

Supporting Information

Improvement of the Water Oxidation Performance of Ti, F Co-modified Hematite by Surface Modification with Co(salen) Molecular Cocatalyst

Ruiling Wang,^a Yasutaka Kuwahara,^{a,b,c} Kohsuke Mori,^{a,b} Catherine Louis,^d Yuyu Bu,^e and Hiromi Yamashita^{*a,b}

^a Division of Material and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

^b Elements Strategy Initiative for Catalysts & Batteries Kyoto University, ESICB, Kyoto University, Katsura, Kyoto 615-8520, Japan

^c JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

^d Sorbonne Université, CNRS, Laboratoire de Réactivité de Surface (LRS), F-75005 Paris, France

^e Key Laboratory of Wide Band-gap Semiconductor Materials and Devices, School of Microelectronics, Xidian University, Xi'an 710071, China

Corresponding Author

* Hiromi Yamashita (yamashita@mat.eng.osaka-u.ac.jp)

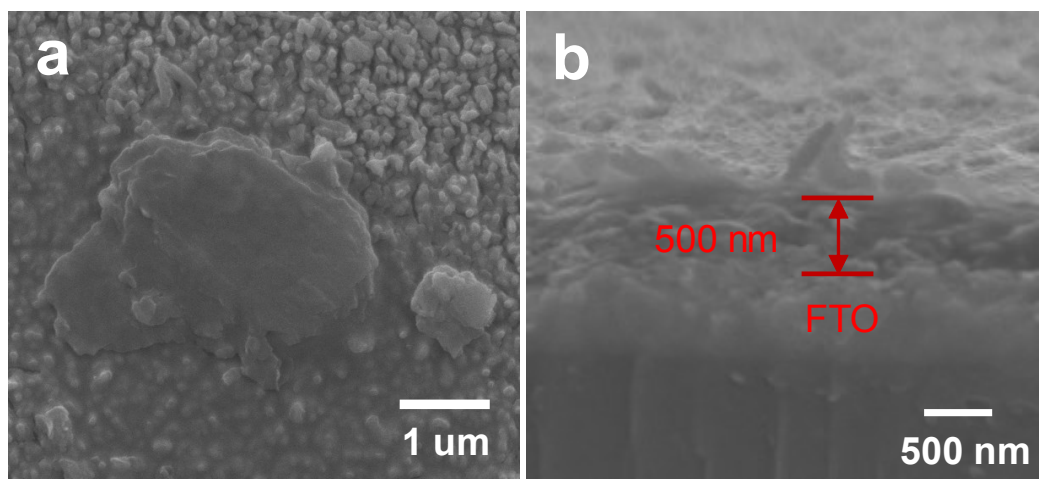


Fig. S1 (a) FE-SEM image of F-Ti-Fe₂O₃/Co(salen); (b) cross-section FE-SEM image of F-Ti-Fe₂O₃/Co(salen).

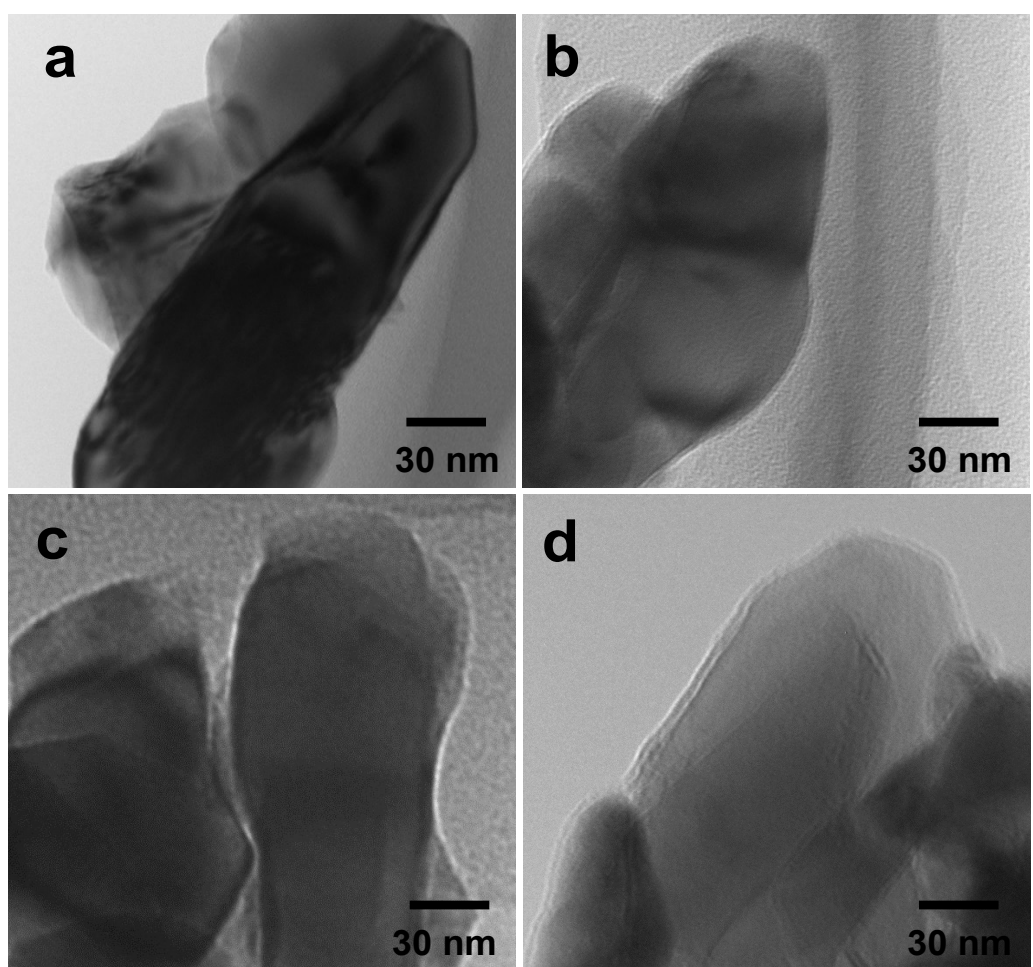


Fig. S2 TEM images of (a) Fe₂O₃, (b) Ti-Fe₂O₃, (c) F-Ti-Fe₂O₃ and (d) F-Ti-Fe₂O₃/Co(salen).

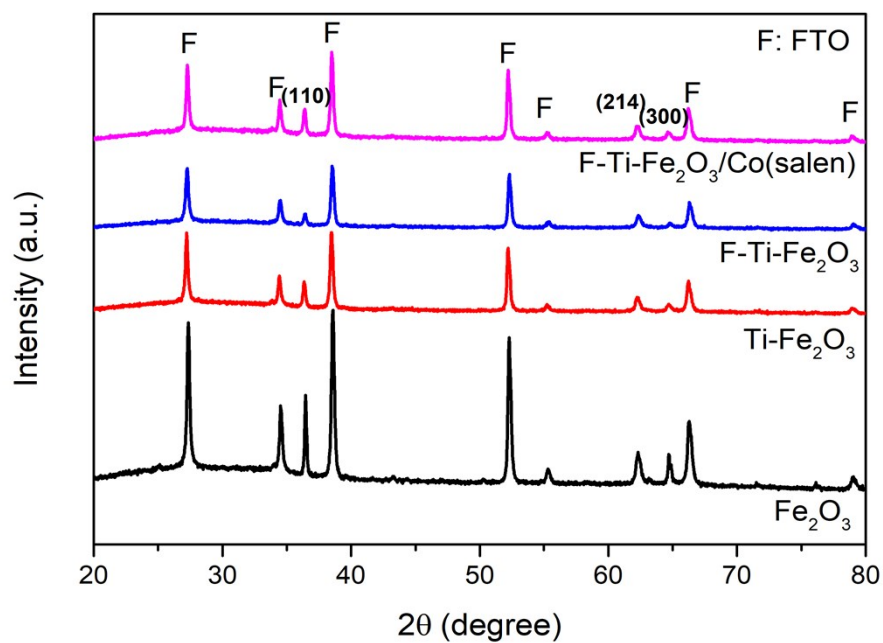


Fig. S3 XRD patterns of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen).

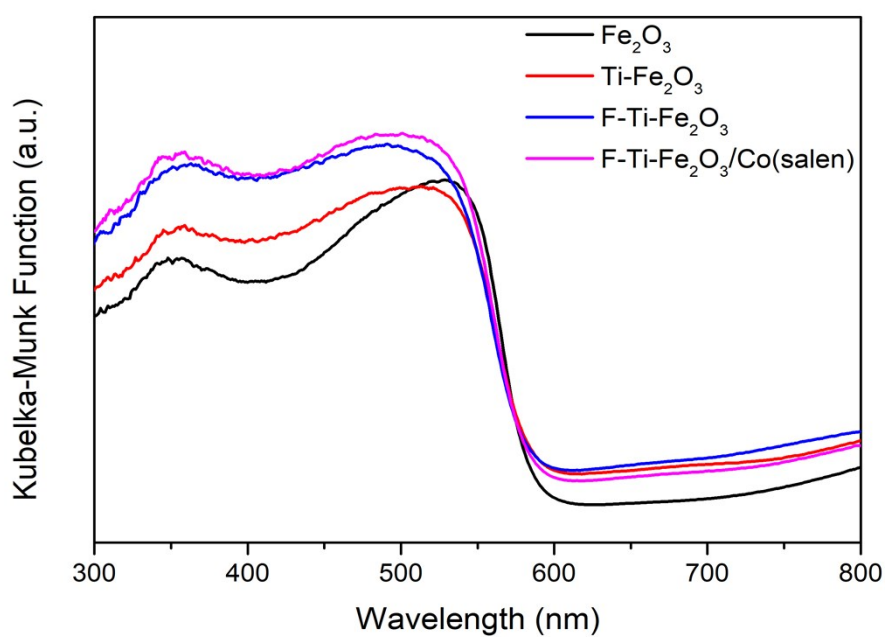


Fig. S4 UV-Vis spectra of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen).

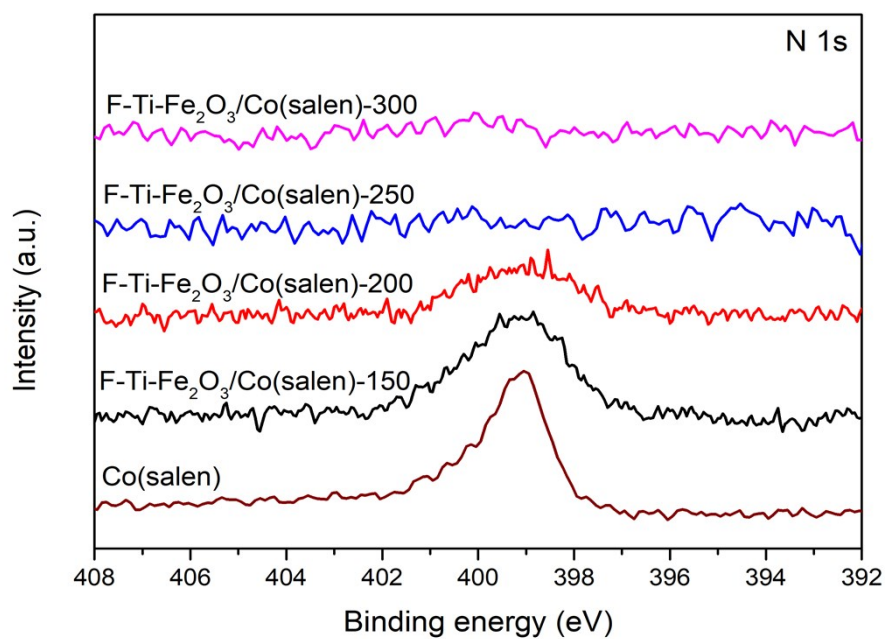


Fig. S5 N 1s XPS spectra of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen).

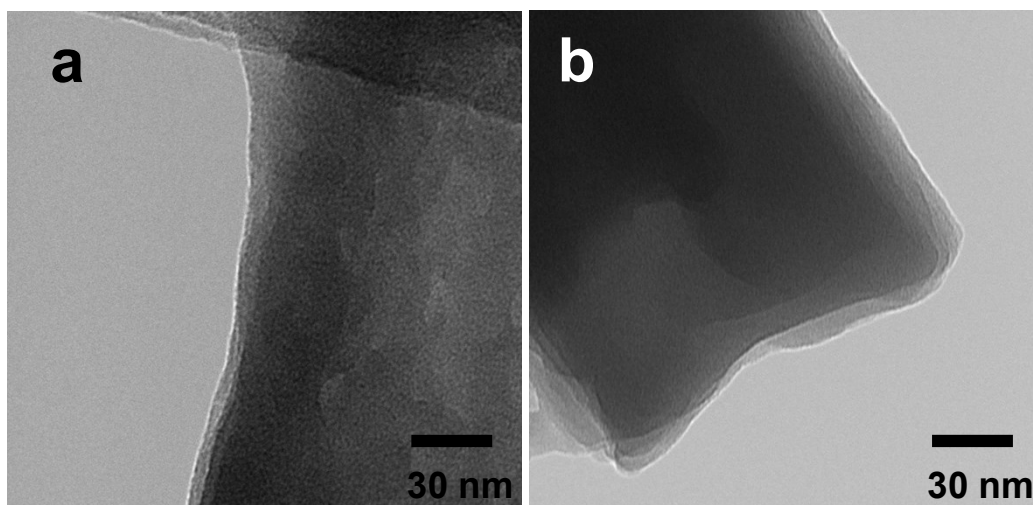


Fig. S6 TEM images of (a) F-Ti-Fe₂O₃/Co(salen)-250 and (b) F-Ti-Fe₂O₃/Co(salen)-300.

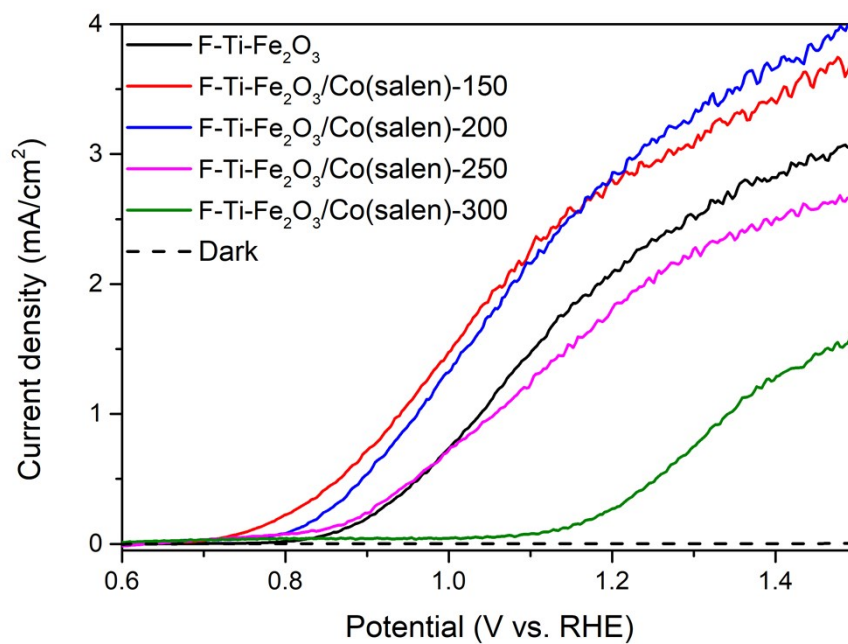


Fig. S7 LSV curves of F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen) at different temperatures photoanodes under illumination.

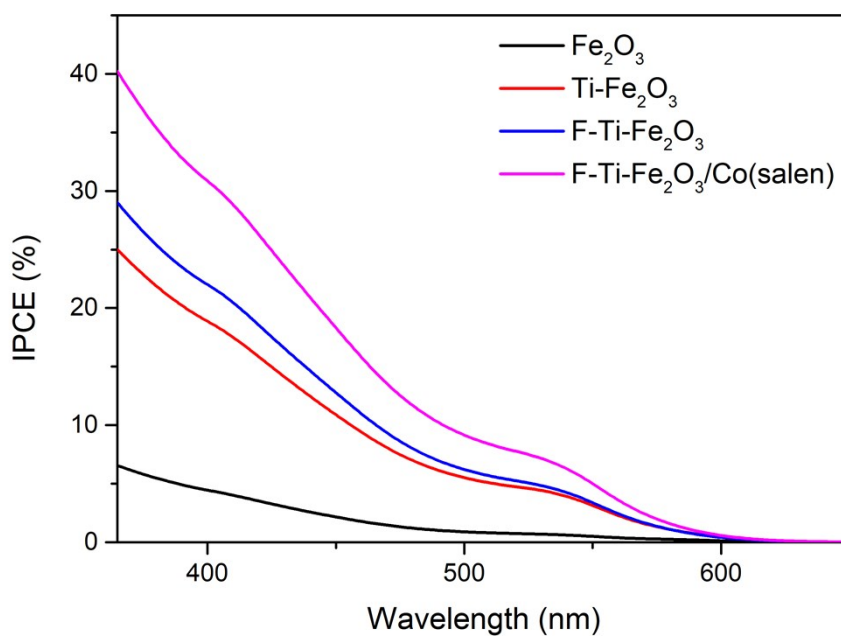


Fig. S8 IPCE curves of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen) photoanodes at 1.23 V vs. RHE under illumination.

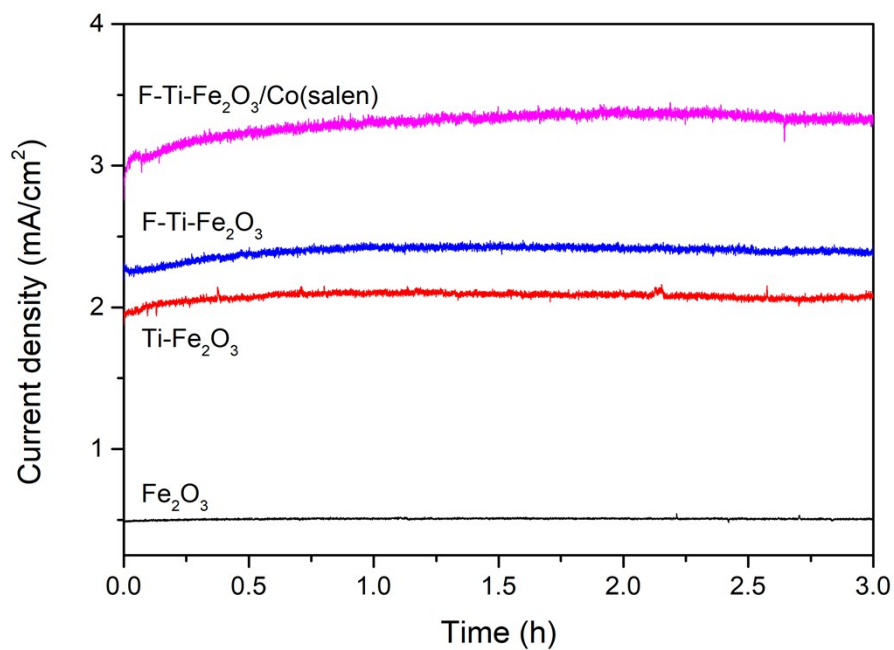


Fig. S9 Amperometric I-t curves of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen) photoanodes.

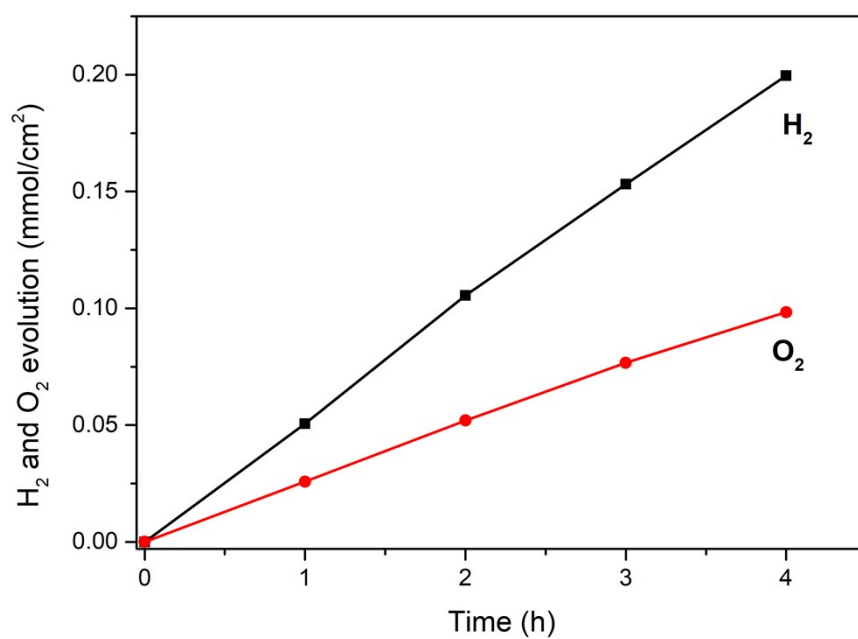


Fig. S10 H₂ and O₂ evolution of the F-Ti-Fe₂O₃/Co(salen) photoanode at 1.23 V vs. RHE under illumination.

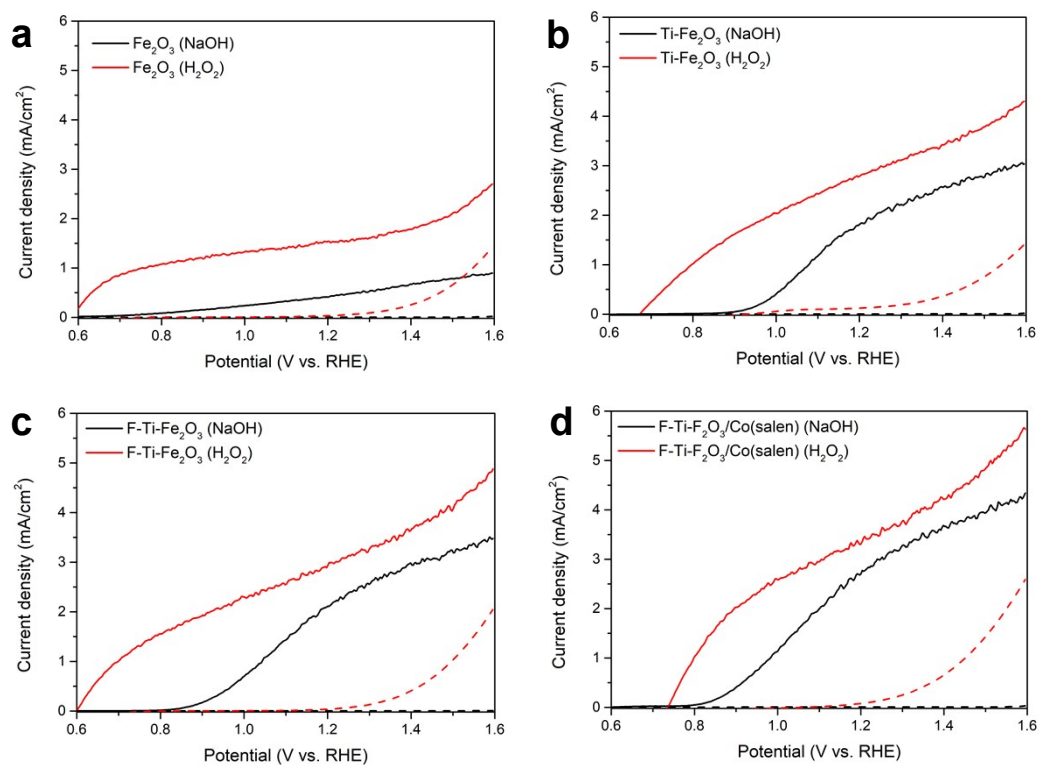


Fig. S11 LSV curves of photoanodes in 1 M NaOH and 1 M NaOH with 0.5 M H_2O_2 solution under illumination: (a) Fe_2O_3 , (b) $\text{Ti-Fe}_2\text{O}_3$, (c) $\text{F-Ti-Fe}_2\text{O}_3$ and (d) $\text{F-Ti-Fe}_2\text{O}_3/\text{Co(salen)}$ photoanodes.

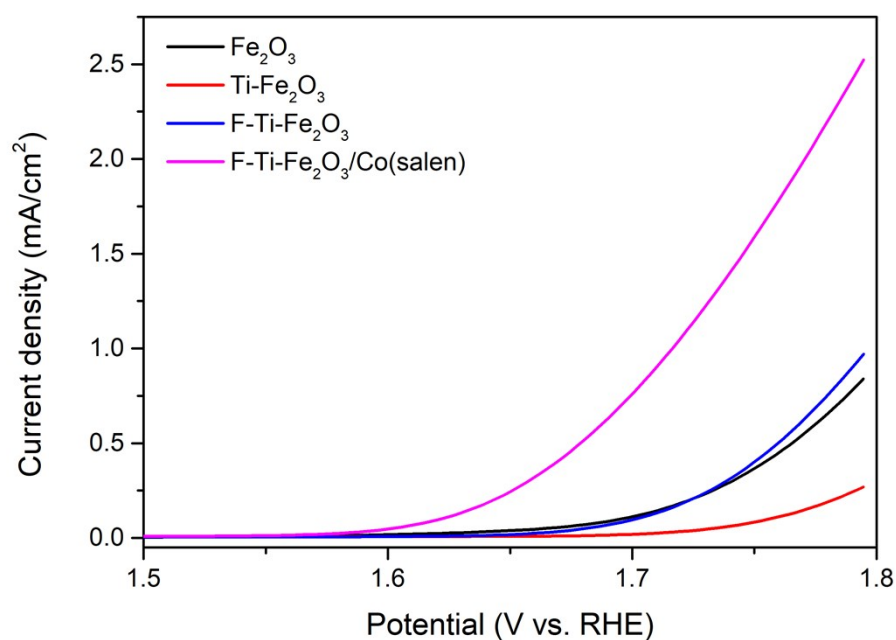


Fig. S12 Polarization curves for OER performance of Fe_2O_3 , $\text{Ti-Fe}_2\text{O}_3$, $\text{F-Ti-Fe}_2\text{O}_3$ and $\text{F-Ti-Fe}_2\text{O}_3/\text{Co(salen)}$ photoanodes in the dark.

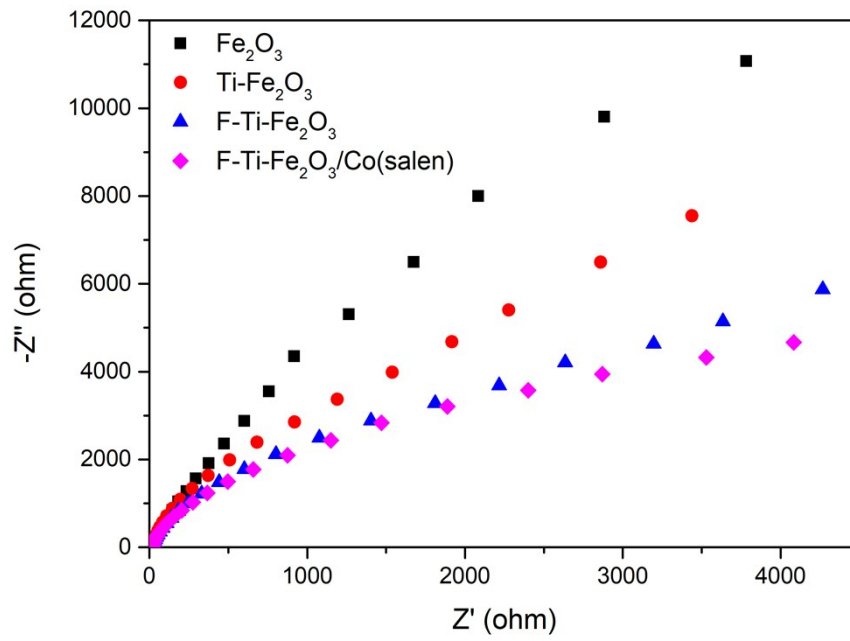


Fig. S13 EIS spectra of Fe_2O_3 , $\text{Ti-Fe}_2\text{O}_3$, $\text{F-Ti-Fe}_2\text{O}_3$ and $\text{F-Ti-Fe}_2\text{O}_3/\text{Co(salen)}$ photoanodes in the dark.

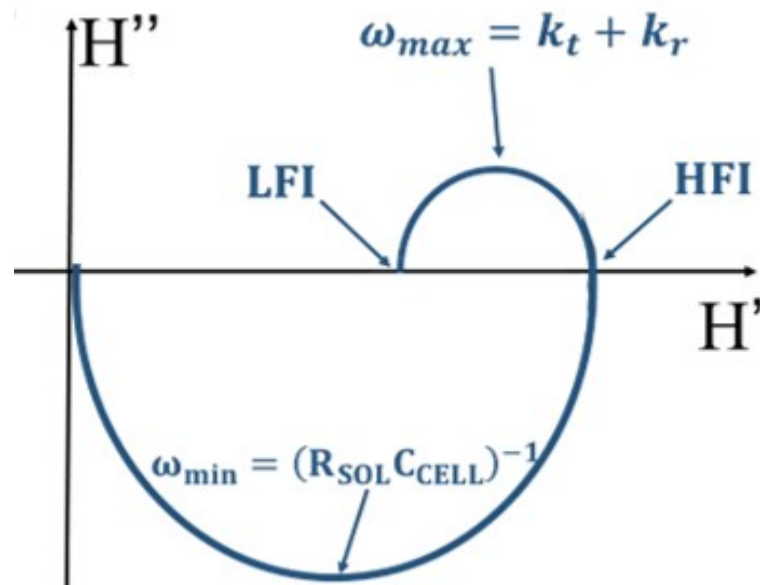


Fig. S14 Standard IMPS spectra in Nyquist coordinates.

Table S1 Comparison of our photoanode to other hematite-based photoanodes

Photoanodes	Electrolyte	J (mA/cm ²) at 1.23 V vs. RHE	Onset potential (V vs. RHE)	Ref.
Co-Pi/Ag/Fe ₂ O ₃	1 M NaOH	4.32	0.70	1
α -Fe ₂ O ₃ /FeOOH/Au	1 M KOH	3.2	0.60	2
Fe ₂ O ₃ -TiP75-Co-Pi	1 M NaOH	2.9	0.85	3
ITO/Fe ₂ O ₃ /Fe ₂ TiO ₅ /Fe ₂ O ₃	1 M NaOH	2.2	1.0	4
Rh-F-TiFeO ₅ /Fe ₂ O ₅	1 M NaOH	2.12	0.72	5
C-Co-Ti- Fe ₂ O ₃	1 M NaOH	2.24	0.70	6
NiOOH/Fe ₂ O ₃ /F-Fe ₂ O ₃	1 M KOH	2.48	0.61	7
Oxygen vacancies+Ti-Fe ₂ O ₃	1 M NaOH	2.25	1.0	8
g-C ₃ N ₄ /Ti-Fe ₂ O ₃	1 M NaOH	2.55	0.95	9
Co-Pi-B-Ti-Fe ₂ O ₃	1 M NaOH	2.61	0.90	10
FeOOH/M:B-Fe ₂ O ₃	1 M NaOH	2.35	0.835	11
Fe ₂ O ₃ :Ti/NH ₂ -MIL-101(Fe)	1 M NaOH	2.27	1.0	12
Co-MOF/Fe ₂ O ₃	1 M NaOH	2.0	0.64	13
F-Ti-Fe ₂ O ₃ /Co(salen)	1 M NaOH	3.02	0.81	This work

Table S2 Fitted parameters of the EIS spectra of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen) photoanodes under illumination.

Sample	R _{sol} ($\Omega \cdot \text{cm}^{-2}$)	R _{ss} ($\Omega \cdot \text{cm}^{-2}$)	R _t ($\Omega \cdot \text{cm}^{-2}$)
Fe ₂ O ₃	18.7	580	215
Ti-Fe ₂ O ₃	17.3	108	33.6
F-Ti-Fe ₂ O ₃	17.6	65.4	32.0
F-Ti-Fe ₂ O ₃ /Co(salen)	17.3	55.4	28.0

Table S3 Transfer time, lifetime and charge collection efficiency of photo-induced electrons obtained from CIMP/VS of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen) photoanodes

Sample	τ_d (ms)	τ_n (ms)	Charge collection efficiency (%)
Fe ₂ O ₃	0.587	4.74	87.6
Ti-Fe ₂ O ₃	0.558	5.42	89.7
F-Ti-Fe ₂ O ₃	0.467	6.15	92.4
F-Ti-Fe ₂ O ₃ /Co(salen)	0.372	6.16	94.0

Table S4 Transfer rate, recombination rate and transfer efficiency of photoinduced carriers obtained from CIMPS of Fe₂O₃, Ti-Fe₂O₃, F-Ti-Fe₂O₃ and F-Ti-Fe₂O₃/Co(salen) photoanodes

Sample	k _{tr} (s ⁻¹)	k _{re} (s ⁻¹)	η _{ct} (%)
Fe ₂ O ₃	0.26	0.60	30.0
Ti-Fe ₂ O ₃	3.59	0.92	79.6
F-Ti-Fe ₂ O ₃	4.09	0.65	86.3
F-Ti-Fe ₂ O ₃ /Co(salen)	6.02	0.75	88.9

Supplementary References

- 1 P. Peerakiatkhajohn, J.H. Yun, H. Chen, M. Lyu, T. Butburee and L. Wang, *Adv. Mater.*, 2016, **28**, 6405.
- 2 L. Wang, H. Hu, N. T. Nguyen, Y. Zhang, P. Schmuki and Y. Bi, *Nano Energy*, 2017, **35**, 171.
- 3 X. Lv, K. Nie, H. Lan, X. Li, Y. Li, X. Sun, J. Zhong and S. T. Lee, *Nano Energy*, 2017, **32**, 526.
- 4 P. Tang, H. Xie, C. Ros, L. Han, M. Biset-Peiró, Y. He, W. Kramer, A. P. Rodríguez, E. Saucedo, J. R. Galán-Mascarós, T. Andreu, J. R. Morante, J. Arbiol, *Energy Environ. Sci.*, 2017, **10**, 2124.
- 5 J. Deng, X. Lv, K. Nie, X. Lv, X. Sun and J. Zhong, *ACS Catal.*, 2017, **7**, 4062.
- 6 H. Lan, Y. Xia, K. Feng, A. Wei, Z. Kang and J. Zhong, *Appl. Catal. B Environ.*, 2019, **258**, 117962.
- 7 F. Li, J. Li, L. Gao, Y. Hu, X. Long, S. Wei, C. Wang, J. Jin and J. Ma, *J. Mater. Chem. A.*, 2018, **6**, 23478.
- 8 A. Pu, J. Deng, M. Li, J. Gao, H. Zhang, Y. Hao, J. Zhong and X. Sun, *J. Mater. Chem. A.*, 2014, **2**, 2491.
- 9 Y. Liu, F.Y. Su, Y.X. Yu and W. De Zhang, *Int. J. Hydrogen Energy*, 2016, **41**, 7270.
- 10 H. Lan, A. Wei, H. Zheng, X. Sun and J. Zhong, *Nanoscale*, 2018, **10**, 7033.
- 11 H. Ahn, K. Yoon, M. Kwak, J. Park and J. Jang, *ACS Catal.*, 2018, **8**, 11932.
- 12 Y. J. Dong, J. F. Liao, Z. C. Kong, Y. F. Xu, Z. J. Chen, H. Y. Chen, D. Bin Kuang, D. Fenske and C. Y. Su, *Appl. Catal. B Environ.*, 2018, **237**, 9.
- 13 Q. Zhang, H. Wang, Y. Dong, J. Yan, X. Ke, Q. Wu and S. Xue, *Solar Energy*, 2018, **171**, 388.