi_{UC} = 0.36 \pm 0.01$ . Since  $\Phi_f = 0.95$  for DPA, the  $\Phi_{TTA} = 0.4$ .



**Figure S6.** Absorption spectra of the upconversion sample (UC) in vacuum degassed toluene and  $Ru(bpy)_3Cl_2$  (std) in aerated water.



**Figure S7.** Photoluminescence spectra of the upconversion sample (UC) as recorded in vacuum degassed toluene and  $Ru(bpy)_3Cl_2$  (std) in aerated water under the same excitation conditions.



**Figure S8.** Simulated photoluminescence spectra of the upconversion sample (UC) in vacuum degassed toluene and  $Ru(bpy)_3Cl_2$  (std) in aerated water under the same excitation conditions.

Full Spectrum of the linear sweep voltammetry at 1 mV/s. All photoelectrochemical measurements in Figure 2 were obtained after dark current stabilization, conditions allowing reproducible photocurrent measurements. Since the current was allowed to stabilize before any shuttered light response measurements, the dark measurements in the linear sweep voltammetry were recorded < 0.7 V vs Ag/AgCl, before turning on the excitation light, Figure S9.



**Figure S9:** Linear sweep voltammetry of WO<sub>3</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub> resulting from long wavelength excitation ( $\lambda_{ex} > 500$  nm, broadband power density of 32 mW/cm<sup>2</sup>) at 1 mV/s of a proximate optical cell containing a mixture of PdOEP (16 µM) and DPA (0.5 mM) in vacuum degassed toluene. The measurements here were not adjusted to zero baseline.

**Control experiments with plain FTO electrode.** Control experiments were performed using controlled potential electrolysis and linear sweep voltammetry to verify that the photocurrent observed when the upconversion cuvette is placed near WO<sub>3</sub> (Figure 2) comes solely from the WO<sub>3</sub> nanostructures rather than from the FTO electrode support. We can clearly see no photoresponse emanating from the plain FTO substrate, confirming that the photocurrents obtained in Figure 2 are indeed due to sub-bandgap excitation of WO<sub>3</sub>.

![](_page_11_Figure_2.jpeg)

**Figure S10:** Shuttered current/time response [starting with light on, 0.066 Hz shopping frequency] of a FTO biased to +0.9 V *vs* Ag/AgCl (**a**) and linear sweep voltammetry of WO<sub>3</sub> at 1 mV/s (**b**) in 1.0 M H<sub>2</sub>SO<sub>4</sub> resulting from long wavelength excitation ( $\lambda_{ex} > 500$  nm, broadband power density of 32 mW/cm<sup>2</sup>) of a proximate optical cell containing a mixture of PdOEP (16  $\mu$ M) and DPA (0.5 mM) in vacuum degassed toluene. The measurements were not adjusted to zero baseline.

### **References:**

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