## **Supporting Information**

## Regulating Zn/Co bimetallic catalyst in metal-organic framework and

## oxyhydroxide for improved photoelectrochemical water oxidation

Xiu-Shuang Xing,<sup>a</sup> Xuyang Zeng,<sup>a,b</sup> Zhongyuan Zhou,<sup>c,d,\*</sup> Xin Song,<sup>c</sup> Xiaohua Jing,<sup>a</sup> Minghao Yuan,<sup>a</sup> Cuiying Xu,<sup>a</sup> Xiaofei Ren,<sup>a,b</sup> and Jimin Du<sup>a,\*</sup>

<sup>a</sup>Henan Key Laboratory of New Optoelectronic Functional Materials, College of

Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, P.

R. China. E-mail: djm@iccas.ac.cn

<sup>b</sup>College of Chemistry, Zhengzhou University, Zhengzhou 450000, P. R. China.

°School of Chemical and Environmental Engineering, Anyang Institute of Technology,

Anyang 455000, P. R. China. Email: 20200038@ayit.edu.cn

<sup>d</sup>Key Lab of Advanced Optical Manufacturing Technologies of Jiangsu Province, Soochow University, Suzhou 215006, China.



Figure S1. The EDS elements composition of  $FTO/Sn@\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode.



Figure S2. The EDS elements composition of  $FTO/Sn@\alpha-Fe_2O_3/Zn_{0.5}Co_{0.5}-ZIF$  photoanode.



Figure S3. The EDS elements composition of FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Zn<sub>0.46</sub>Co<sub>0.54</sub>OOH photoanode.



**Figure S4.** The (a and d) XRD patterns, (b and e) UV–vis reflectance spectra and (c and f) XPS survey spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes decorated by ZnCo-ZIF and ZnCoOOH catalyst, respectively.



**Figure S5.** The *J-V* curves and transient photocurrent density curves of (a and b) FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Zn-ZIF, (c and d) FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Co-ZIF, (e and f) FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnCo-ZIF photoanodes for different optimization time.



**Figure S6.** The *J-V* curves and transient photocurrent density curves of (a and b) FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnOOH, (c and d) FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CoOOH, (e and f) FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnCoOOH photoanodes for different optimization time.



Figure S7. *J-t* curves of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode with ZnCo-ZIF and ZnCoOOH catalyst at 1.23 V<sub>RHE</sub>.



**Figure S8.** The SEM images before (a and c) and after (b and d) stability test of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode with ZnCo-ZIF and ZnCoOOH catalyst for 5 hours.



Figure S9. Schematic diagram of carriers transports in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode with ZnCo-ZIF or ZnCoOOH catalyst.

**Table S1.** The ion contents of Fe, Zn and Co in FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Zn<sub>0.5</sub>Co<sub>0.5</sub>-ZIF (10min) and FTO/Sn@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Zn<sub>0.46</sub>Co<sub>0.54</sub>OOH (5 min) photoanodes.

Concentration	$FTO/Sn@\alpha-Fe_2O_3/Zn_{0.5}Co_{0.5}-ZIF$	$FTO/Sn@\alpha-Fe_2O_3/Zn_{0.46}Co_{0.54}OOH$
	(10 min)	(5 min)
Fe (mol/cm <sup>2</sup> )	2.97×10 <sup>-6</sup>	1.90×10 <sup>-6</sup>
Zn (mol/cm <sup>2</sup> )	3.85×10 <sup>-7</sup>	5.0×10 <sup>-7</sup>
Co (mol/cm <sup>2</sup> )	3.83×10 <sup>-7</sup>	5.83×10 <sup>-7</sup>

Table S2. The fitting EIS data of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes based on equivalent circuits.

	FTO/Sn@α-Fe <sub>2</sub> O <sub>3</sub>	$FTO/Sn@\alpha-Fe_2O_3/Zn_{0.5}Co_{0.5}-ZIF$	FTO/Sn@α-Fe <sub>2</sub> O <sub>3</sub> /Zn <sub>0.46</sub> Co <sub>0.54</sub> OOH
$R_{\rm s} \left(\Omega \ {\rm cm}^2\right)$	9.18	11.55	12.24
$R_{ m trap}$ ( $\Omega \  m cm^2$ )	6.1	9.1	19.7
$C_{\text{bulk}}$ (F/cm <sup>2</sup> )	1.6×10-6	1.4×10 <sup>-6</sup>	1.6×10 <sup>-6</sup>
$R_{\rm ct} (\Omega { m cm}^2)$	2019.0	433.2	36.24
$C_{\rm ss}~({\rm F/cm^2})$	3.6×10-6	1.7×10 <sup>-3</sup>	1.1×10 <sup>-3</sup>