## Supporting Information

## Photoenhanced Interfacial Electron Transfer of Dual Functional Hematite Biophotoelectrode

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Fig. S1. Assembled S-MPEC chambers Fe<sub>2</sub>O<sub>3</sub> as the working electrode.



**Fig. S2.** The plot of  $E_p$  against the log of scan rate at low and high scan rates of oxidation reaction using (a) CC-MR-1, (c) Fe<sub>2</sub>O<sub>3</sub> and (e) Fe<sub>2</sub>O<sub>3</sub>-MR-1, as well as reduction reaction using (b) CC-MR-1, (d) Fe<sub>2</sub>O<sub>3</sub> and (f) Fe<sub>2</sub>O<sub>3</sub>-MR-1 to determine of critical scan rate (V<sub>c</sub>).



**Fig. S3.** Tafel plot of the oxidation peak of (a) CC-MR-1, (c)  $Fe_2O_3$  and (e)  $Fe_2O_3$ -MR-1 and the reduction peak of (b) CC-MR-1, (d)  $Fe_2O_3$  and (f)  $Fe_2O_3$ -MR-1.



Fig. S4. (a) UV-Vis diffuse reflectance spectrum and (b) Tauc plot of  $Fe_2O_3$ ,  $Fe_2O_3$  after PEC measurement, and  $Fe_2O_3$ -MR-1.



Fig. S5. Linear sweep voltammetry curve of the  $Fe_2O_3$  photoanodes in 1M NaOH under 100 mW cm<sup>-2</sup> irradiation.



Fig. S6. Linear sweep voltammetry curve of the  $Fe_2O_3$  photoanodes in 1M NaOH with 100mM  $H_2O_2$  as hole scavenger under 100 mW cm<sup>-2</sup> irradiation.



**Fig. S7.** The I-t curve of the 24-hour operation under the external bias of 0.8V of 3 trials.

**Table S1.** The Chemical Oxygen Demand (COD) in mg/L of CC-MR-1,  $Fe_2O_3$ ,  $Fe_2O_3$ -MR-1 (dark condition), and  $Fe_2O_3$ -MR-1 (irradiated condition) at T0 (0hr), T12 (12hrs), and T24 (24 hrs) under the external bias of 0.8V.

	CC-MR-1	CC-MR-1 Fe <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> -MR-1 (Light)	Fe <sub>2</sub> O <sub>3</sub> -MR-1	
			(Light)	(Dark)
T0 (mg/L)	13,954	14,049	13,932	14,910
T12 (mg/L)	12,654	13,159	12,187	14,143
T24 (mg/L)	12,143	12,579	11,321	13,532
COD removal (mg/L)	1,811	1,470	2,611	1,378

**Table S2.** Fitted parameters extracted from the Nyquist plots of all prepared sample electrodes.

	CC-MR-1	Bare Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> -MR-1
Rs	4.99	143.2	141
CPE1-Anode-T	1.11 × 10 <sup>-4</sup>	$8.95 \times 10^{-9}$	$2.95 \times 10^{-8}$
CPE1-Anode-P	0.5833	1.141	1
Ra	3.769	79.27	75.88
CPE1-Cathode-T	0.00177	$5.13 \times 10^{-5}$	$6.22 \times 10^{-5}$
CPE1- Cathode -P	0.742	0.526	0.581
Rc	1007	5967	757.1