

## Supporting Information

### **Transition metal-promoted Fe-based catalysts for photothermal catalytic CO<sub>2</sub> hydrogenation**

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## Supporting Text

### Catalysts preparation

Typically, metal nitrates were firstly dissolved in water to give solution A with total concentration of 0.4 M (M : Fe = 1 : 4). Then solution A was dropwise added into excess NaOH solution with addition of 2 ml PEG in advance under vigorous stirring. After aging for 4 h, the obtained precipitation was collected by a filter and washed repeatedly by DI water until the filtrate reached neutral pH. The filter cake was dried overnight and calcined at 450 °C for 3 h in a muffle furnace. Finally, all samples were pre-activated under hydrogen atmosphere at 400 °C for 2 h followed by passivation by 1% O<sub>2</sub>/N<sub>2</sub> to give MFeO<sub>x</sub> catalysts. For ZnFe sample, the NaOH solution was replaced by NaOH/Na<sub>2</sub>CO<sub>3</sub> mixed solution in case of redissolution of zincates.

### Photothermocatalytic CO<sub>2</sub> hydrogenation evaluation

In a typical batch test, 100 mg catalyst was dispersed on a quartz fiber filter to form a radiation area around 3.14 cm<sup>2</sup>. Then the catalyst film was placed on the bottom center of the reactor followed by sealing the reactor and purging the chamber with feeding gas (CO<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub> = 3:9:1). The batch tests were carried out under 2.8 W cm<sup>-2</sup> and 0.2 MPa for 2 h. During the reaction, the temperature of catalyst bed was monitored by thermocouples and the results were illustrated in Fig. S2. After the reaction, the reactor was heated to 220 °C to vaporize liquid products and they directly flowed to a gas chromatograph equipped with TCD and FID detectors (Panna 91 Plus) along 200 °C heating tube. The dark contrast tests were conducted under the same conditions except for light irradiation.

For flow type tests, the temperature of catalyst bed was fixed at 300 °C by irradiation of 2.0 W cm<sup>-2</sup> and external heating to rule out the difference in light-heat conversion between different MFeO<sub>x</sub> catalysts. In addition, the reaction atmosphere was identical to the batch type with a total flow rate of 13 mL min<sup>-1</sup>. The online product was collected and analyzed after 2 h reaction. The dark contrast tests were conducted under the same conditions besides the introduction of light.

Equations used to calculate the CO<sub>2</sub> conversion and products selectivity are listed below:

$$\chi(\text{CO}_2) = \frac{c(\text{CO}_2)_{\text{inlet}} - \frac{c(\text{N}_2)_{\text{inlet}}}{c(\text{N}_2)_{\text{outlet}}} \times c(\text{CO}_2)_{\text{outlet}}}{c(\text{CO}_2)_{\text{inlet}}} \times 100\% \quad S(\text{CO}) = \frac{c(\text{CO})}{c(\text{CO}) + c(\text{CH}_4) + c(\text{C}_2+)} \times 100\% \quad (1)$$

$$(2) \quad (3)$$

$$S(CH_4) = \frac{c(CH_4)}{c(CO) + c(CH_4) + c(C_{2+})} \times 100\% \quad (4)$$

$$S(C_{2+}) = \frac{c(C_{2+})}{c(CO) + c(CH_4) + c(C_{2+})} \times 100\%$$

where  $\chi(CO_2)$  represents the  $CO_2$  conversion while  $S(CO)$ ,  $S(CH_4)$  and  $S(C_{2+})$  stand for the selectivity toward  $CO$ ,  $CH_4$  and  $C_{2+}$  respectively. The gas molar concentration  $c(CO)$ ,  $c(CH_4)$ ,  $c(C_{2+})$  and  $CO_2$  molar concentration for inlet  $c(CO_2)_{inlet}$ , outlet  $c(CO_2)_{outlet}$  were obtained from gas chromatograph standardization. Besides, the space-time yield was calculated by formula listed below.

$$STY(CO) = \frac{F_{inlet}(mmol/h) \times c(CO) \times c(N_2)_{outlet}}{m_{catalyst}(g) \times c(N_2)_{outlet}} \times 100\% \quad (5)$$

$$STY(CH_4) = \frac{F_{inlet}(mmol/h) \times c(CH_4) \times c(N_2)_{outlet}}{m_{catalyst}(g) \times c(N_2)_{outlet}} \times 100\% \quad (6)$$

$$STY(C_{2+}) = \frac{F_{inlet}(mmol/h) \times c(C_{2+}) \times c(N_2)_{outlet}}{m_{catalyst}(g) \times c(N_2)_{outlet}} \times 100\% \quad (7)$$

where  $STY(CO)$ ,  $STY(CH_4)$  and  $STY(C_{2+})$  are space-time yield of  $CO$ ,  $CH_4$  and  $C_{2+}$  respectively. Total inlet molar flow rate  $F_{inlet}$  was obtained from mass flowmeters.

## Supporting Tables

**Table S1** Textural properties of the MFeO<sub>x</sub> catalysts.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	D <sub>p</sub> (nm)	Fe/M mole ratio
Fe	12.3	0.047	1.51	-
CoFe	12.2	0.190	6.24	4.02
MnFe	17.0	0.236	5.53	3.95
ZnFe	13.3	0.190	5.73	3.91
CuFe	7.7	0.033	1.70	4.03

**Table S2** Summarization of photothermal CO<sub>2</sub> hydrogenation catalysts for C<sub>2+</sub> production.

Catalysts	Reaction conditions					CO <sub>2</sub> Conversion (%)	Product Selectivity (%)			C <sub>2+</sub> product ion rate (mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	Ref.
	Light intensity (W/m <sup>2</sup> )	Press ure (MPa)	Test type	Feed rate (ml/min)	T ( °C)		CO	CH <sub>4</sub>	C <sub>2+</sub>		
Co- CoO <sub>x</sub> /MA O	1.2	0.3	flow	2400 ml h <sup>-1</sup> g <sup>-1</sup>	32 5	23.7	35. 2	24.3	40.5	1.303	[1]
FeNi <sub>x</sub> /Fe <sub>2</sub> O <sub>3</sub> and NiO	0.56	0.1	flow	8	25 0	~24	~45	40	15	0.673	[2]
CoFe	-	0.18	flow	25	25 0	7.76	59. 18	25.5 7	15.2 5	-	[3]
CoFe/CoF e <sub>2</sub> O <sub>4</sub>	2	0.1	flow	2.5	30 0	12.9	-	-	29.8	1.1	[4]
K- Ru/Fe <sub>3</sub> O <sub>4</sub>	2.05	0.1	flow	2	42 0	~35.0	~65	~12 .3	~22 .7	0.63	[5]
<b>CoFe</b>	<b>2.8</b>	<b>0.2</b>	<b>flow</b>	<b>13</b>	<b>30</b> <b>0</b>	<b>20.8</b>	<b>77.</b> <b>3</b>	<b>11.5</b>	<b>11.2</b>	<b>1.73</b>	<b>This work</b>

## Supporting Figures

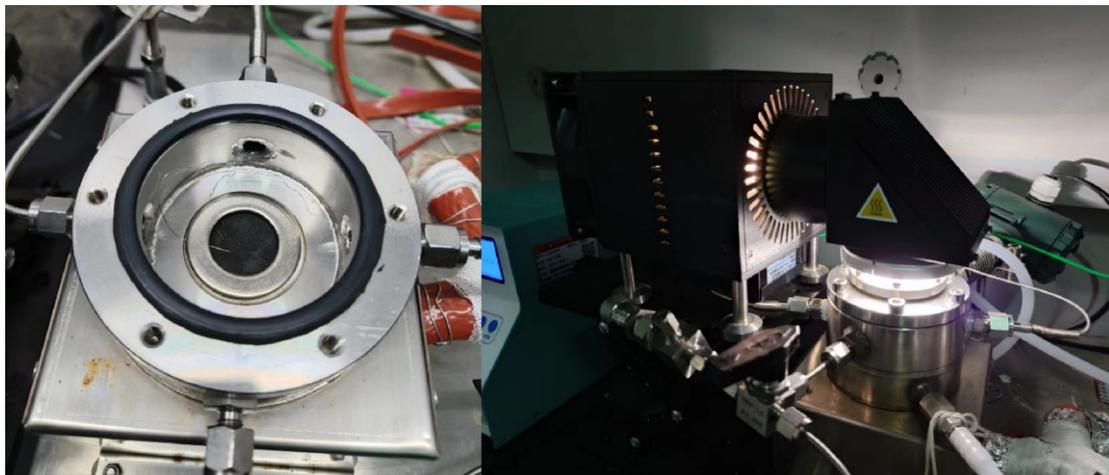


Fig. S1. The images of the photothermal reactor with thermocouples buried in the catalyst bed and Xenon lamp.

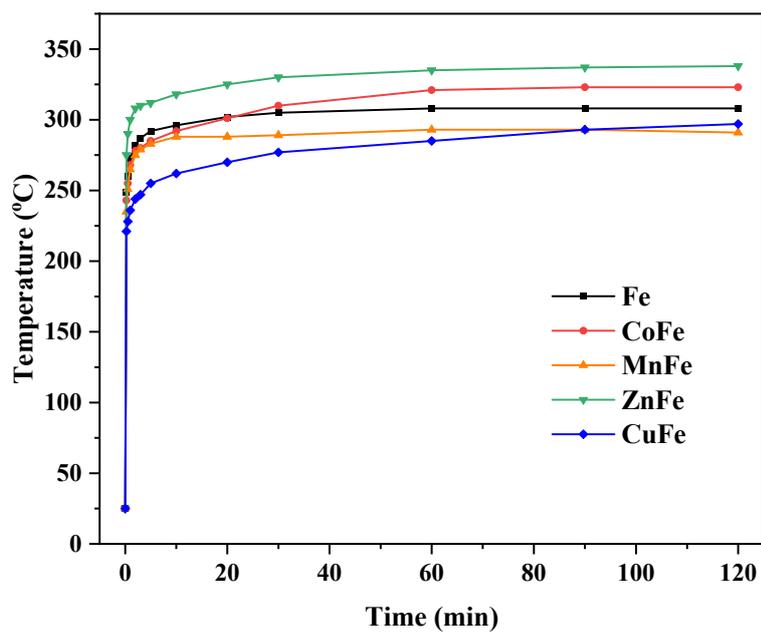


Fig. S2. Temperature profiles in batch-type tests for prepared  $MFeO_x$  catalysts.

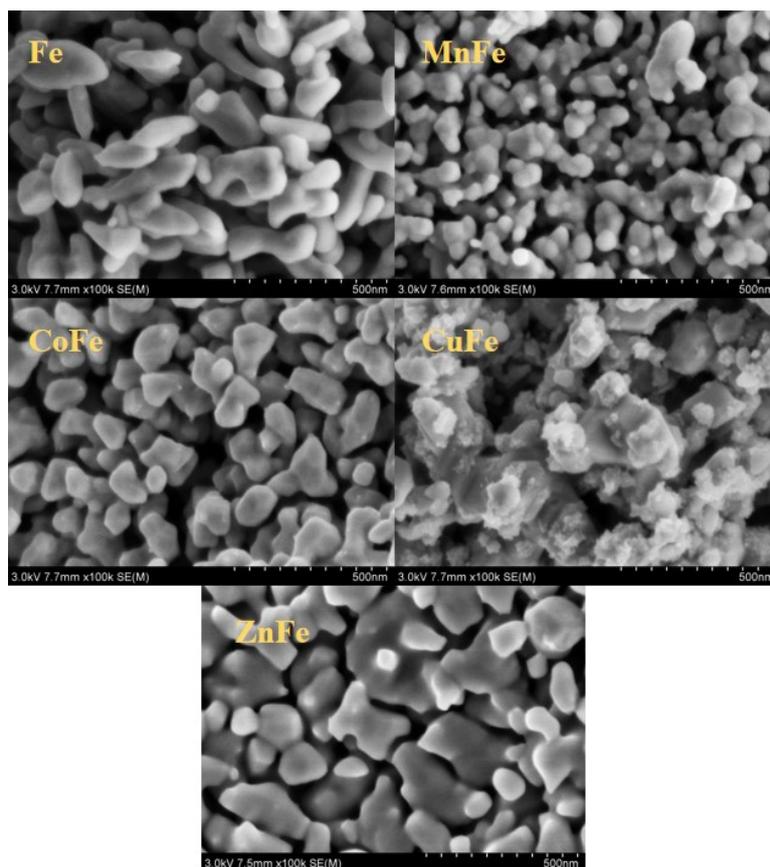


Fig. S3. SEM images of prepared  $MFeO_x$  catalysts.

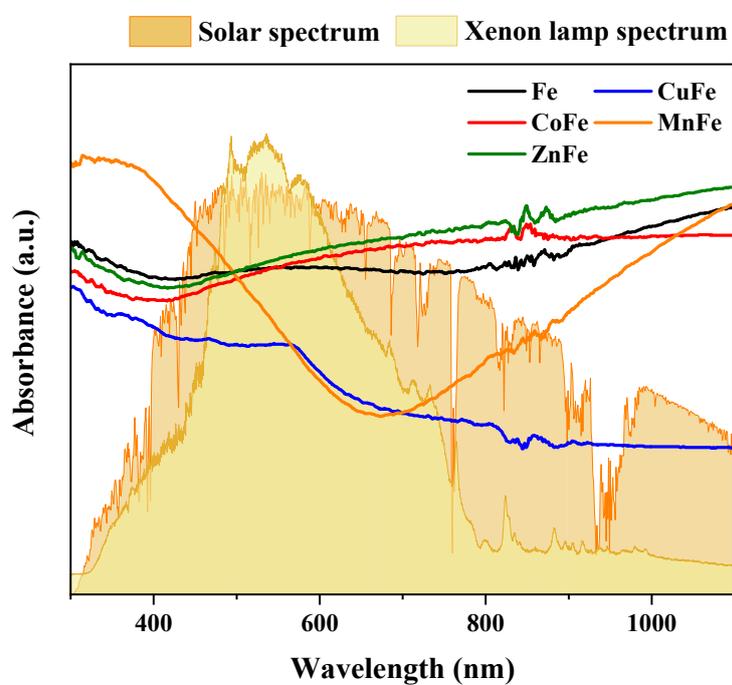


Fig. S4. UV-vis spectra of the prepared  $MFeO_x$  catalysts in comparison of the spectra from light sources.

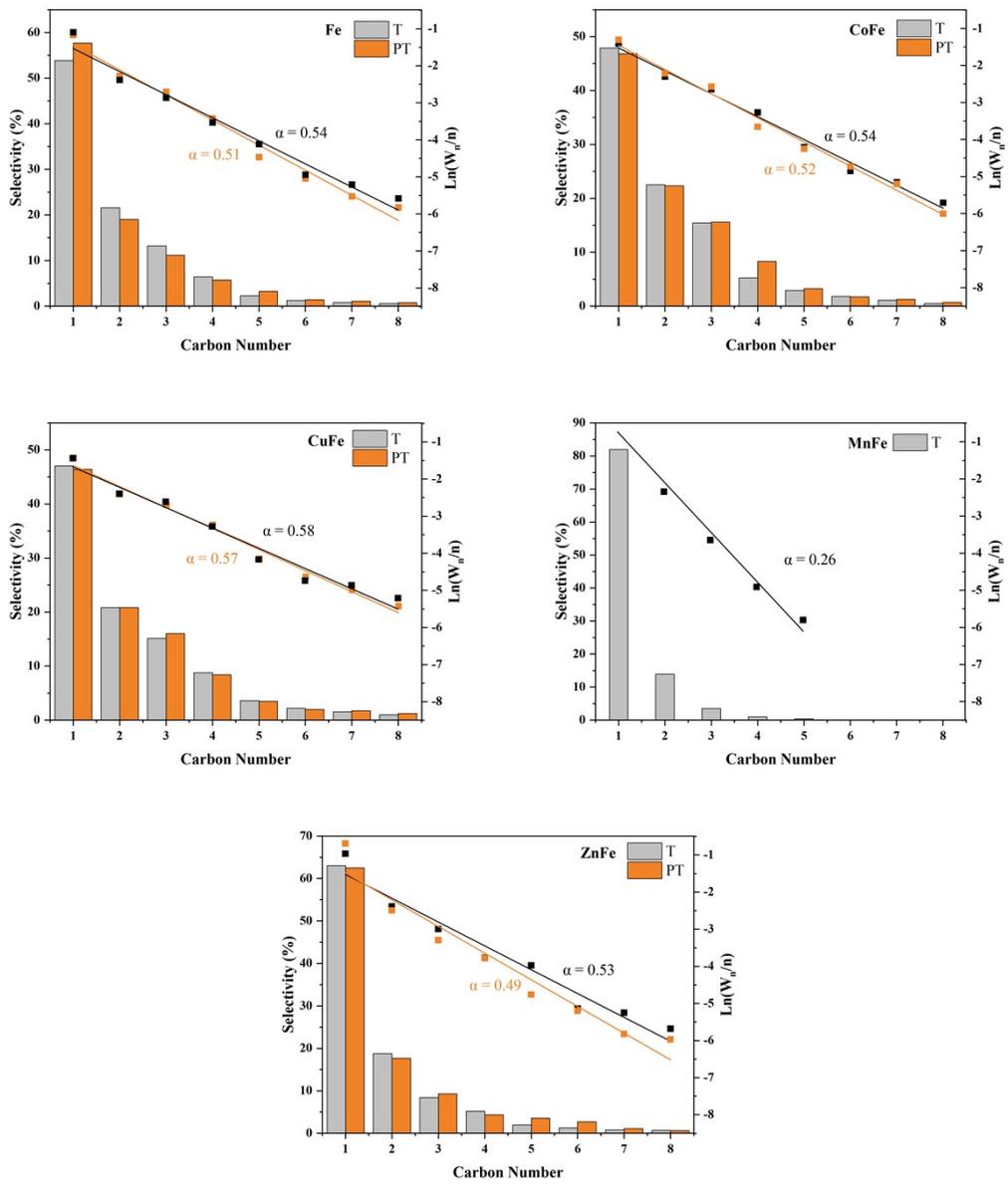


Fig. S5 Hydrocarbon distribution for C<sub>2+</sub> and chain growth factor over MFeO<sub>x</sub> catalysts.

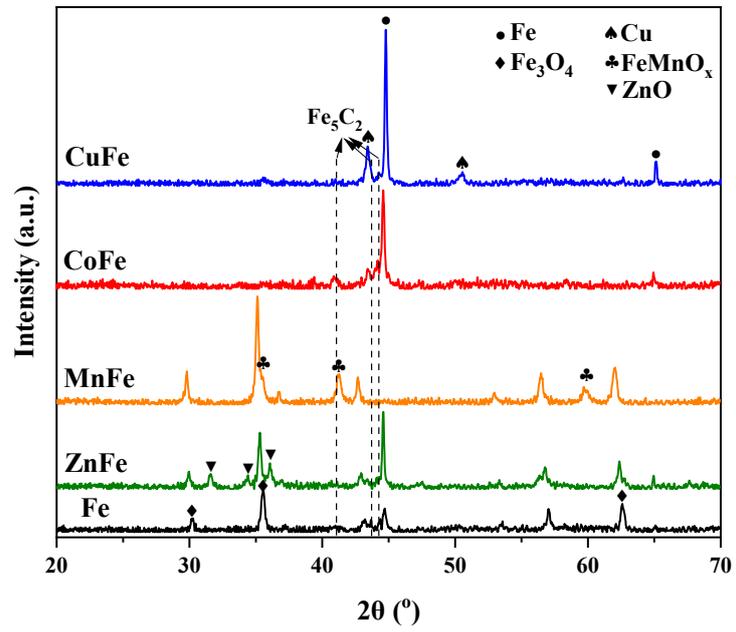


Fig. S6. XRD patterns of  $\text{MFeO}_x$  catalysts spent in photothermal  $\text{CO}_2$  hydrogenation.

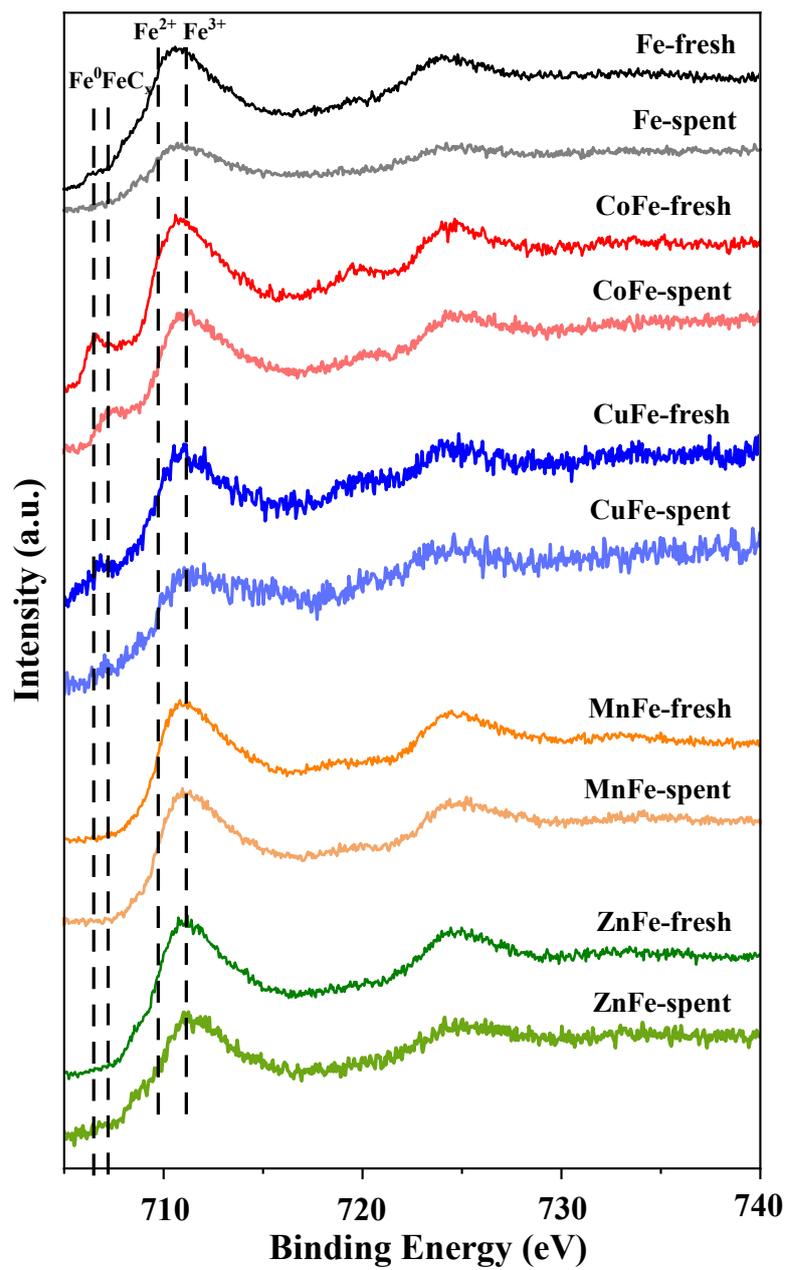


Fig. S7. Fe 2p XPS of MFeO<sub>x</sub> catalysts spent in photothermal CO<sub>2</sub> hydrogenation.

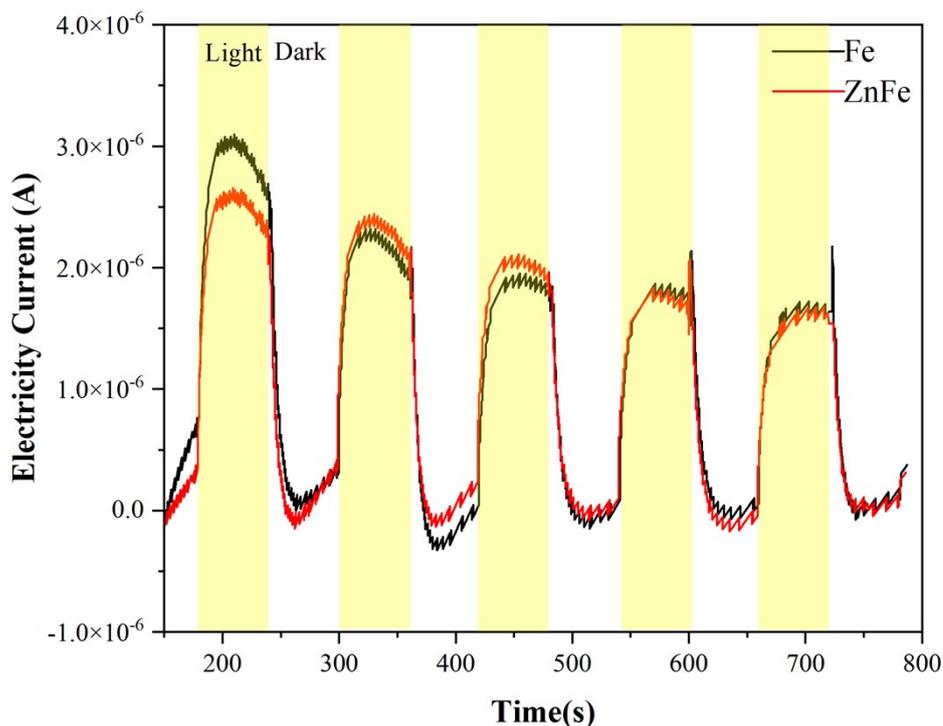


Fig. S8. Typical photocurrent of Fe and ZnFe catalyst in 0.1 M sodium sulfate electrolyte.

## Reference

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