## An effective strategy of constructing multi-junction structure by

## integrating heterojunction and homojunction to promote charge

## separation and transfer efficiency of WO<sub>3</sub>

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## **Supplemental Informations:**

Fig. S1 Schematic illustration for the fabrication process of Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub> homojunction photoanode

Fig. S2 LSV plots of WO<sub>3</sub> photoanodes with different Mo doping amounts (a) and with different Fe doping amounts (b) mearsured in  $0.2 \text{ M} \text{ Na}_2\text{SO}_4$  solution under AM 1.5 G illumination

Fig. S3 XRD patterns of WO<sub>3</sub>, Mo-WO<sub>3</sub> and Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub> homojunction. Bottom peaks are standard positions of  $SnO_2$  (red) and WO<sub>3</sub> (green)

Fig. S4 EDS elemental analysis spectrum and corresponding elemental mapping images of W, O and Mo in Mo-WO<sub>3</sub>, respectively

Fig. S5 Incident photon conversion efficiencies (IPCEs) plots of WO<sub>3</sub>, Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>, Mo-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> and Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> photoanodes

Fig. S6 (a) Schematic diagram of SPV measurement configuration. (b) The equivalent circuit of electrochemical impedance spectroscopy

Fig. S7 XRD pattern of Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub>. Bottom peaks are standard positions of SnO<sub>2</sub>, WO<sub>3</sub> and Bi<sub>2</sub>S<sub>3</sub>

Fig. S8 High resolution XPS spectra of (a) W 4f, (b) O 1s, (c) Fe 2p, (d) Mo 3d and S 2s and (e) Bi 4f and S 2p for Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> composite

Fig. S9 (a) UV-Vis absorption spectrum of Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub>. (b) IPCEs plots. (c) Time-dependent photocurrent density curves of WO<sub>3</sub>, Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>, Mo-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> and Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> photoanodes measured at 1.23V vs. RHE under simulated sunlight illumination for 7200 s

Fig. S10 LSV curves of WO<sub>3</sub>, Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>, Mo-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> and Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> photoanodes measured in 0.2 M Na<sub>2</sub>SO<sub>4</sub> electrolyte solution with the addition of 0.1 M Na<sub>2</sub>SO<sub>3</sub>

Tab. S1 The flat band potential ( $V_{FB}$ ) and carrier density ( $N_d$ ) of WO<sub>3</sub>, Mo-WO<sub>3</sub>, Fe-WO<sub>3</sub> and Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub> photoanodes

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Sample	V <sub>FB</sub> (V vs RHE)	N <sub>d</sub> (cm <sup>-3</sup> )			
WO <sub>3</sub>	0.62	5.30×10 <sup>19</sup>			
Mo-WO <sub>3</sub>	0.56	1.19×10 <sup>19</sup>			
Fe-WO <sub>3</sub>	0.69	1.46×10 <sup>19</sup>			
Mo-WO <sub>3</sub> /Fe-WO <sub>3</sub>	0.65	$1.65 \times 10^{20}$			

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WO<sub>3</sub> and Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub> photoanodes

Sample	$R_s \left( \frac{\Omega \ cm^2}{2} \right)$	$R_{ct}$ ( $\Omega cm^2$ )	CPE(F/cm <sup>2</sup> )
WO <sub>3</sub>	25	1752	2.10×10 <sup>-3</sup>
Mo-WO <sub>3</sub>	28	1598	1.12×10 <sup>-4</sup>
Fe-WO <sub>3</sub>	28	1407	2.67×10 <sup>-4</sup>
Mo-WO <sub>3</sub> /Fe-WO <sub>3</sub>	24	487	1.08×10 <sup>-3</sup>

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Sample	V <sub>FB</sub> (V vs RHE)	N <sub>d</sub> (cm <sup>-3</sup> )
Mo-WO <sub>3</sub> /Bi <sub>2</sub> S <sub>3</sub>	0.50	1.77×10 <sup>22</sup>
Mo-WO <sub>3</sub> /Fe-WO <sub>3</sub> /Bi <sub>2</sub> S <sub>3</sub>	0.59	3.62×10 <sup>22</sup>

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Mo-WO<sub>3</sub>/Fe-WO<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub> photoanodes

Sample	$R_s (\Omega cm^2)$	$R_{ct}$ ( $\Omega cm^2$ )	CPE(F/cm <sup>2</sup> )
Mo-WO <sub>3</sub> /Bi <sub>2</sub> S <sub>3</sub>	26	334	9.00×10 <sup>-4</sup>
Mo-WO <sub>3</sub> /Fe-WO <sub>3</sub> /Bi <sub>2</sub> S <sub>3</sub>	22	238	6.94×10 <sup>-4</sup>