

Supporting Information

Tunable Surface Modification of Hematite Photoanode by Co(salen)-Based Cocatalyst for Boosting Photoelectrochemical Performance

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Supplementary Figures and Tables

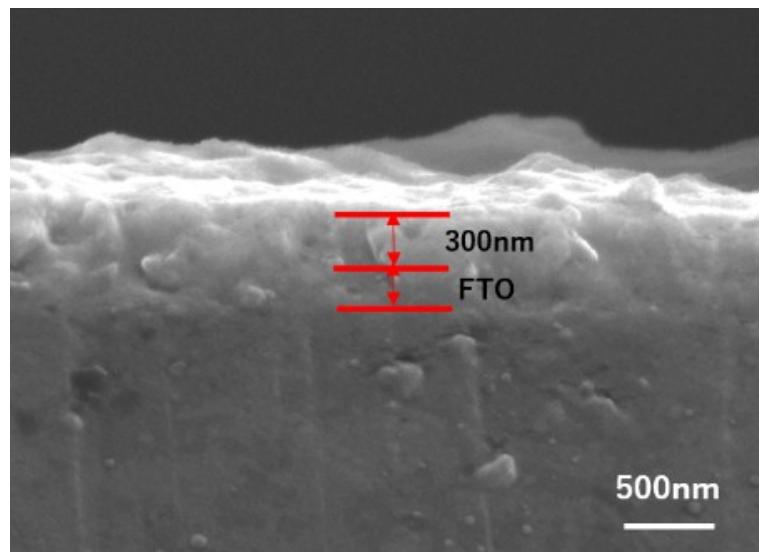


Figure S1. Cross-section FE-SEM image of $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})\text{-250}$.

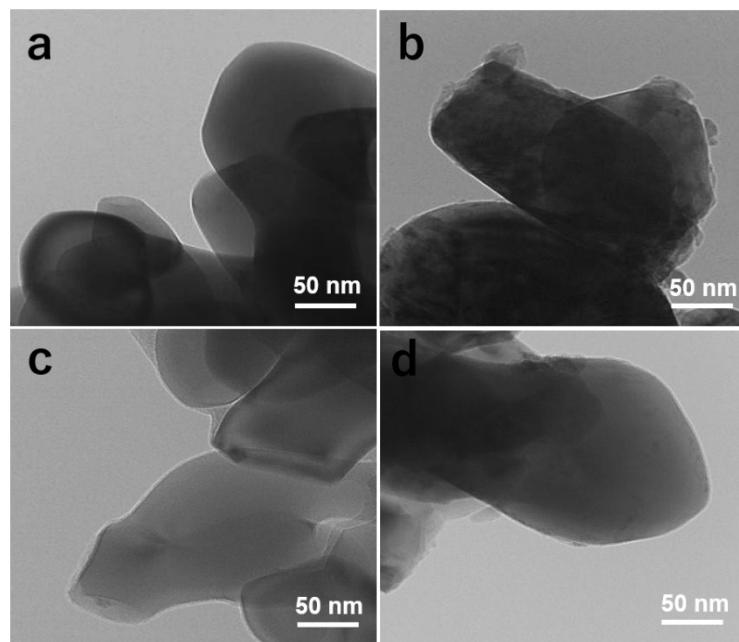


Figure S2. TEM images of (a) $\alpha\text{-Fe}_2\text{O}_3$, (b) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})\text{-250}$, (c) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})\text{-350}$ and (d) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})\text{-450}$.

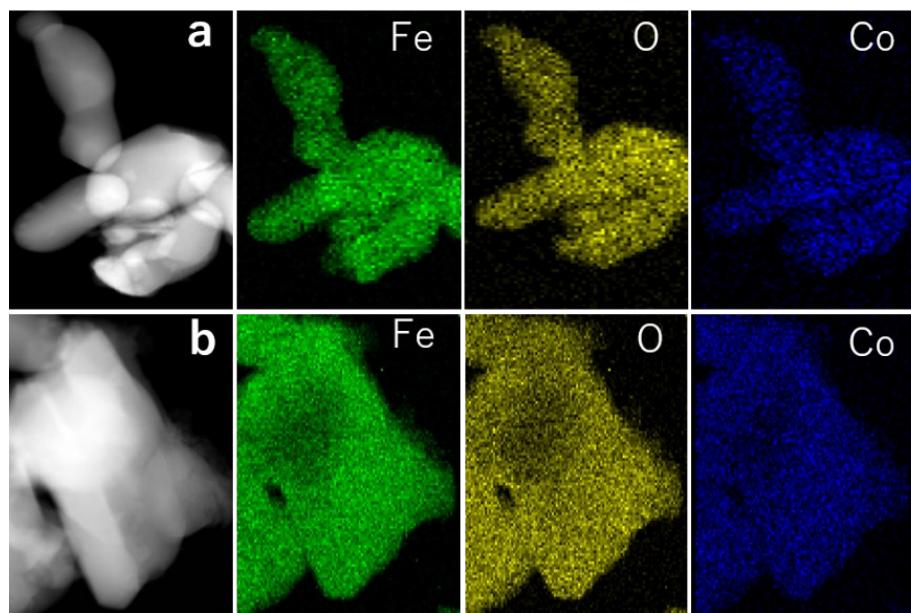


Figure S3. TEM-EDS mapping images of (a) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -250 and (b) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -350 refer to the signals of Fe, O and Co, respectively.

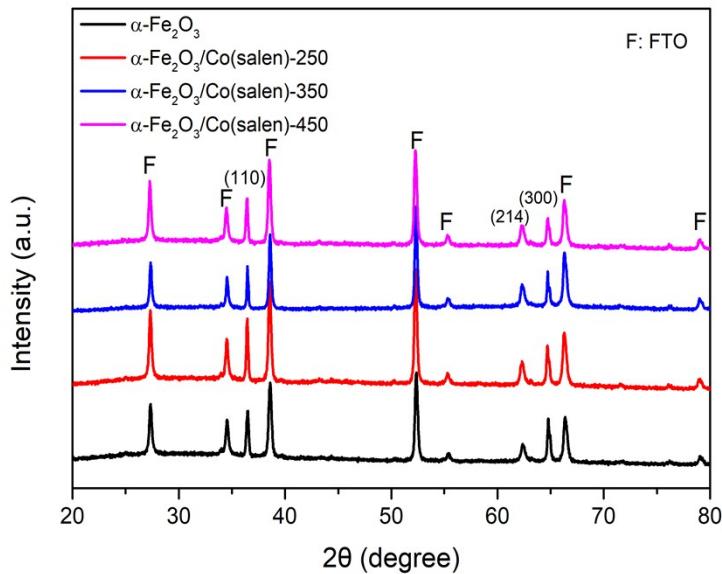


Figure S4. XRD of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -250, $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -350 and $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -450.

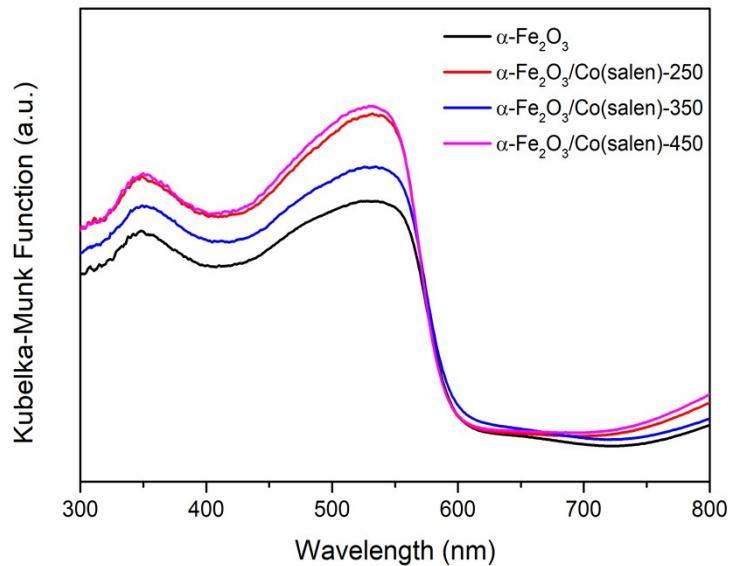


Figure S5. UV-Visible diffuse reflectance spectra of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-250}$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-350}$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-450}$.

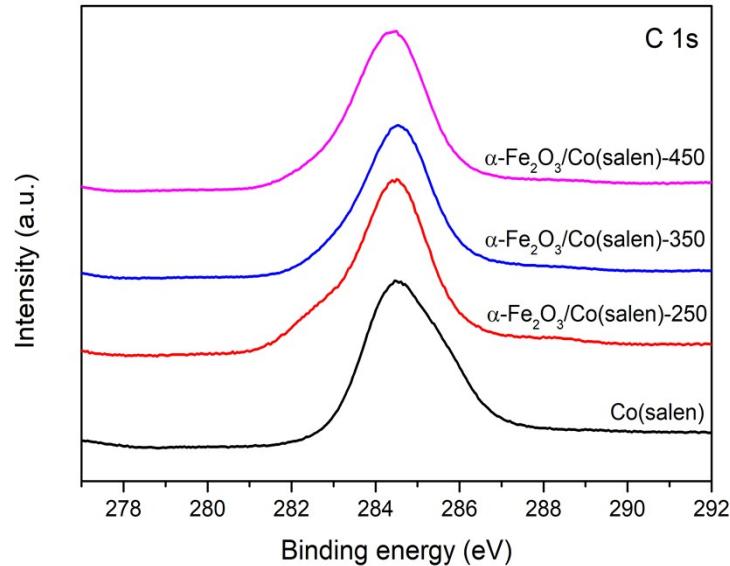


Figure S6. C 1s XPS spectra of Co(salen), $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-250}$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-350}$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-450}$.

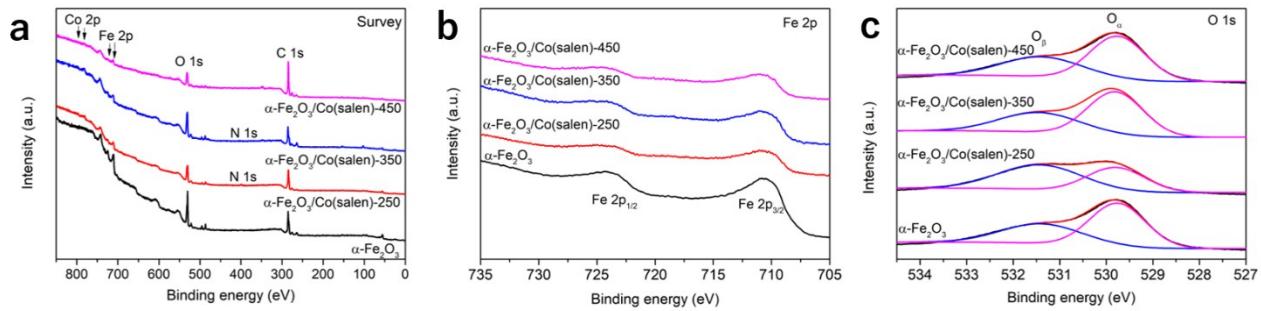


Figure S7. XPS spectra of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -250, $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -350 and $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -450. (a) The total survey spectra, (b) Fe 2p, (c) O 1s.

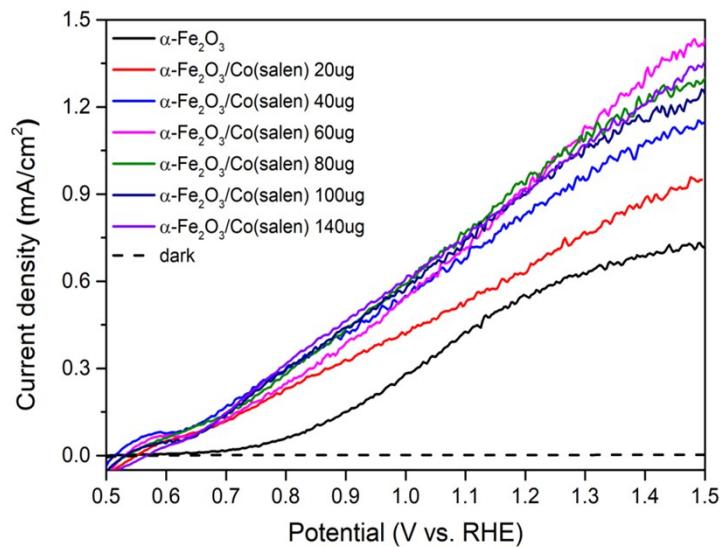


Figure S8. Photo-induced liner sweep voltammetry (LSV) curves of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})$ -250 photoanodes with different Co(salen) contents in 1 M NaOH solution under the simulated solar light source illumination (100 mW/cm²).

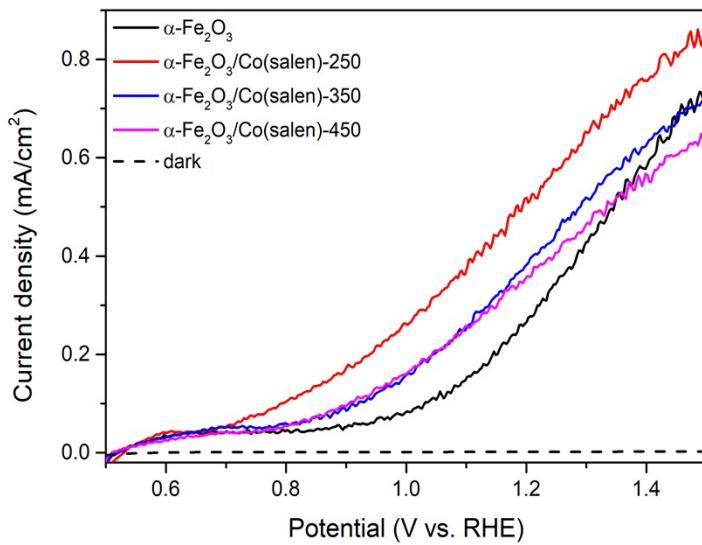


Figure S9. Photo-induced liner sweep voltammetry (LSV) curves of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-250}$, $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-350}$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-450}$ photoanodes in 1 M NaOH solution under the simulated solar light source illumination ($100 \text{ mW}/\text{cm}^2$).

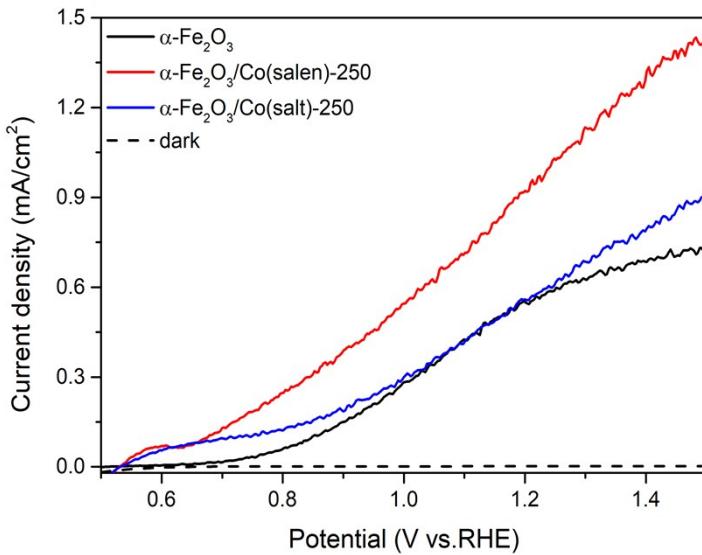


Figure S10. Photo-induced liner sweep voltammetry (LSV) curves of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salen)}\text{-250}$ and $\alpha\text{-Fe}_2\text{O}_3/\text{Co(salt)}\text{-250}$ photoanodes in 1 M NaOH solution under the simulated solar light source illumination ($100 \text{ mW}/\text{cm}^2$).

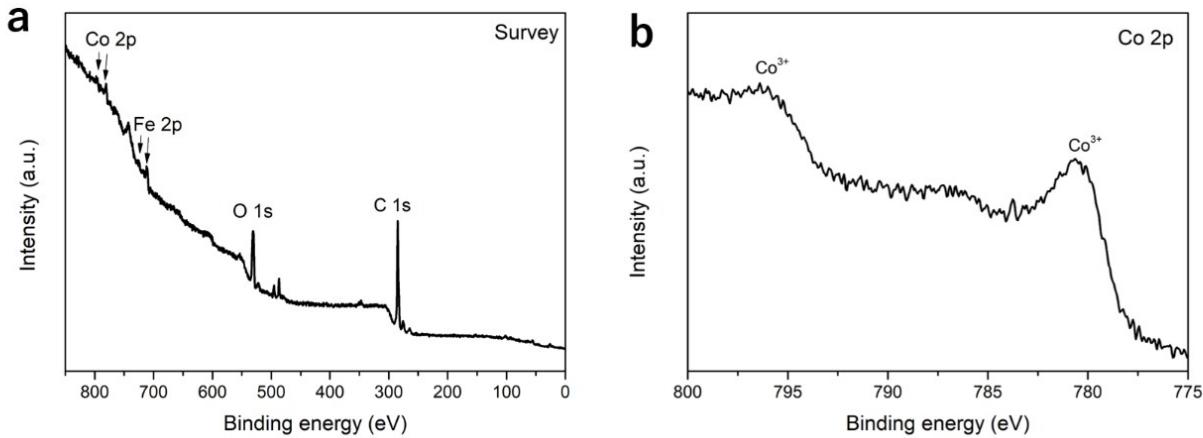


Figure S11. XPS spectra of $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salt})\text{-250}$. (a) The total survey spectra, (b) Co 2p.

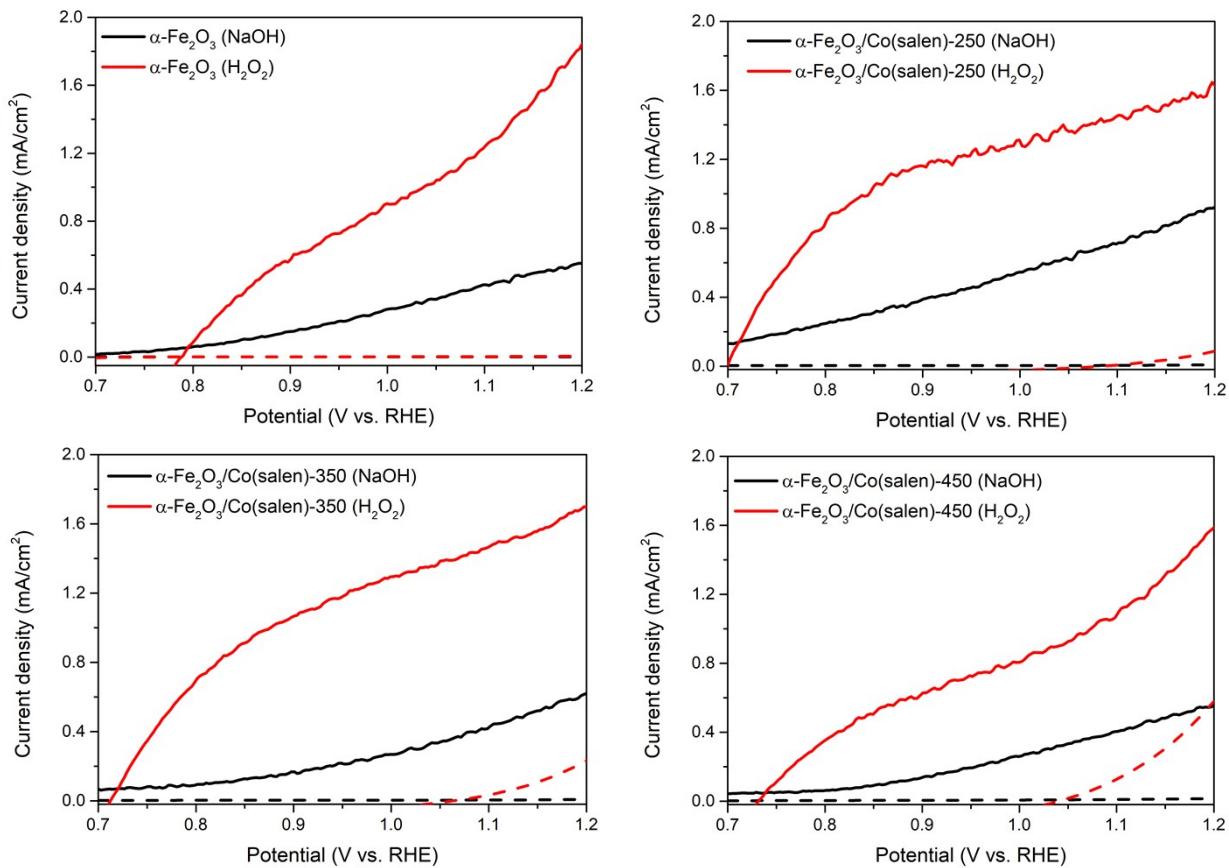


Figure S12. Photo-induced linear sweep voltammetry (LSV) curves of photoanodes in 1 M NaOH solution and 1 M NaOH with 0.5 M H_2O_2 solution under the simulated solar light source illumination (100 mW/cm^2). (a) $\alpha\text{-Fe}_2\text{O}_3$, (b) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})\text{-250}$, (c) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})\text{-350}$ and (d) $\alpha\text{-Fe}_2\text{O}_3/\text{Co}(\text{salen})\text{-450}$.

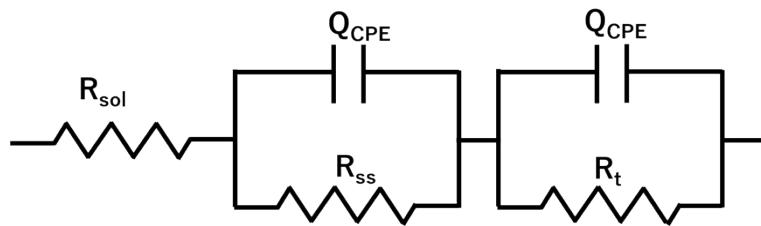


Figure S13. The equivalent circuit of EIS spectra.

Table S1. Comparison of our photoanode to other hematite photoanodes coupled Co-based cocatalysts

Catalyst	Electrolyte	J with	J without	Ratio	Onset potential	Ref.
		cocatalyst ^{a)}	cocatalyst		cathodic shift ^{b)}	
Co-N-C- Fe ₂ O ₃	1 M NaOH	0.98	0.57	1.72	180	This work
Co ₃ O ₄ - Fe ₂ O ₃	1 M NaOH	1.2	0.72	1.67	40	1
C/Co ₃ O ₄ - Fe ₂ O ₃	1 M NaOH	1.48	0.83	1.78	60	2
CoPi- Fe ₂ O ₃	1 M NaOH	1.28	0.856	1.50	100	3
CoPi- Fe ₂ O ₃	1 M NaOH	0.6	0.41	1.46	350	4
CoO _x - Fe ₂ O ₃	1 M KOH	0.65	0.25	2.6	250	5
CoO _x (POM)- Fe ₂ O ₃	1 M NaOH	2.4	1.2	2.0	100	6
CoFeO _x - Fe ₂ O ₃	1 M NaOH	1.2	0.88	1.36	200	7

a) J (mA/cm²) at 1.23 V vs. RHE under AM 1.5G 100 mW/cm²; b) Onset potential cathodic shift (mV).

Table S2. Fitted parameters of the EIS of α -Fe₂O₃, α -Fe₂O₃/Co(salen)-250, α -Fe₂O₃/Co(salen)-350 and α -Fe₂O₃/Co(salen)-450 photoanodes under dark.

Sample	R _{sol} ($\Omega \text{ cm}^{-2}$)	R _{ss} ($\Omega \text{ cm}^{-2}$)	R _t ($\Omega \text{ cm}^{-2}$)
α -Fe ₂ O ₃	19.5	87.6 k	3.08 k
α -Fe ₂ O ₃ /Co(salen)-250	23.4	24.6 k	1.32 k
α -Fe ₂ O ₃ /Co(salen)-350	20.3	13.5 k	1.25 k
α -Fe ₂ O ₃ /Co(salen)-450	18.2	13.6 k	2.16 k

Table S3. Fitted parameters of the EIS of α -Fe₂O₃, α -Fe₂O₃/Co(salen)-250, α -Fe₂O₃/Co(salen)-350 and α -Fe₂O₃/Co(salen)-450 photoanodes under irradiation.

Sample	R _{sol} ($\Omega \text{ cm}^{-2}$)	R _{ss} ($\Omega \text{ cm}^{-2}$)	R _t ($\Omega \text{ cm}^{-2}$)
α -Fe ₂ O ₃	18.9	16.6 k	57.0
α -Fe ₂ O ₃ /Co(salen)-250	20.0	317	95.3
α -Fe ₂ O ₃ /Co(salen)-350	22.3	449	67.5
α -Fe ₂ O ₃ /Co(salen)-450	19.4	445	70.5

Supplementary References

- 1 P. Zhang, T. Wang, X. Chang, L. Zhang and J. Gong, *Angew. Chem. Int. Ed.*, 2016, **55**, 5851–5855.
- 2 L. Xi, P. D. Tran, S. Y. Chiam, P. S. Bassi, W. F. Mak, H. K. Mulmudi, S. K. Batabyal, J. Barber, J. S. C. Loo and L. H. Wong, *J. Phys. Chem. C*, 2012, **116**, 13884-13889.
- 3 J. Xiao, H. Huang, Q. Huang, L. Zhao, X. Li, X. Hou and H. Chen, *J. Catal.*, 2017, **350**, 48-55.
- 4 D. K. Zhong, J. Sun, H. Inumaru and D. R. Gamelin, *J. Am. Chem. Soc.*, 2009, **131**, 6086-6087.
- 5 C. Du, J. Wang, X. Liu, J. Yang, K. Cao, Y. Wen, R. Chen and B. Shan, *Phys. Chem. Chem. Phys.*, 2017, **19**, 14178-14184.
- 6 X. Cao, Y. Wang, J. Lin and Y. Ding, *J. Mater. Chem. A*, 2019, **7**, 6294-6303.
- 7 J. Zhang, R. García-Rodríguez, P. Cameron and S. Eslava, *Energy Environ. Sci.*, 2018, **11**, 2972–2984.