

Supplementary Materials: High Performance of Manganese Porphyrin Sensitized p-Type CuFe_2O_4 Photocathode for Solar Water Splitting to Produce Hydrogen in a Tandem Photoelectrochemical Cell

Xia Li ¹, Aijuan Liu ¹, Dongmei Chu ¹, Chunyong Zhang ¹, Yukou Du ¹, Jie Huang ² and Ping Yang ^{1,*}

2. Results

2.1. Morphology and Structure

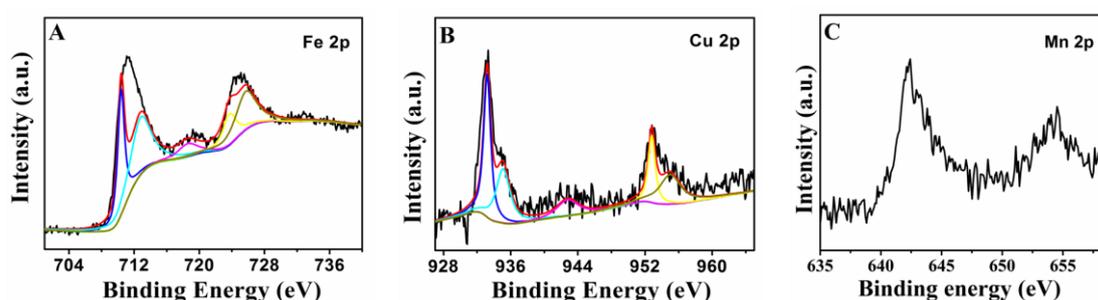


Figure S1. High-resolution XPS spectra of **A)** Fe 2p and **B)** Cu 2p of CuFe_2O_4 nanospheres; **C)** Mn 2p from MnTPP/ CuFe_2O_4 hybrid.

2.3. Photocatalytic Activity

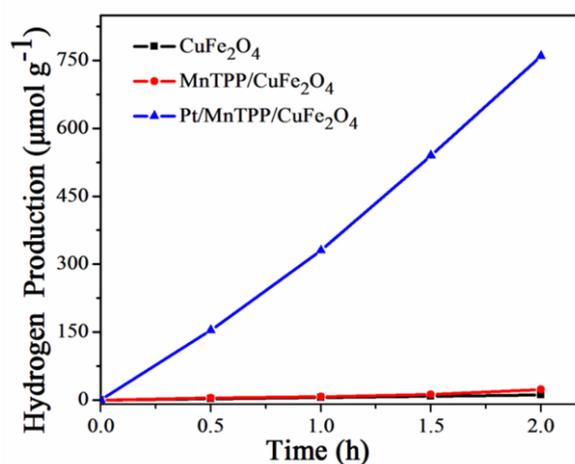


Figure S2. Amount of hydrogen evolved from the PEC device with CuFe_2O_4 , MnTPP/ CuFe_2O_4 and Pt/MnTPP/ CuFe_2O_4 at -0.2 V applied bias vs. RHE. Reaction conditions: electrolyte 0.2 M phosphate buffer solution. Light intensity 16 mW cm^{-2} .

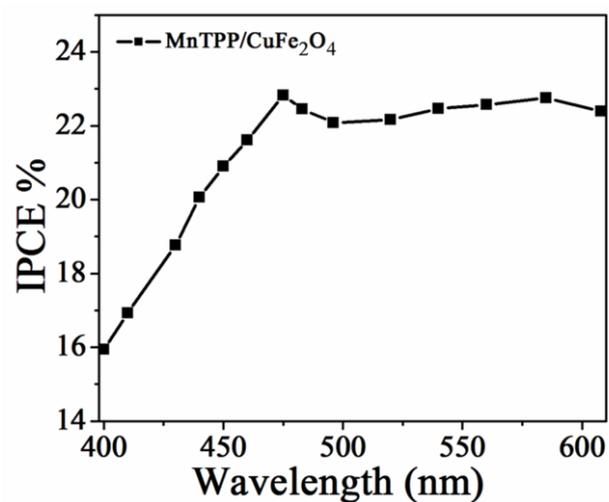


Figure S3. IPCE spectra of the PECs in 0.2 M phosphate buffer solution without any bias voltage.

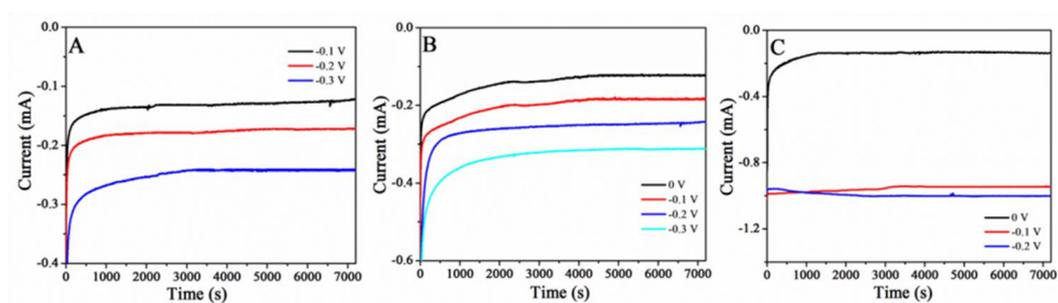
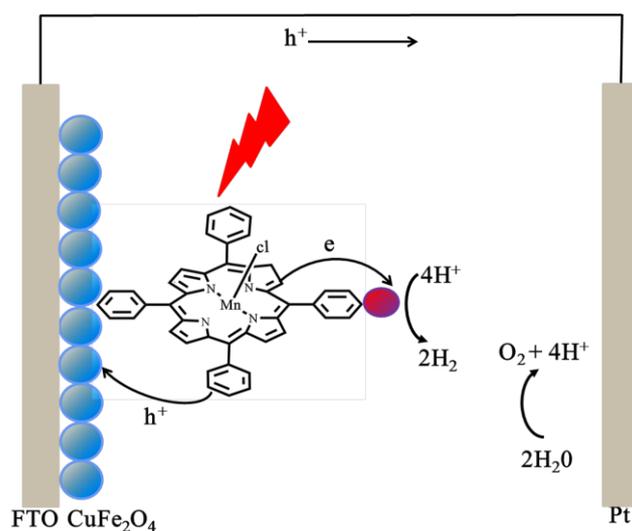


Figure S4. Current density vs time behavior from the PEC device with (A) CuFe_2O_4 , (B) $\text{MnTPP}/\text{CuFe}_2\text{O}_4$ and (C) $\text{Pt}/\text{MnTPP}/\text{CuFe}_2\text{O}_4$ as the photocathode at different applied voltages vs. RHE. Reaction conditions: electrolyte 0.2 M phosphate buffer solution. Light intensity 16 mW cm^{-2} .



Scheme 1. Scheme of three-electrode PEC device.

Table S1. Comparison of the performance of photocathodes

photocathode	E/V	n/H ₂	Electrolyte condition	Light source	Ref
ZnPc/C ₆₀ /Pt	0.2 V vs. RHE	110 μL	H ₃ PO ₄ solution (pH 2)	90 mW cm ⁻²	[1]
Pt/TiO ₂ /N, Zn-Fe ₂ O ₃ /Cr ₂ O ₃	0.1 V vs. RHE	11 μmol cm ⁻²	0.5 M Na ₂ CO ₃ -NaHCO ₃ (1:1) buffer electrolyte (pH 9.7)	300 W Xenon lamp	[2]
TiO ₂ /CaFe ₂ O ₄ /Pt	1.2 V vs. RHE	1.8 μmol	0.1 M NaOH	A solar simulator (400 mW cm ⁻²)	[3]
Pt/In ₂ S ₃ /CdS/CZTS	0.5 V vs. RHE	9.5 μmol	0.2 M Na ₂ HPO ₄ /NaH ₂ PO ₄ (pH 6.5)	AM 1.5G light irradiation	[4]
N-Ta ₂ O ₅ /Pt	-0.4 V vs. Ag/AgCl	0.58 μmol cm ⁻²	0.2 M K ₂ SO ₄	A 500 W Xeon lamp	[5]
CuFe ₂ O ₄ /MnTPP/Pt	-0.2 V vs. RHE	760 μmol g ⁻¹	0.2 M phosphate buffer solution (pH 7)	A 300 W solar simulator	This work

References:

- Abe, T.; Fukui, K.; Kawai, Y.; Nagai, K.; Kato, H. A water splitting system using an organo-photocathode and titanium dioxide photoanode capable of bias-free H₂ and O₂ evolution, *Chem. Commun.* **2016**, *52*, 7735–7737.
- Sekizawa, K.; Oh-ishi, K.; Kataoka, K.; Arai, T.; Suzuki T.M.; Morikawa T. Stoichiometric water splitting using a p-type Fe₂O₃ based photocathode with the aid of a multi-heterojunction, *J. Mater. Chem. A* **2017**, *5*, 6483–6493.
- Ida, S.; Kearney, K.; Futagami, T.; Hagiwara, H.; Sakai, T.; Watanabe, M.; Rockett, A.; Ishihara, T. Photoelectrochemical H₂ evolution using TiO₂-coated CaFe₂O₄ without an external applied bias under visible light irradiation at 470 nm based on device modeling, *Sustainable Energy & Fuels* **2017**, *1*, 280–287.
- Jiang, F.; Gunawan.; Harada, T.; Kuang, Y.; Minegishi, T.; Domen, K.; Ikeda, S. Pt/In₂S₃/CdS/Cu₂ZnSnS₄ Thin film as an efficient and stable photocathode for water reduction under sunlight radiation, *J. Amer. Chem. Soc.* **2015**, *137*, 13691–13697.
- Suzuki, T.M.; Saeki, S.; Sekizawa, K.; Kitazumi, K.; Takahashi, N.; Morikawa, T. Photoelectrochemical hydrogen production by water splitting over dual-functionally modified oxide: p-Type N-doped Ta₂O₅ photocathode active under visible light irradiation, *Appl. Catal. B: Environ.* **2017**, *202*, 597–604.