

Supporting information

CoMoO₄ modified hematite with oxygen vacancy for high-efficiency solar water splitting

Gaoteng Zhang^{1†}, Cheng Lu^{1†}, Chang Li¹, Shuo Li¹, Xiaoquan Zhao¹, Kaiqi Nie², Jiaou Wang², Kun Feng^{2*} and Jun Zhong^{2*}

¹ *Institute of Functional Nano and Soft Materials Laboratory (FUNSOM), Jiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, Suzhou 215123, China.*

² *Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*

† These authors contribute equally to this work.

* Corresponding authors.

E-mail address: fengkun0520@163.com (Kun Feng), jzhong@suda.edu.cn (Jun Zhong)

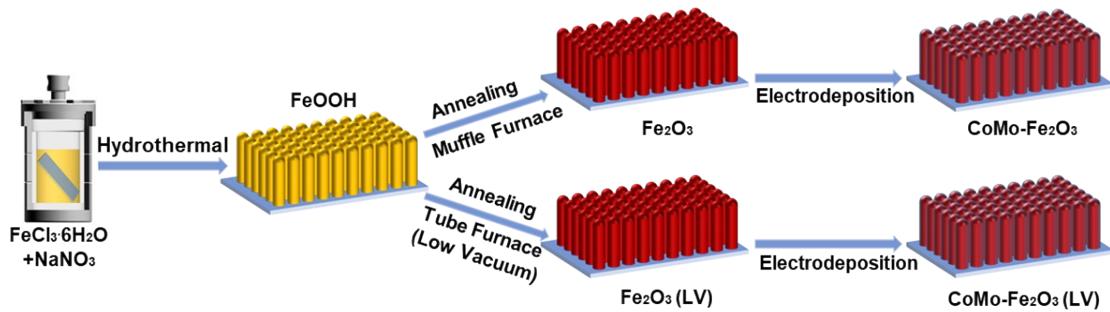


Fig. S1. Schematic illustration of the synthesis processes for Fe_2O_3 , Fe_2O_3 (LV) and $\text{CoMo-Fe}_2\text{O}_3$ (LV) photoanodes.

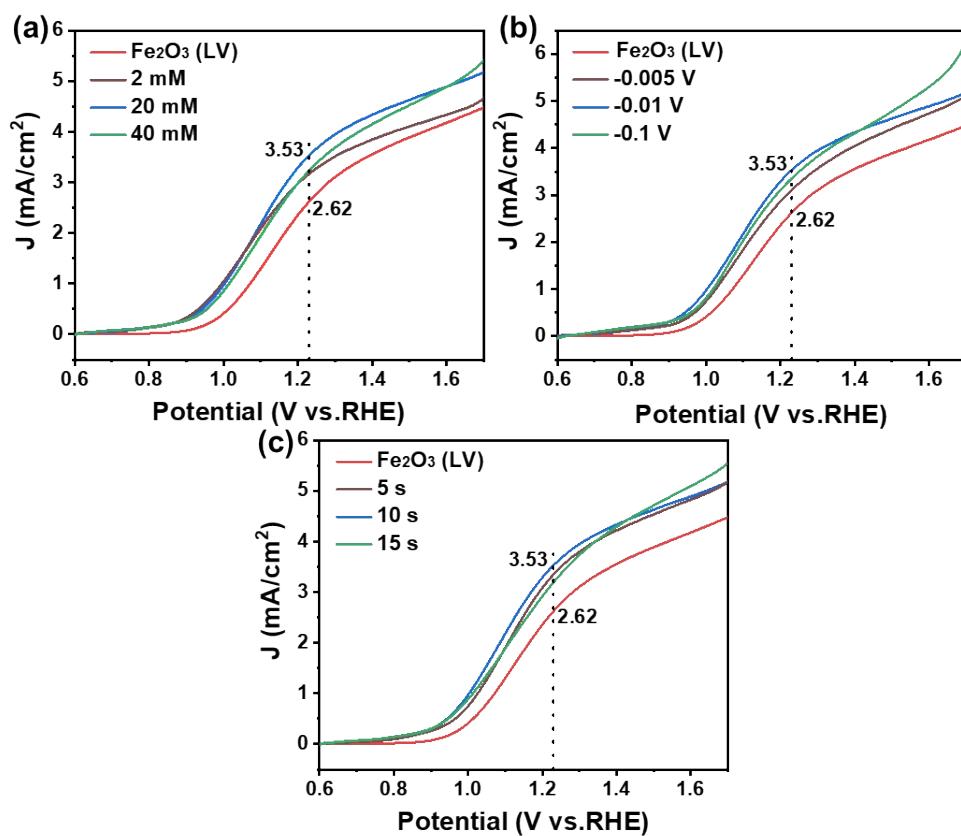


Fig. S2. J - V curves of CoMo- Fe_2O_3 (LV) photoanodes treated with (a) different precursor solution concentrations, (b) different deposition voltage and (c) different electrodeposition times.

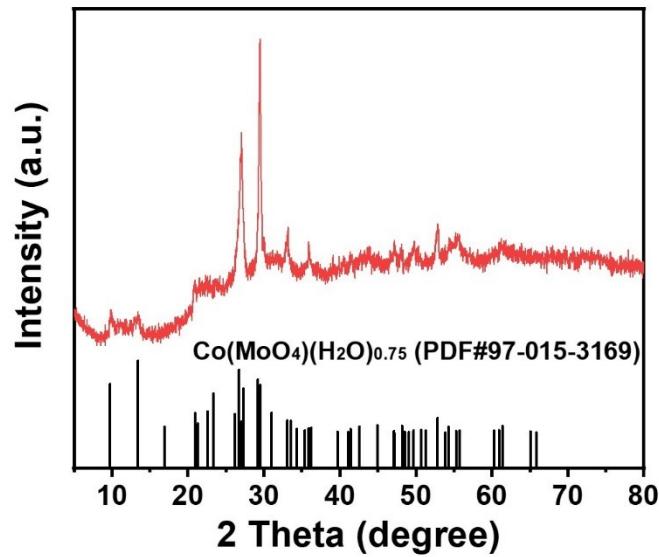


Fig. S3. XRD spectrum of CoMoO_4 with a deposition time of 10 hours.

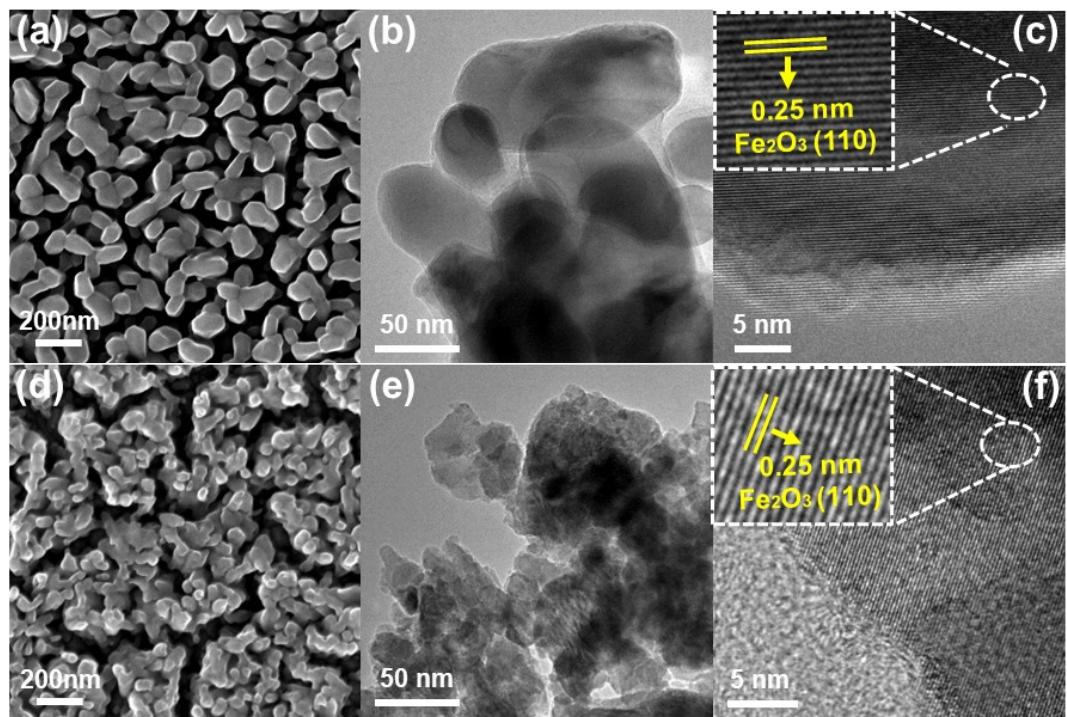


Fig. S4. (a) SEM, (b) TEM and (c) HRTEM images of Fe_2O_3 . (d) SEM, (e) TEM and (f) HRTEM images of Fe_2O_3 (LV).

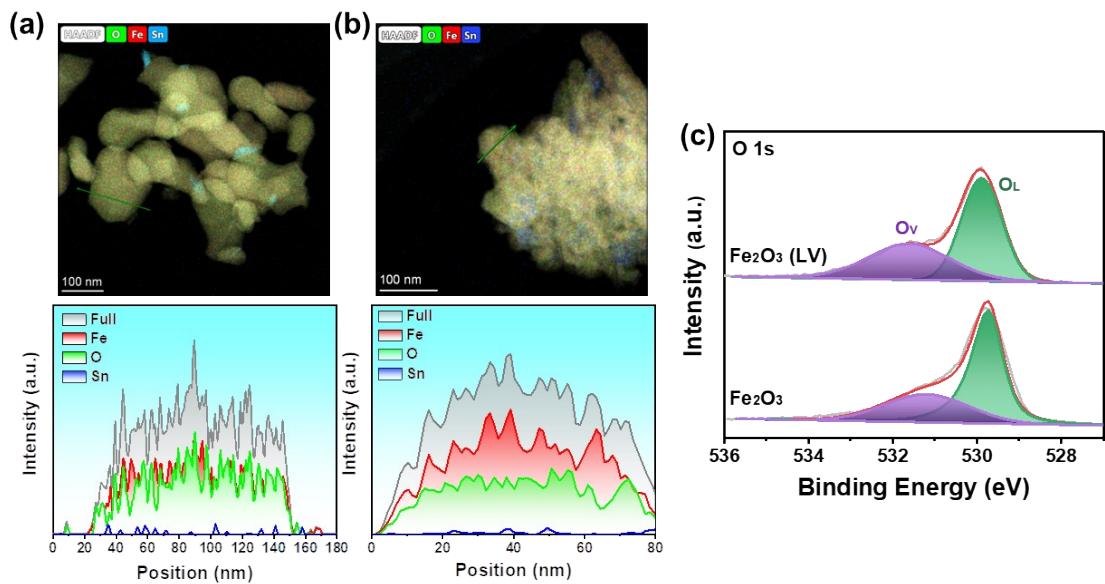


Fig. S5. TEM line scan analysis of (a) Fe₂O₃ and (b) Fe₂O₃ (LV) photoanodes. (c) O 1s high-resolution XPS spectra of Fe₂O₃ and Fe₂O₃ (LV) photoanodes.

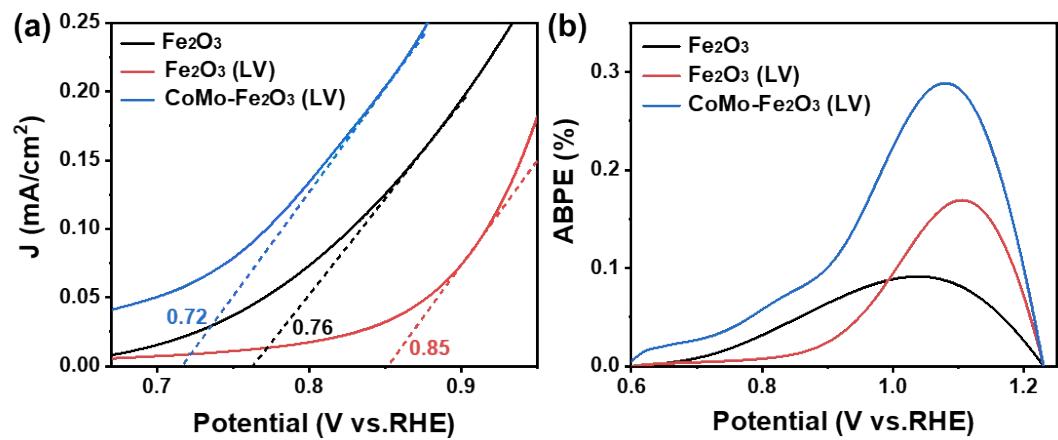


Fig. S6. (a) Magnified onset potential diagrams and (b) the ABPE curves of Fe_2O_3 , Fe_2O_3 (LV) and $\text{CoMo-Fe}_2\text{O}_3$ (LV) photoanodes.

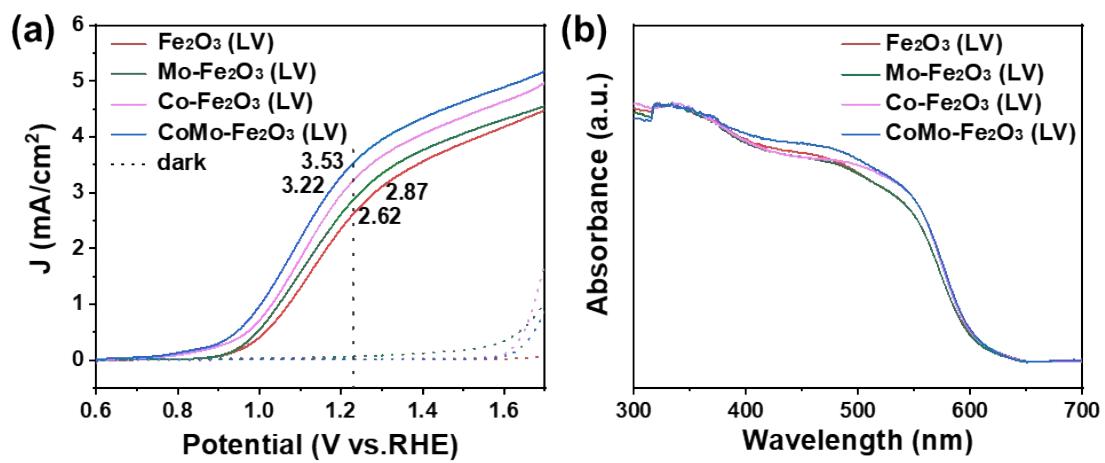


Fig. S7. (a) J - V curves and (b) UV-visible absorption spectra of Fe_2O_3 (LV), $\text{Mo-Fe}_2\text{O}_3$ (LV), $\text{Co-Fe}_2\text{O}_3$ (LV) and $\text{CoMo-Fe}_2\text{O}_3$ (LV).

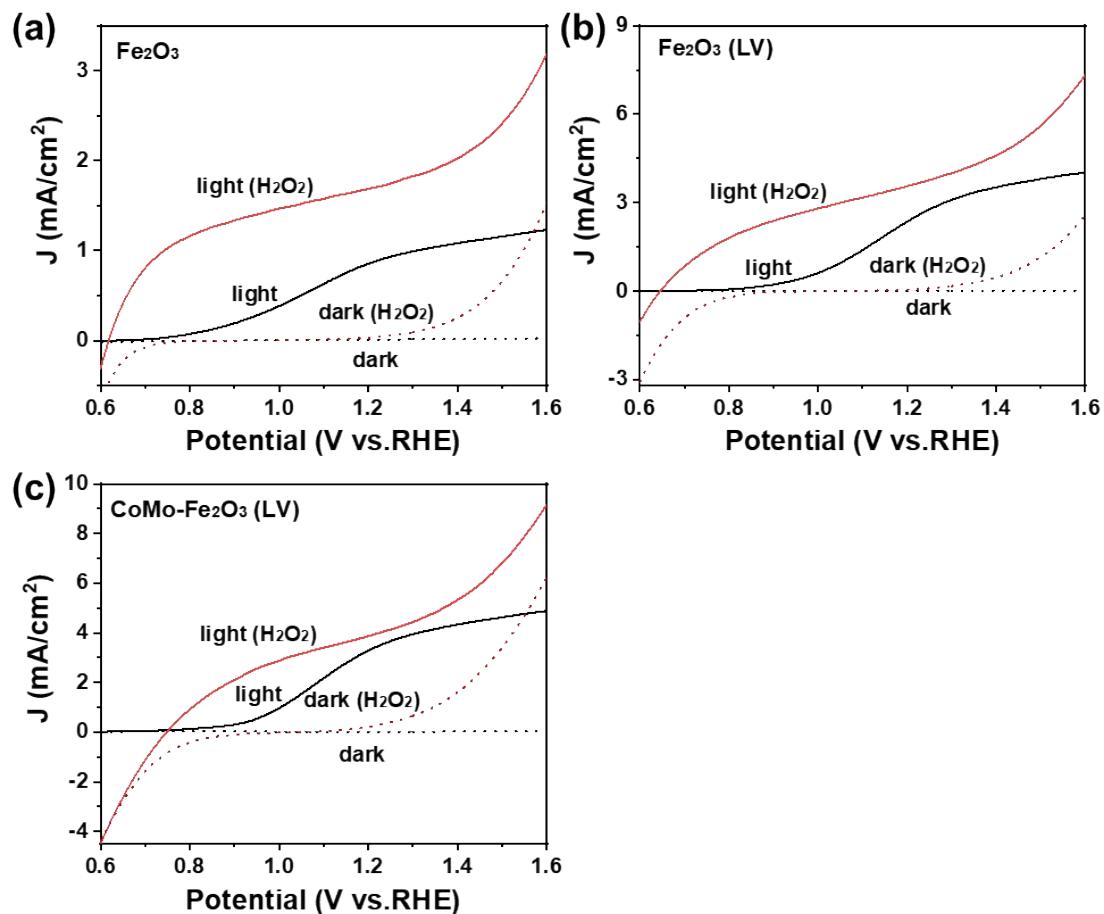


Fig. S8. J - V curves with (red) and without (black) H_2O_2 (0.5 M) for Fe_2O_3 (a), Fe_2O_3 (LV) (b) and $\text{CoMo-Fe}_2\text{O}_3$ (LV) (c), respectively.

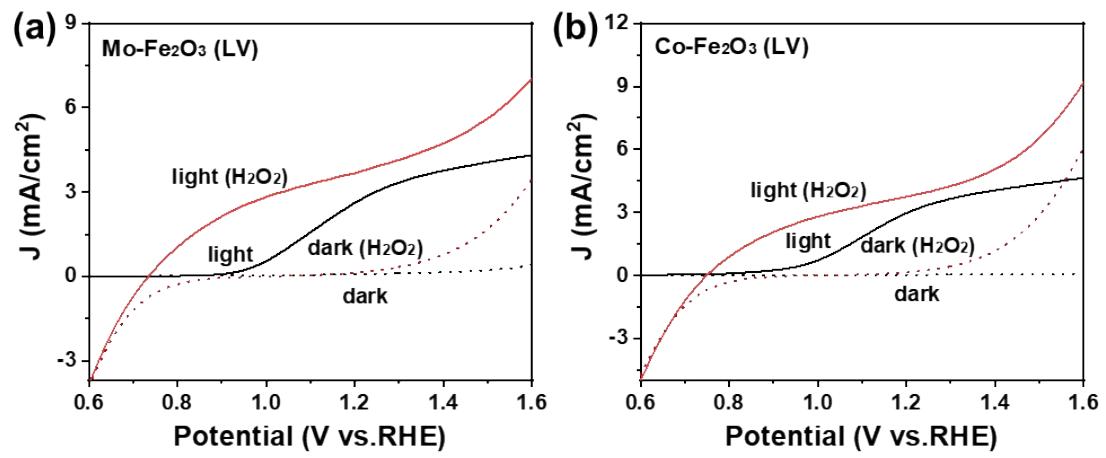


Fig. S9. J - V curves with (red) and without (black) H_2O_2 (0.5 M) for $\text{Mo-Fe}_2\text{O}_3$ (LV) (a) and $\text{Co-Fe}_2\text{O}_3$ (LV) (b), respectively.

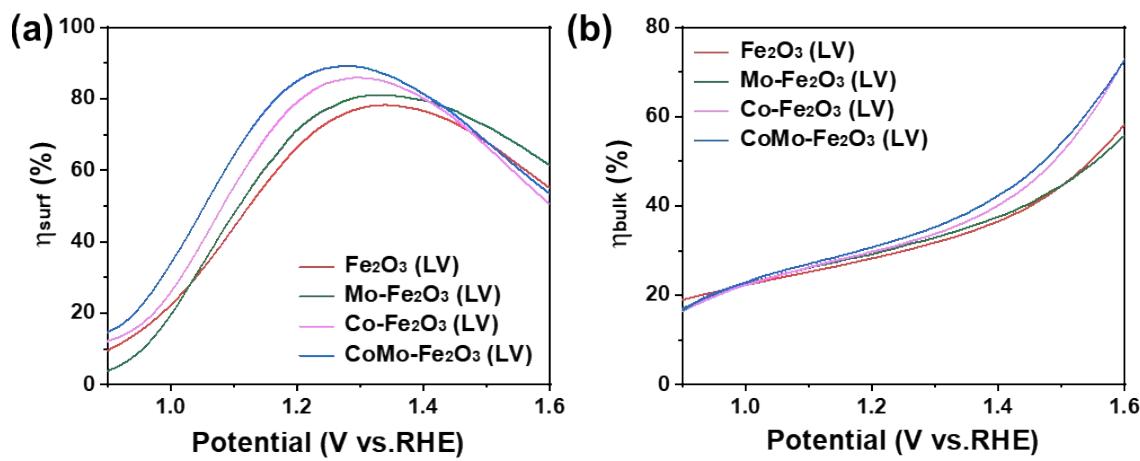


Fig. S10. (a) Surface charge separation efficiencies ($\eta_{surface}$) and (b) bulk charge separation efficiencies (η_{bulk}) of Fe₂O₃ (LV), Mo-Fe₂O₃ (LV), Co-Fe₂O₃ (LV) and CoMo-Fe₂O₃ (LV), respectively.

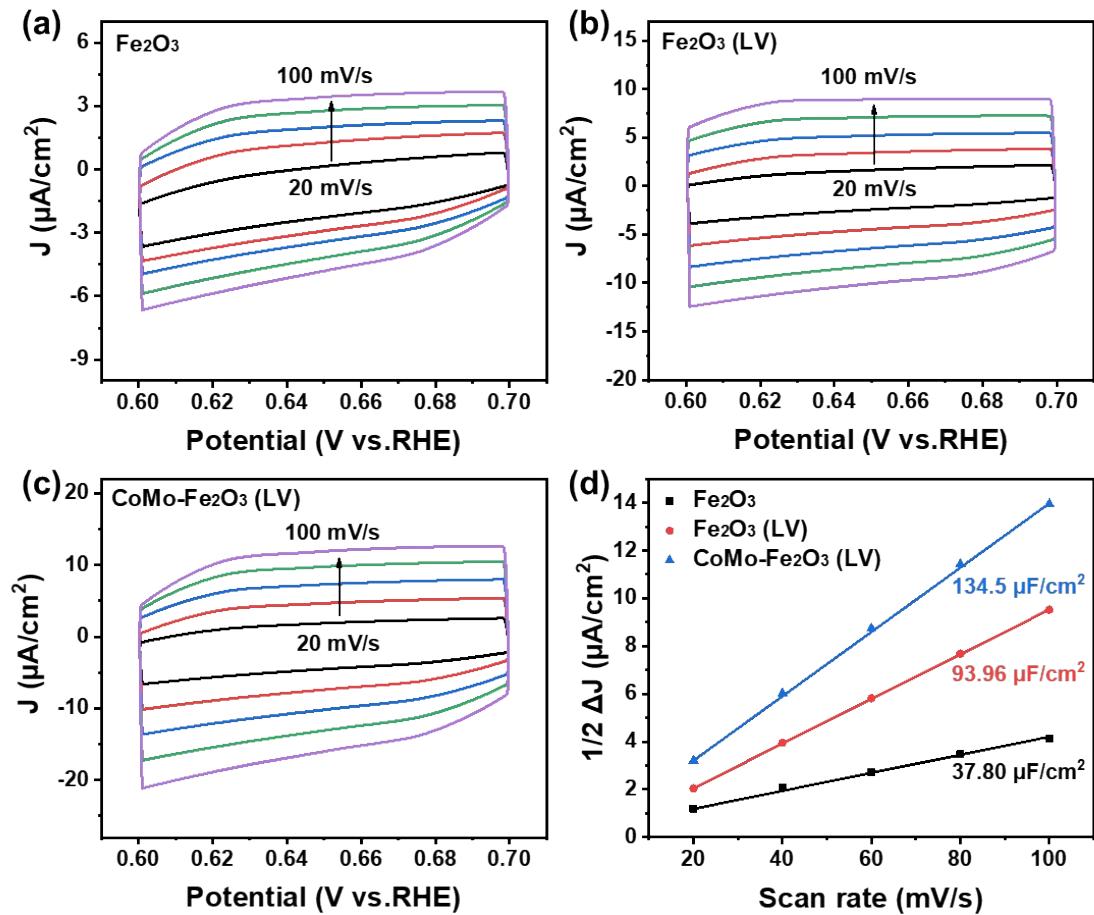


Fig. S11. CV curves recorded at different scan rates (20, 40, 60, 80, and 100 mV/s) for (a) Fe_2O_3 , (b) Fe_2O_3 (LV) and (c) $\text{CoMo-Fe}_2\text{O}_3$ (LV) electrodes in the dark. (d) The average capacitive current against scan rate for Fe_2O_3 , Fe_2O_3 (LV) and $\text{CoMo-Fe}_2\text{O}_3$ (LV) electrodes.

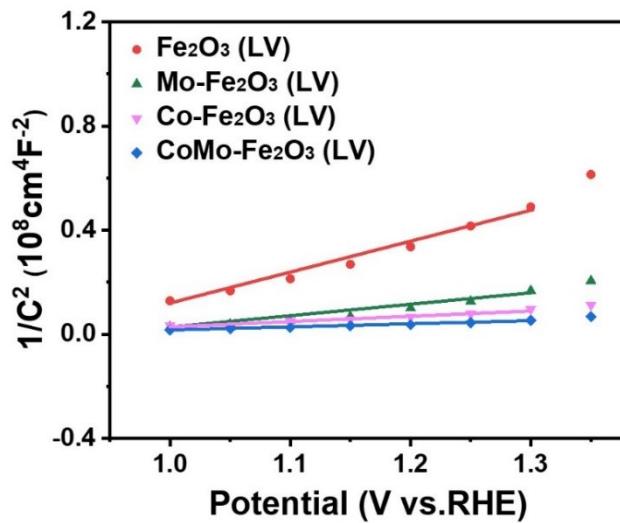


Fig. S12. Mott-Schottky plots of Fe_2O_3 (LV), $\text{Mo-Fe}_2\text{O}_3$ (LV), $\text{Co-Fe}_2\text{O}_3$ (LV) and $\text{CoMo-Fe}_2\text{O}_3$ (LV).

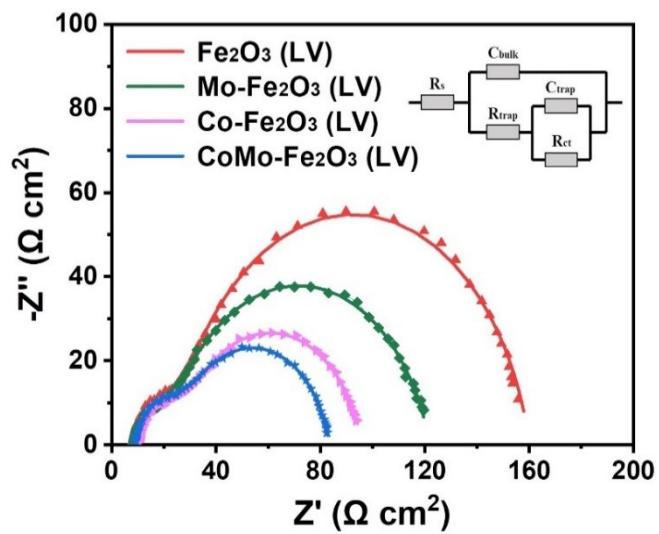


Fig. S13. EIS spectra of Fe_2O_3 (LV), $\text{Mo}-\text{Fe}_2\text{O}_3$ (LV), $\text{Co}-\text{Fe}_2\text{O}_3$ (LV) and $\text{CoMo}-\text{Fe}_2\text{O}_3$ (LV).

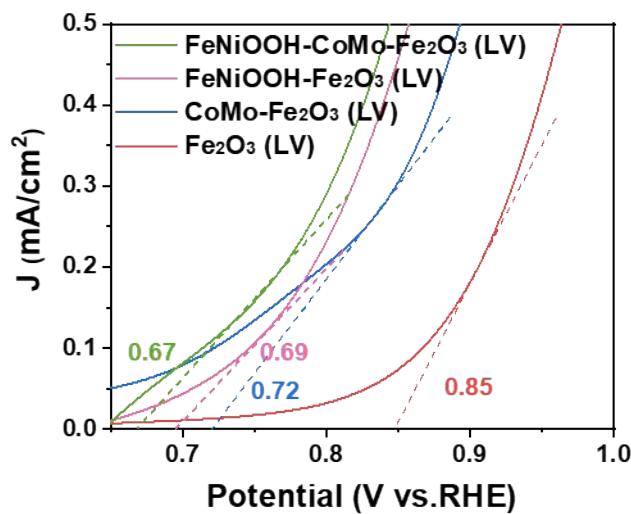


Fig. S14. Magnified onset potential diagrams of Fe_2O_3 (LV), $\text{CoMo-Fe}_2\text{O}_3$ (LV), $\text{FeNiOOH-Fe}_2\text{O}_3$ (LV) and $\text{FeNiOOH-CoMo-Fe}_2\text{O}_3$ (LV) photoanodes.

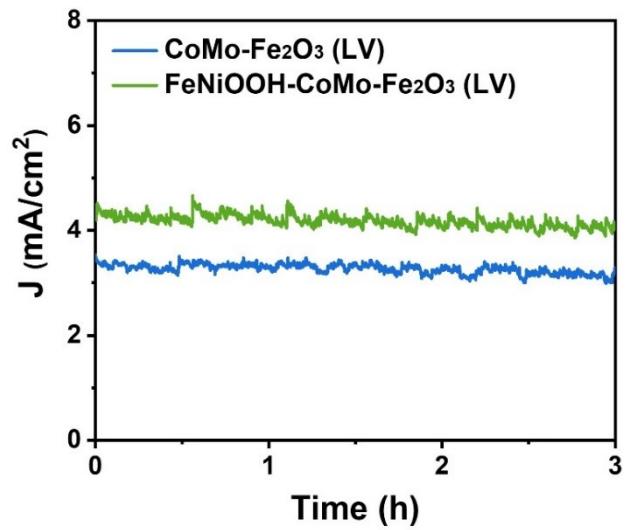


Fig. S15. Photochemical stability curves of CoMo-Fe₂O₃ (LV) and FeNiOOH-CoMo-Fe₂O₃ (LV) measured at 1.23 V_{RHE}.

Table S1. Parameters of the equivalent circuit elements.

	R_s (Ω)	C_{bulk} (μF)	R_{trap} (Ω)	C_{trap} (mF)	R_{ct} (Ω)
Fe₂O₃ (LV)	8.11±0.06	65.14±6.81	24.02±0.80	0.57±0.02	128.00±1.50
Mo-Fe₂O₃ (LV)	8.34±0.04	101.60±9.63	19.96±0.65	0.90±0.02	93.65±1.00
Co-Fe₂O₃ (LV)	10.11±0.05	105.80±9.54	23.17±0.70	1.08±0.03	62.74±0.99
CoMo-Fe₂O₃ (LV)	8.99±0.04	121.10±9.82	25.56±0.77	0.99±0.04	48.89±0.92

Table S2. Comparison of the photocurrents on hematite-based photoanodes (at 1.23 V RHE).

Electrodes	Solutions	J (mA/cm ²)	Reference
FeNiOOH-CoMo-Fe₂O₃ (LV)	1 M NaOH (pH 13.6)	4.18	This work
FH/TH/Co	1 M NaOH (pH 13.6)	6.0	(1)
NiFeO_x@Ge-PH	1 M NaOH (pH 13.6)	4.60	(2)
NiFeO_x/Si:Ti-Fe₂O₃	1 M NaOH (pH 13.6)	4.30	(3)
Ti:Fe₂O₃/SiO_x/Ti-FeOOH	1 M NaOH (pH 13.6)	4.06	(4)
NiFeO_x/Ti:Si-Fe₂O₃ (Dual photoanode)	1 M NaOH (pH 13.6)	4.00	(5)
Fe₂O₃-MA-18 min	1 M NaOH (pH 13.6)	3.90	(6)
Co-Pi/Sn-Fe₂O₃	1 M NaOH (pH 13.6)	3.90	(7)
IrO₂/Fe₂O₃	1 M NaOH (pH 13.6)	3.75	(8)
F/Sn: Fe₂O₃	1 M NaOH (pH 13.6)	3.64	(9)
NiFeO_x/P,Ti-Fe₂O₃	1 M NaOH (pH 13.6)	3.54	(10)
Co-Pi/Mn-Fe₂O₃	1 M NaOH (pH 13.6)	3.50	(11)
Ti-Fe₂O₃ MC/Co-Pi	1 M NaOH (pH 13.6)	3.50	(12)
InO₂ layer / Fe₂O₃	1 M NaOH (pH 13.6)	3.40	(13)
CoPi-Ti/Au/ Fe₂O₃	1 M NaOH (pH 13.6)	3.39	(14)
Sn:Fe₂O₃ with V_O	1 M NaOH (pH 13.6)	3.30	(15)
NiFe(OH)_x/Ta:Fe₂O₃@Fe₂O₃	1 M NaOH (pH 13.6)	3.22	(16)
Fe₂O₃/FeOOH/Au	1 M KOH (pH 13.6)	3.20	(17)
Ti:Fe₂O₃/SiO_x/Co-Pi	1 M NaOH (pH 13.6)	3.19	(18)
Co-Pi/(3D) Ti-Fe₂O₃/NTO	1 M NaOH (pH 13.6)	3.16	(19)
Fe₂O₃/TiO₂/FeOOH	1 M KOH (pH 13.6)	3.15	(20)
Fe₂O₃/SiMWs	1 M NaOH (pH 13.6)	3.12	(21)
P:Fe₂O₃ /Co-Pi	1 M NaOH (pH 13.6)	3.10	(22)
TiO₂/Ti: Fe₂O₃ BNR/FeOOH	1 M KOH (pH 13.6)	3.10	(23)
Sb₂Se₃-Fe₂O₃	1 M NaOH (pH 13.6)	3.07	(24)
CoPi-Ti :Fe₂O₃	1 M NaOH (pH 13.6)	3.05	(25)
Co-Pi/CQDs/Fe₂O₃/TiO₂	1 M NaOH (pH 13.6)	3.00	(26)
Ni₂P/Ta:α-Fe₂O₃	1 M KOH (pH 13.6)	2.98	(27)
A:Ce-Fe₂O₃@Fe₂O₃	1 M KOH (pH 13.6)	2.50	(28)
Cu@α-Fe₂O₃-Vo-pn	1 M KOH (pH 13.6)	2.49	(29)

References :

- 1 T. Jeon, G. Moon, H. Park and W. Choi, *Nano Energy*, 2017, **39**, 211-218.
- 2 K. Yoon, J. Park, M. Jung, S. Ji, H. Lee, J. Seo, M. Kwak, S. Seok, J. Lee and J. Jang, *Nat. Commun.*, 2021, **12**, 4309.
- 3 K. Yoon, J. Park, H. Lee, J. Seo, M. Kwak, J. Lee and J. Jang, *ACS Catal.*, 2022, **12**, 5112-5122.
- 4 K. Yoon, H. Ahn, M. Kwak, S. Kim, J. Park and J. Jang, *J. Mater. Chem. A*, 2016, **4**, 18730-18736.
- 5 J. Park, K. Yoon, T. Kim, H. Jang, M. Kwak, J. Kim and J. Jang, *Nano Energy*, 2020, **76**, 105089.
- 6 Y. Hou, C. Zheng, Z. Zhu and X. Wang, *Chem. Commun.*, 2016, **52**, 6888-6891.
- 7 Gurudayal, R. John, P. Boix, C. Yi, C. Shi, M. Scott, S. Veldhuis, A. Minor, S. Zakeeruddin, L. Wong, M. Grätzel and N. Mathews, *ChemSusChem*, 2017, **10**, 2449-2456.
- 8 S. Tilley, M. Cornuz, K. Sivula and M. Gratzel, *Angew. Chem. Int. Ed.*, 2010, **49**, 6405-6408.
- 9 N. Quang, P. Van, D. Le, S. Majumder, N. Chinh, J. Jeong, C. Kim and D. Kim, *Appl. Surf. Sci.*, 2021, **558**, 149898.
- 10 J. Kang, K. Yoon, J. Lee, J. Park, S. Chaule and J. Jang, *Nano Energy*, 2023, **107**, 108090.
- 11 Gurudayal, D. Sabba, M. Kumar, L. Wong, J. Barber, M. Grätzel and N. Mathews, *Nano Lett.*, 2015, **15**, 3833-3839.
- 12 Z. Zhang, I. Karimata, H. Nagashima, S. Muto, K. Ohara, K. Sugimoto and T. Tachikawa, *Nat. Commun.*, 2019, **10**, 4832.
- 13 S. Yi, Z. Wang, H. Li, Z. Zafar, Z. Zhang, L. Zhang, D. Chen, Z. Liu and X. Yue, *Appl. Catal. B: Environ.*, 2021, **283**, 119649.
- 14 J. Li, Y. Qiu, Z. Wei, Q. Lin, Q. Zhang, K. Yan, H. Chen, S. Xiao, Z. Fan and S. Yang, *Energy Environ. Sci.*, 2014, **7**, 3651-3658.
- 15 J. Wang, Y. Hu, R. Toth, G. Fortunato and A. Braun, *J. Mater. Chem. A*, 2016, **4**, 2821-2825.
- 16 H. Zhang, D. Li, W. Byun, X. Wang, T. Shin, H. Jeong, H. Han, C. Li and J. Lee, *Nat. Commun.*, 2020, **11**, 4622.
- 17 L. Wang, H. Hu, N. Nguyen, Y. Zhang, P. Schmuki and Y. Bi, *Nano Energy*, 2017, **35**, 171-

- 18 H. Ahn, K. Yoon, M. Kwak and J. Jang, *Angew. Chem. Int. Ed.*, 2016, **55**, 9922-9926.
- 19 K. Yan, Y. Qiu, S. Xiao, J. Gong, S. Zhao, J. Xu, X. Meng, S. Yang and J. Xu, *Mater. Today Energy*, 2017, **6**, 128-135.
- 20 F. Feng, C. Li, J. Jian, X. Qiao, H. Wang and L. Jia, *Chem. Eng. J.*, 2019, **368**, 959-967.
- 21 Z. Zhou, S. Wu, L. Qin, L. Li, L. Li and X. Li, *J. Mater. Chem. A*, 2018, **6**, 15593-15602.
- 22 Y. Zhang, S. Jiang, W. Song, P. Zhou, H. Ji, W. Ma, W. Hao, C. Chen and J. Zhao, *Energy Environ. Sci.*, 2015, **8**, 1231-1236.
- 23 Z. Luo, T. Wang, J. Zhang, C. Li, H. Li and J. Gong, *Angew. Chem. Int. Ed.*, 2017, **56**, 12878-12882.
- 24 A. Liao, Y. Zhou, L. Xiao, C. Zhang, C. Wu, A. Asiri, M. Xiao and Z. Zou, *Nanoscale*, 2019, **11**, 109-114.
- 25 Y. Qiu, S. Leung, Q. Zhang, B. Hua, Q. Lin, Z. Wei, K. Tsui, Y. Zhang, S. Yang and Z. Fan, *Nano Lett.*, 2014, **14**, 2123-2129.
- 26 X. Hu, J. Huang, F. Zhao, P. Yi, B. He, Y. Wang, T. Chen, Y. Chen, Z. Li and X. Liu, *J. Mater. Chem. A*, 2020, **8**, 14915-14920.
- 27 X. Cao, P. Wen, R. Ma, Y. Liu, S. Sun, Q. Ma, P. Zhang and Y. Qiu, *Chem. Eng. J.*, 2022, **449**, 137792.
- 28 J. Bai, R. Gao, X. Guo, J. He, X. Liu, X. Zhang and L. Wang, *Chem. Eng. J.*, 2022, **448**, 137602.
- 29 H. Wang, Y. Hu, G. Song and D. Zheng, *Chem. Eng. J.*, 2022, **435**, 135016.