

## Supplementary Information

### **Solar-charged Photoelectrochemical Wastewater Fuel Cell for Efficient and Sustainable Hydrogen Production**

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## Calculation of photocarrier density

The photocarrier density was calculated by the equation

$$\frac{1}{C^2} = \frac{2}{NDe\epsilon\epsilon_0} \left( E_S - E_{FB} - \frac{kT}{e} \right) \quad (1)$$

$$N_D = \frac{2}{e\epsilon_0\epsilon} \left( \frac{dE}{d\left(\frac{1}{C^2}\right)} \right) \quad (2)$$

where, C is the space charge capacity of the semiconductor material, e is the element charge quantity ( $1.6 \times 10^{-19}$  C), ND is the carrier density,  $\epsilon_0$  is the vacuum dielectric constant ( $8.86 \times 10^{-12}$  F m<sup>-1</sup>),  $\epsilon$  is the relative permittivity of the WO<sub>3</sub> nanostructures (a value of 50 has been assumed for the WO<sub>3</sub>), E<sub>S</sub> is the applied potential, E<sub>FB</sub> is the flat band potential, T is absolute temperature and k is Boltzmann's constant ( $1.38 \times 10^{-23}$  J K<sup>-1</sup>). Thus, the equation of ND can be described as follow:

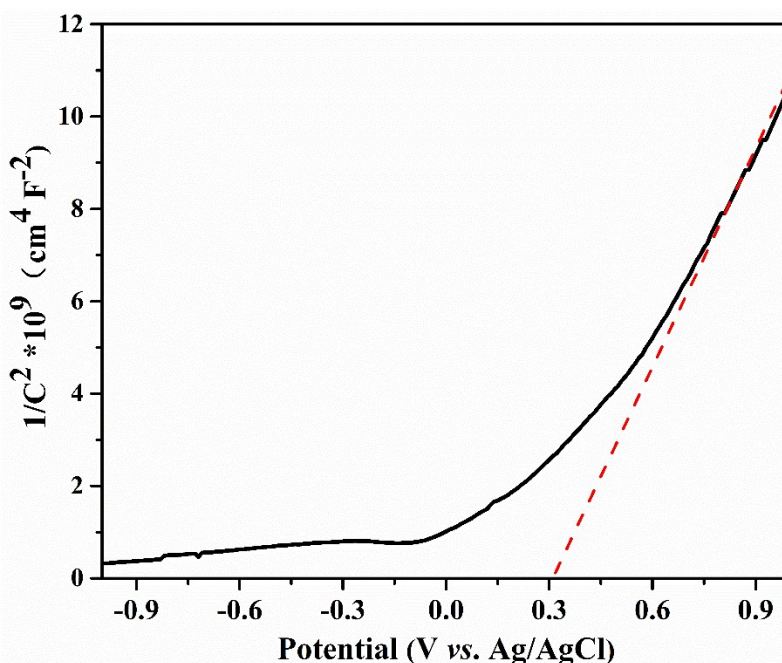


Figure.S1. Mott-Schottky plots of WO<sub>3</sub> NFs/W electrode measured in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution with a frequency of 1000 Hz and scan rate of 0.01 V·s<sup>-1</sup>.

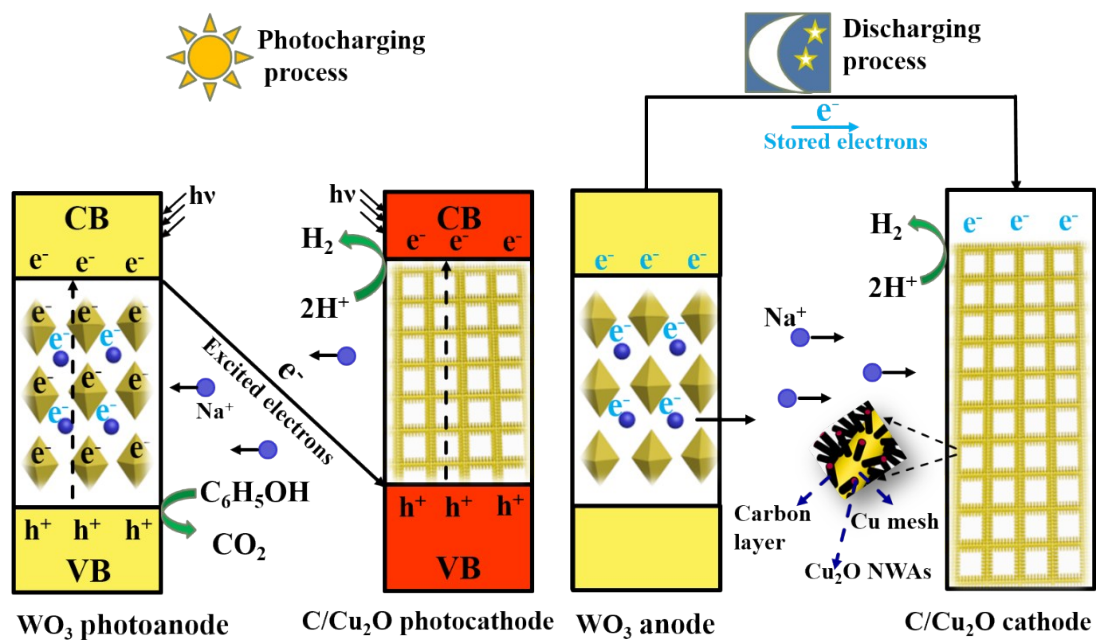


Fig.S2.The working mode diagram of scPEWFC system for simultaneous pollutant removal and hydrogen production under the photocharging-discharging process.

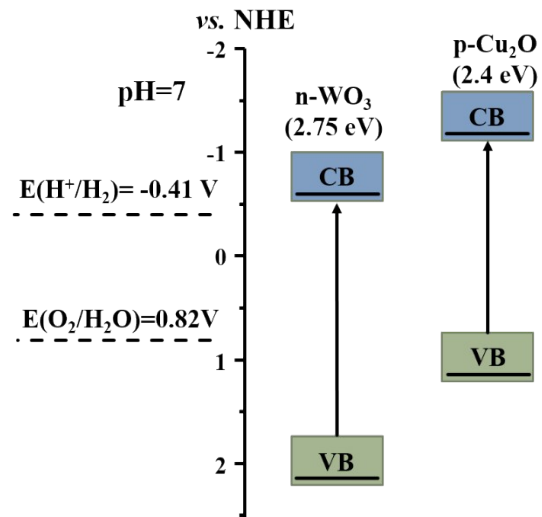


Fig. S3 The relative band positions for the WO<sub>3</sub> NFs-C/Cu<sub>2</sub>O NWAs visible-light response dual-photoelectrodes

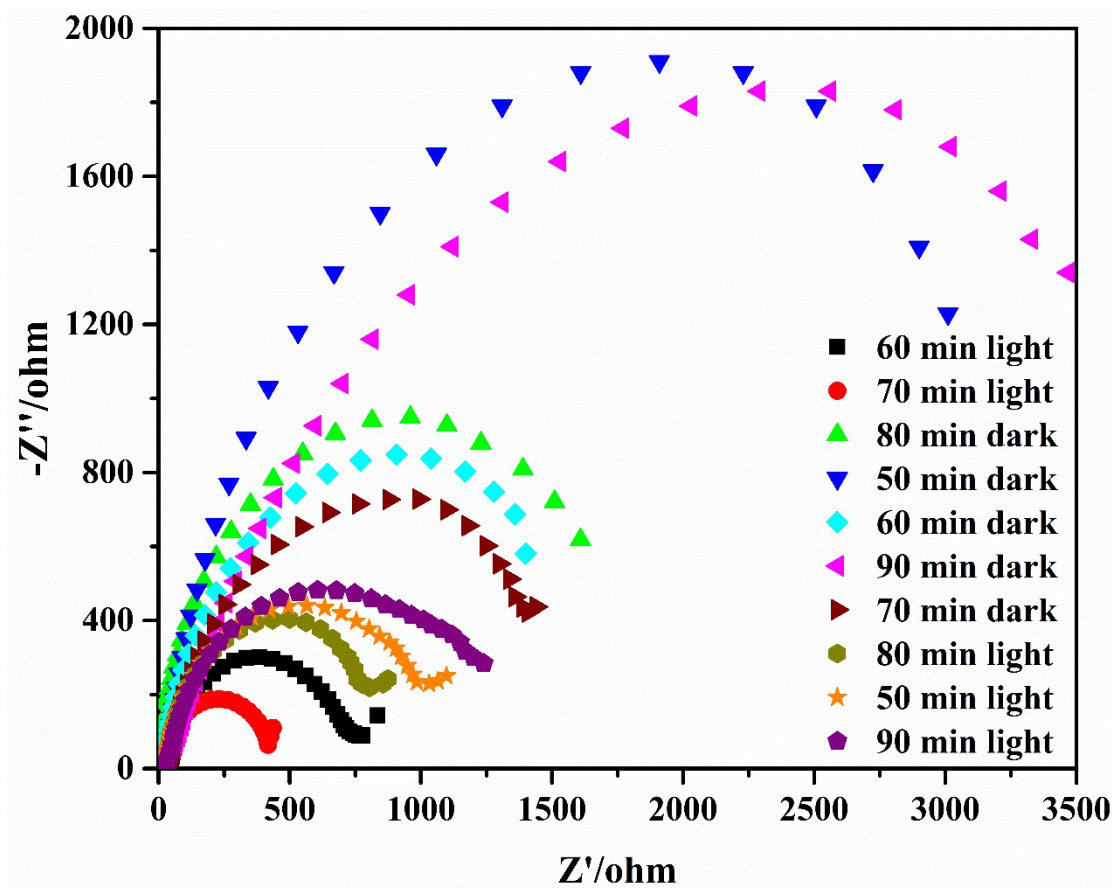


Figure.S4. The Nyquist curve of different anodizing time prepared  $\text{WO}_3$  NFs electrode by using the two-electrode system without any bias in the  $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$  solution containing  $20 \text{ mg L}^{-1}$  phenol.

**Table S1.** The photoelectrochemical performance, TOC removal and hydrogen production of scPEWFC.

<b>Parameters</b>	<b>50min</b>	<b>60min</b>	<b>70min</b>	<b>80min</b>	<b>90min</b>
$V_{OC}$ (V)	0.24	0.26	0.25	0.24	0.24
$J_{SC}$ ( $\text{mA}\cdot\text{cm}^{-2}$ )	0.33	0.42	0.44	0.40	0.36
$P_{max}$ ( $\text{mW}\cdot\text{cm}^{-2}$ )	0.011	0.014	0.015	0.013	0.011
FF	0.139	0.128	0.136	0.135	0.127
TOC (%)	77.53	80.51	82.12	79.93	78.01
$\text{H}_2$ ( $\mu\text{mol}\cdot\text{cm}^{-2}$ )	80.67	87.15	93.08	85.65	82.41

**Table S2.** The WO<sub>3</sub> NFs/W-C/Cu<sub>2</sub>O NWAs/Cu scPEWFC performance parameters in different concentrations of electrolyte solution.

<b>Parameters</b>	<b>0.01mol L<sup>-1</sup></b>	<b>0.05 mol L<sup>-1</sup></b>	<b>0.1 mol L<sup>-1</sup></b>	<b>0.5 mol L<sup>-1</sup></b>
J <sub>SClight</sub> (mA cm <sup>-2</sup> )	0.482	0.488	0.523	0.589
J <sub>SCdark</sub> (mA cm <sup>-2</sup> )	0.067	0.075	0.098	0.080
H <sub>2 light</sub> (μmol cm <sup>-2</sup> )	78.97	81.15	85.58	80.89
H <sub>2 dark</sub> (μmol cm <sup>-2</sup> )	6.23	6.71	7.50	7.15