## **Supplemental Information**:

Fig. S1 (a)-(b) TEM images, (c)-(d) HRTEM images of the interface between WO<sub>3</sub> and PANI with different measurement condition for WO<sub>3</sub>/PANI hybrid structure Fig. S2 The IPCE plots in the range of 350~600 nm measured at 1.23 V vs RHE for bare WO<sub>3</sub> and WO<sub>3</sub>/PANI hybrid heterojunction

Fig. S3 The dark I-T curves measured at 1.23 V vs. RHE for 300s

Fig. S4 The cyclic voltammogram curves of pure WO3 and WO3 hybrid photoelectrode

Fig. S5 The curves of photovoltage with time for bare WO<sub>3</sub> and WO<sub>3</sub>/PANI

Fig. S6 The Mott-Schottky curves measured with the frequency of (a) 3000 Hz and (b) 5000 Hz under dark

Fig. S7 The schematic diagram for bending of energy band and extender depletion layer at the interface of photoelectrode/electrolyte

Fig. S8 (a)-(b) The LSV curves and EIS measurements of all as-obtained WO<sub>3</sub>/PANI hybrid heterojunction, (c) the results of M-S measurements of WO<sub>3</sub>/PANI-30s and WO<sub>3</sub>/PANI-90s

Tab. S1 The  $V_{FB}$  and  $N_d$  of bare WO<sub>3</sub> and WO<sub>3</sub>/PANI hybrid heterojunction through M-S measurements with frequency of 3000 Hz and 5000 Hz under dark Tab. S2 The values of all parameters for the fitting circuit diagram of EIS measured

without illumination and with illumination



Fig. S1 (a)-(b) TEM images, (c)-(d) HRTEM images of the interface between WO<sub>3</sub> and PANI with different measurement condition for WO<sub>3</sub>/PANI hybrid structure



Fig. S2 The IPCE plots in the range of 350~600 nm measured at 1.23 V vs RHE for bare WO<sub>3</sub> and WO<sub>3</sub>/PANI hybrid heterojunction



Fig. S3 The dark I-T curves measured at 1.23 V vs. RHE for 300s



Fig. S4 The cyclic voltammogram curves of pure WO<sub>3</sub> and WO<sub>3</sub> hybrid photoelectrode



Fig. S5 The curves of photovoltage with time for bare WO<sub>3</sub> and WO<sub>3</sub>/PANI



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Fig. S8 (a)-(b) The LSV curves and EIS measurements of all as-obtained WO<sub>3</sub>/PANI hybrid heterojunction, (c) the results of M-S measurements of WO<sub>3</sub>/PANI-30s and WO<sub>3</sub>/PANI-90s

3000 Hz	Workelectrode	V <sub>FB</sub> (V vs RHE)	N <sub>d</sub> (cm <sup>-3</sup> )	
	WO <sub>3</sub>	0.59	5.60 x 10 <sup>21</sup>	
	WO <sub>3</sub> /PANI	0.55	4.40 x 10 <sup>21</sup>	
5000 Hz	Workelectrode	V <sub>FB</sub> (V vs RHE)	N <sub>d</sub> (cm <sup>-3</sup> )	
	WO <sub>3</sub>	0.62	3.68 x 10 <sup>21</sup>	
	WO <sub>3</sub> /PANI	0.52	2.72 x 10 <sup>21</sup>	

Tab. S1 The  $V_{FB}$  and  $N_d$  of bare WO<sub>3</sub> and WO<sub>3</sub>/PANI hybrid heterojunction through M-S measurements with frequency of 3000 Hz and 5000 Hz under dark

Tab. S2 The values of all parameters for the fitting circuit diagram of EIS measured without illumination and with illumination

Dark	Workelectrode	$R_{s} \left(\Omega \ cm^{2} ight)$	$R_{int} (\Omega \ cm^2)$	CPE <sub>1</sub> (F/cm <sup>2</sup> )	$R_{pt}$ ( $\Omega$ cm <sup>2</sup> )	CPE <sub>2</sub> (F/cm <sup>2</sup> )
	WO <sub>3</sub>	39.16	3.52	9.88 x 10-6	235.2	7.28 x 10 <sup>-5</sup>
	WO <sub>3</sub> /PANI	29.53	2.08	5.78 x 10 <sup>-6</sup>	194.1	1.23 x 10 <sup>-5</sup>
Light	Workelectrode	$R_{s} \left(\Omega \ cm^{2} ight)$	$R_{int} (\Omega \ cm^2)$	CPE <sub>1</sub> (F/cm <sup>2</sup> )	$R_{pt}$ ( $\Omega$ cm <sup>2</sup> )	CPE <sub>2</sub> (F/cm <sup>2</sup> )
	WO <sub>3</sub>	37.23	3.17	8.39 x 10-6	144	9.28 x 10 <sup>-5</sup>
	WO <sub>3</sub> /PANI	30.84	2.12	5.89 x 10 <sup>-6</sup>	127	1.42 x 10 <sup>-5</sup>