

Electronic Supplementary Information

Microwave-assisted surface attachment of aluminium ions on *in-situ* diluted titanium-doped hematite photoanodes for efficient photoelectrochemical water-splitting

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Supporting experimental details

1. Preparation of without dilution titanium-doped Fe₂O₃ photoanodes by in situ hydrothermal method

In a typical procedure, a piece of cleaned FTO substrate (1 cm × 2.5 cm) is placed inside a 20 mL volume vial, containing a 10 mL aqueous solution of FeCl₃·6H₂O (150 mM; Fe) and NaNO₃ (1 M), appropriate amount of HCl to adjust the pH 1.5. Then, 1 mL of titanium diisopropoxide-bis (acetylacetonate) precursor (4 mol% of the Fe) dissolved in ethanol precursor solution is added dropwise to the resultant hydrothermal solution. Remaining, hydrothermal reaction and calcination conditions were kept similar to the one mentioned in main manuscript, the sample can then be denoted as Ti(4%):Fe₂O₃ (W/O dilution).

2. Preparation of ex situ titanium-doped Fe₂O₃ photoanodes by dip-coating method

Further, *ex situ* Ti-doped Fe₂O₃ photoanode was prepared via dip-coating method. As-prepared EtOH:FeOOH photoanode was dipped in titanium diisopropoxide-bis (acetylacetonate) ethanol based precursor solution (4 mol% of the Fe) for 2 min, as reported previously for Ti *ex situ* doping.^[1] After that, the dipped photoanode was dried and thermally quenched at same calcination condition as similar as mentioned earlier to prepare *titanium-doped* photoanodes. The as-prepared photoanode was denoted as Ti(4%):Fe₂O₃ (*ex situ*).

Tables

Table S1. XPS data, showing peak assignment, area under the curve.

Samples	Peak assign	B.E (eV)	Area
EtOH:Fe ₂ O ₃	Fe ²⁺	709.4551	78844.5
	Fe ³⁺	710.48	202557
	Fe ³⁺	712.15	320595
	Satellite (Fe ³⁺)	718.46	262556
	Fe ²⁺	723.33	112925
	Fe ³⁺	724.86	63088.6
	Fe ³⁺	726.21	178865
	Satellite (Fe ²⁺)	732.36	84147.9
Ti(4%):Fe ₂ O ₃	Fe ²⁺	709.53	79351.6
	Fe ³⁺	710.55	177724
	Fe ³⁺	712.3	227096
	Satellite (Fe ³⁺)	718.81	198971
	Fe ²⁺	723.22	51100.1
	Fe ³⁺	724.63	101269
	Fe ³⁺	726.46	94806.5
	Satellite (Fe ²⁺)	732.54	57527.9
Ti(8%):Fe ₂ O ₃	Fe ²⁺	709.52	75881.8
	Fe ³⁺	710.56	152247
	Fe ³⁺	712.3	190738
	Satellite (Fe ³⁺)	718.89	142938
	Fe ²⁺	723.16	43491.6
	Fe ³⁺	724.49	78099.8
	Fe ³⁺	726.14	78179.9
	Satellite (Fe ²⁺)	732.49	38874.1

Table S2. The EIS fitting results for (1) Ti(4%):Fe₂O₃ (W/O dilution), (2) Ti(4%):Fe₂O₃ and (3) Ti(4%):Fe₂O₃ (*ex-situ*) photoanodes.

Samples measured at 1.23 V vs. RHE	R_s (Ω)	R_1 (Ω)	CPE_1 (μ F)	R_2 (Ω)	CPE_2 (μ F)
(1)	35.72	34.41	37.05	233.8	139.5
(2)	29.25	34.36	32.91	119.0	194.8
(3)	27.77	91.94	37.23	132.6	253.9

Table S3. The EIS fitting results for (1) EtOH:Fe₂O₃, (2) Ti(4%):Fe₂O₃ and (3) Ti(8%):Fe₂O₃ photoanodes.

Samples/ parameters	R_s (Ω)	R_1 (Ω)	CPE_1 (μ F)	R_2 (Ω)	CPE_2 (μ F)
(1)	29.48	182.7	17.09	148.4	61.09
(2)	29.25	34.36	32.91	119.0	194.8
(3)	31.65	47.63	43.00	145.6	47.30

Table S4. Minimum imaginary component f_{\min} (Hz) and electron transport time in the IMPS spectra for (1) EtOH:Fe₂O₃, (2) Ti(4%):Fe₂O₃, (3) Al(5mM):Fe₂O₃ and (4) Al(5mM)/Ti(4%):Fe₂O₃ photoanodes at 1.23 V vs. RHE.

Samples	f_{\min} (Hz)	Electron transport time (μ s)
(1)	493.6	323
(2)	501.8	317
(3)	246.7	645
(4)	731.8	218

Table S5. Faradaic efficiency for hydrogen and oxygen evolution.

Sampling time	FE (%) for H ₂ evolution			FE (%) for O ₂ evolution		
	I st	II nd	Avg.	I st	II nd	Avg.
0 min	0	0	--	0	0	--
60 min	79.36	81.61	80.485	82.92	84.90	83.91
120 min	83.32	84.53	83.925	86.11	83.57	84.84
180 min	82.53	83.20	82.865	85.05	84.72	84.885
240 min	85.70	86.51	86.105	84.52	82.35	83.435
300 min	84.75	87.32	86.035	84.20	83.49	83.845

Figures

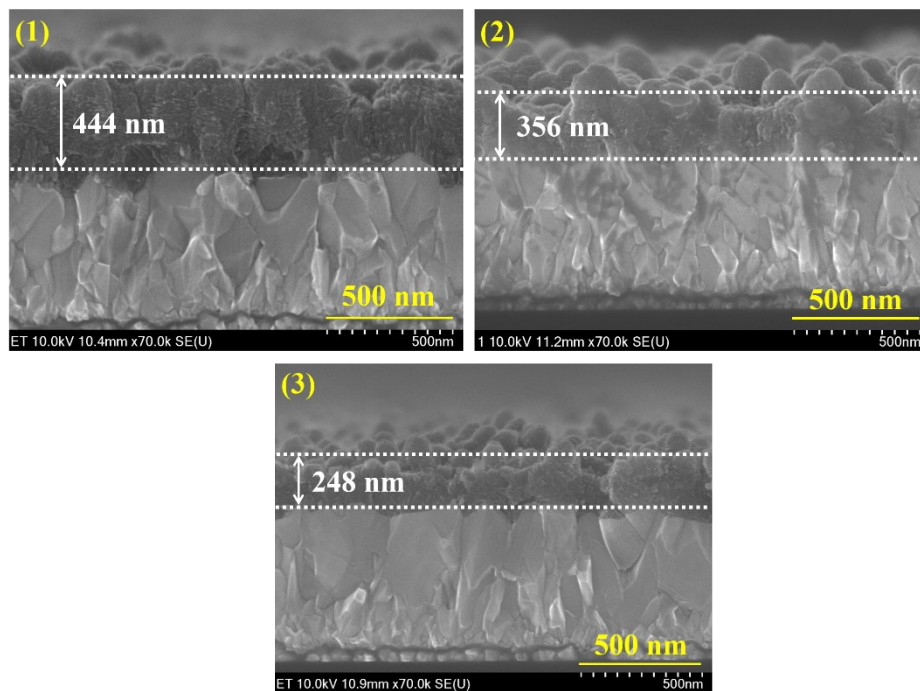


Fig. S1. HR-FESEM cross-section images of (1) EtOH:FeOOH, (2) Ti(4%):FeOOH and (3) Ti(8%):FeOOH photoanodes, respectively.

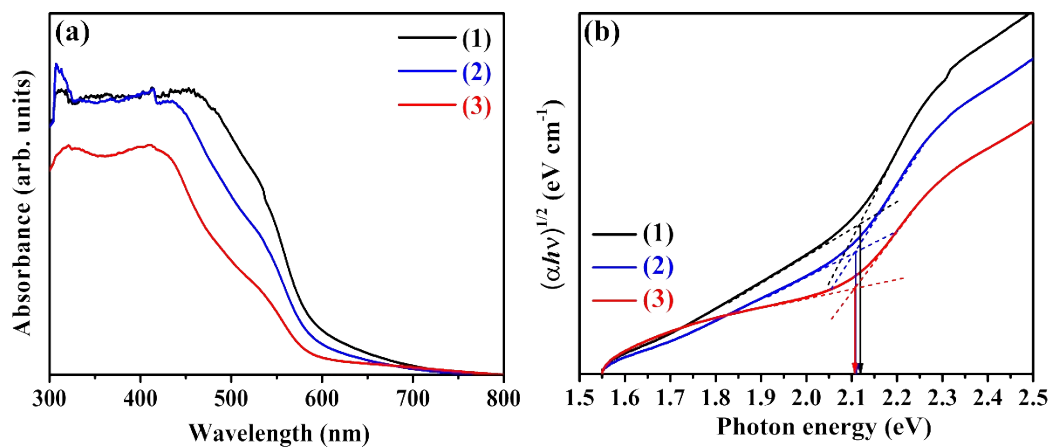


Fig. S2. (a) UV-vis-absorbance curves. (b) Tauc plot (In-direct) of (1) EtOH:Fe₂O₃, (2) Ti(4%):Fe₂O₃ and (3) Ti(8%):Fe₂O₃ photoanodes, respectively.

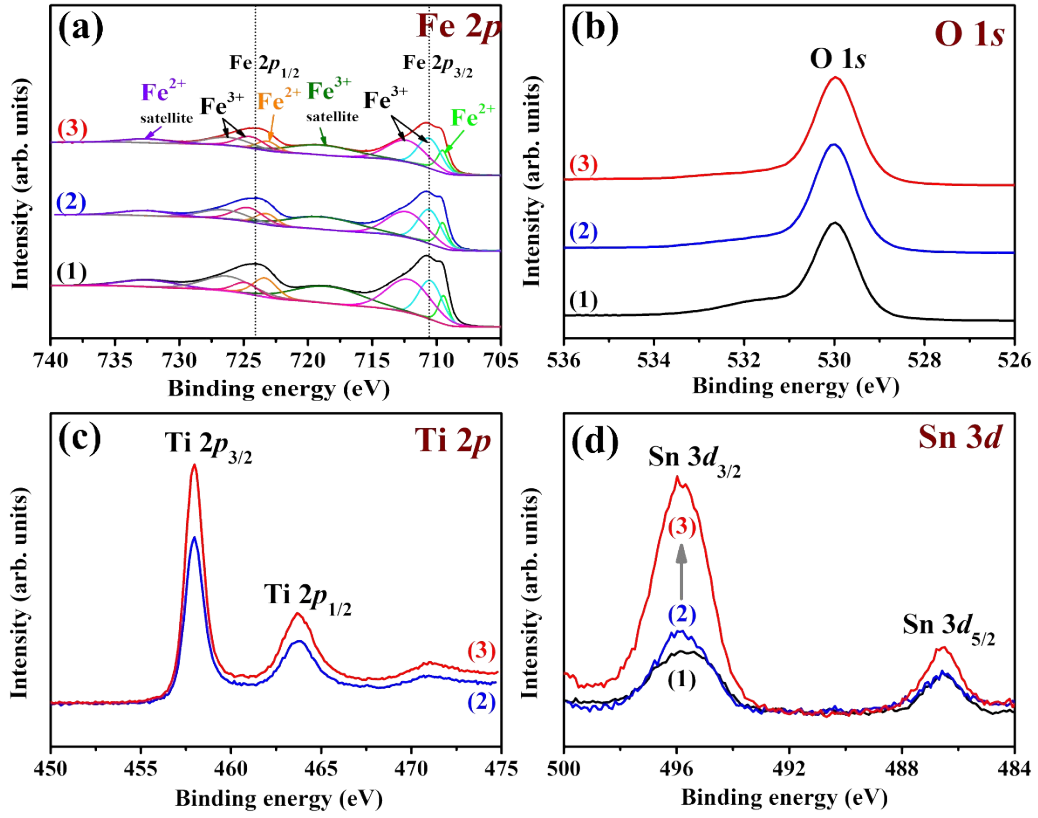


Fig. S3. XPS spectra of (1) EtOH:Fe₂O₃, (2) Ti(4%):Fe₂O₃ and (3) Ti(8%):Fe₂O₃ photoanodes with (a) Fe 2p, (b) O 1s, (c) Ti 2p and (d) Sn 3d, respectively.

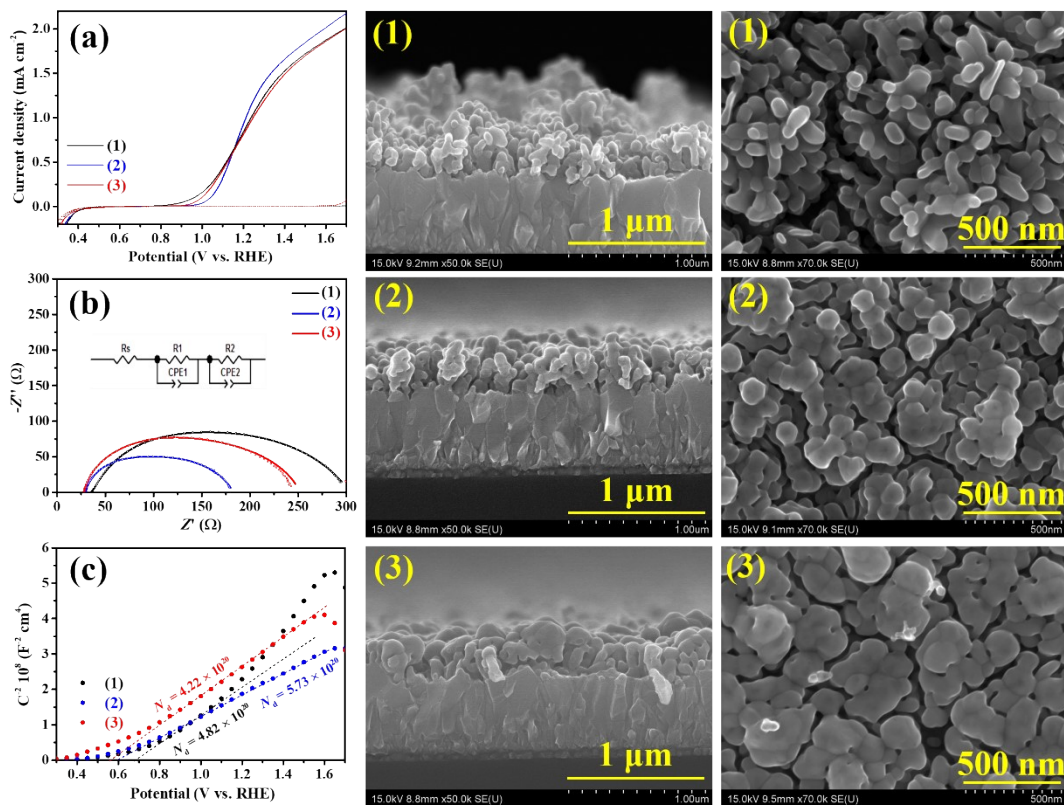


Fig. S4. (a) Photocurrent-potential ($J-V$) curves. (b) electrochemical impedance spectroscopy (EIS) Nyquist plots using 1 M NaOH electrolyte under 1 sun standard illumination conditions at 1.23 V vs. RHE. (c) Mott-Schottky plots using 1 M NaOH electrolyte under dark condition, and corresponding HR-FESEM images for (1) Ti(4%):Fe₂O₃ (W/O dilution), (2) Ti(4%):Fe₂O₃ and (3) Ti(4%):Fe₂O₃ (*ex-situ*) hematite photoanodes, respectively.

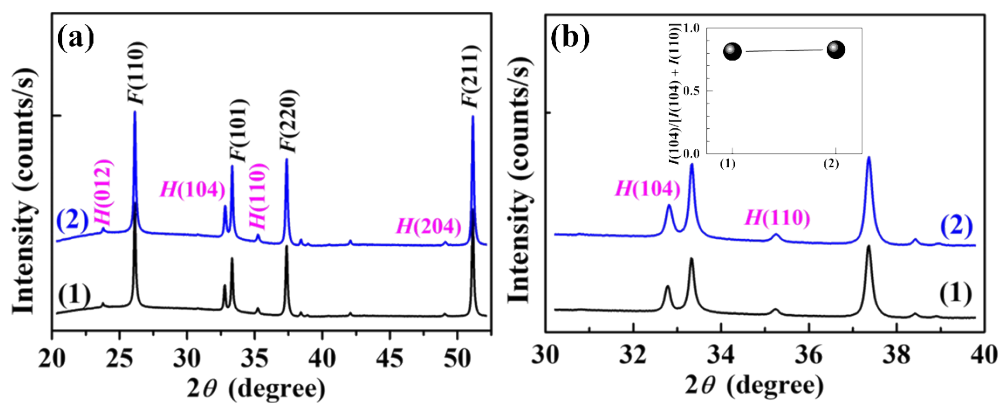


Fig. S5. (a) SR X-ray diffraction patterns and (b) XRD profiles near the (104) and (110) peaks (Inset: the (104) intensity fraction indicating its tendency of preferential orientation) of the (1) Ti(4%):Fe₂O₃ and (2) Al(5mM)/Ti(4%):Fe₂O₃ photoanodes.

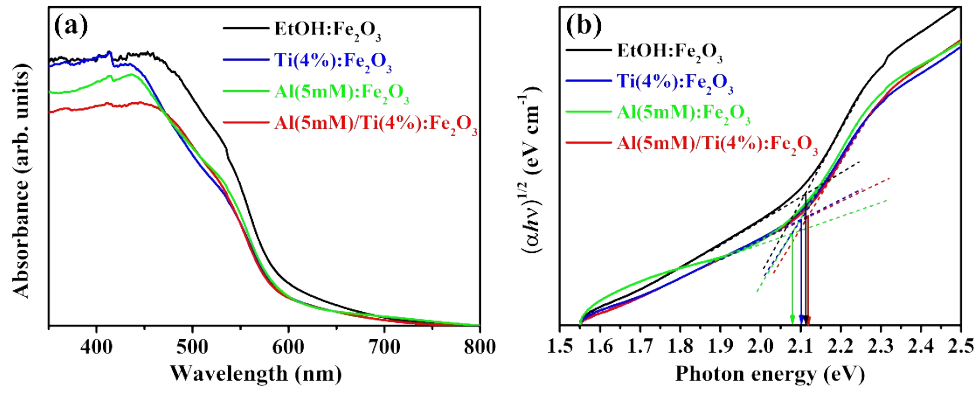


Fig. S6. (a) UV-vis-absorbance curve. (b) Tauc plot (In-direct) of EtOH:Fe₂O₃, Ti(4%):Fe₂O₃, Al(5mM):Fe₂O₃ and Al(5mM)/Ti(4%):Fe₂O₃ photoanodes.

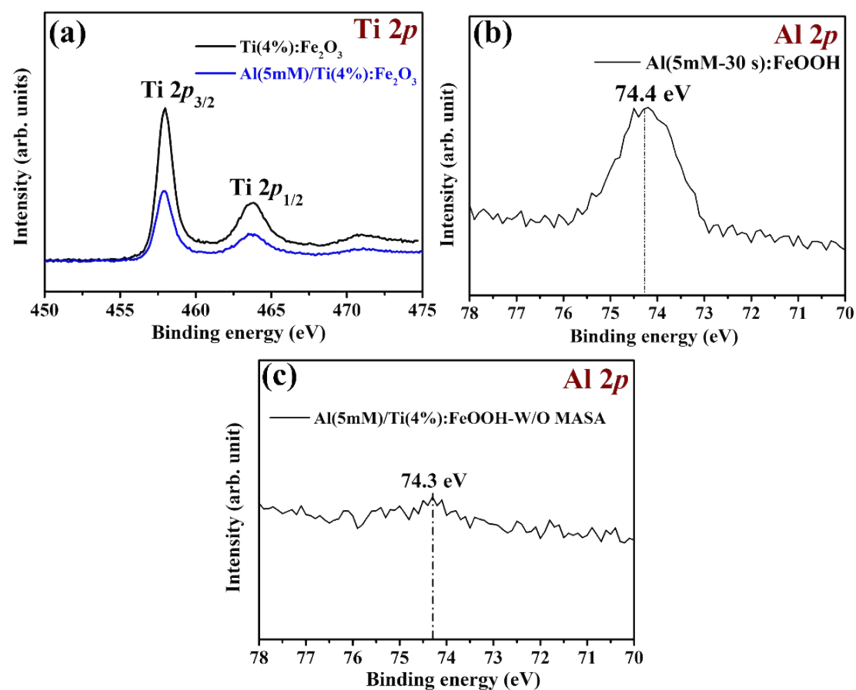


Fig. S7. (a) XPS Ti 2p spectra of Ti(4%):Fe₂O₃ and Al(5mM)/Ti(4%):Fe₂O₃ photoanodes. (b and c) XPS Al 2p spectra of Al(5mM-30 s):FeOOH and Al(5mM)/Ti(4%):FeOOH-W/O MASA, respectively.

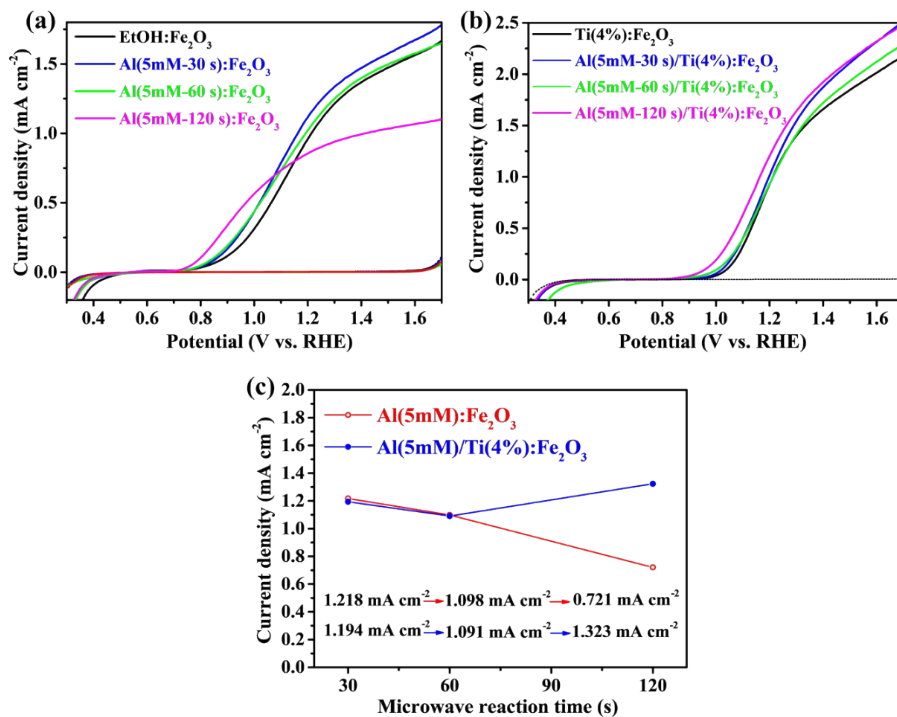


Fig. S8. Photocurrent-potential ($J-V$) curves for synthesized by different MASA time (30, 60, 120 s) on (a) Al(5mM):Fe₂O₃ and (b) Al(5mM)/Ti(4%):Fe₂O₃ using 1 M NaOH electrolyte under 1 sun standard illumination conditions. (c) Photocurrent vs. reaction time for Al(5mM):Fe₂O₃ and Al(5mM)/Ti(4%):Fe₂O₃ photoanodes, respectively.

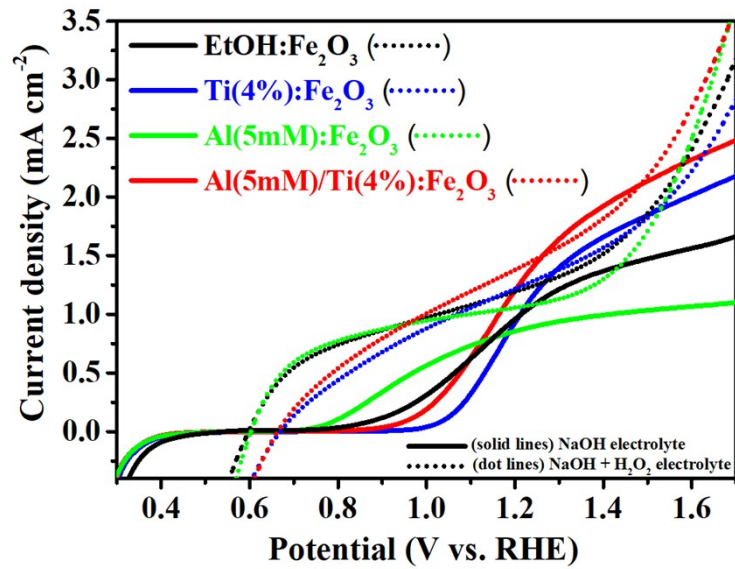


Fig. S9. (a) Photocurrent-potential (J - V) curves for EtOH:Fe₂O₃, Ti(4%):Fe₂O₃, Al(5mM):Fe₂O₃ and Al(5mM)/Ti(4%):Fe₂O₃ photoanodes with and without H₂O₂ in the electrolyte.

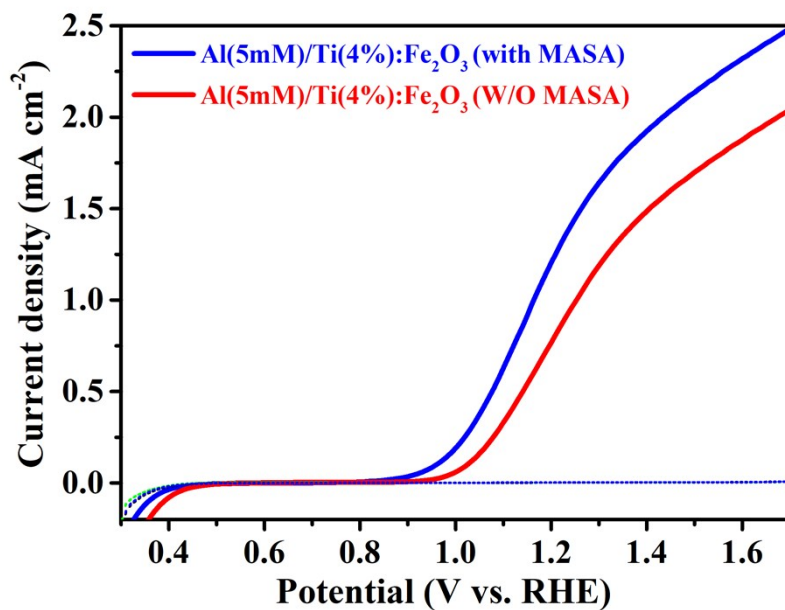


Fig. S10. Photocurrent-potential ($J-V$) curves for Al(5mM)/Ti(4%):Fe₂O₃-with MASA, Al(5mM)/Ti(4%):Fe₂O₃-W/O MASA using 1 M NaOH electrolyte under 1 sun standard illumination conditions.

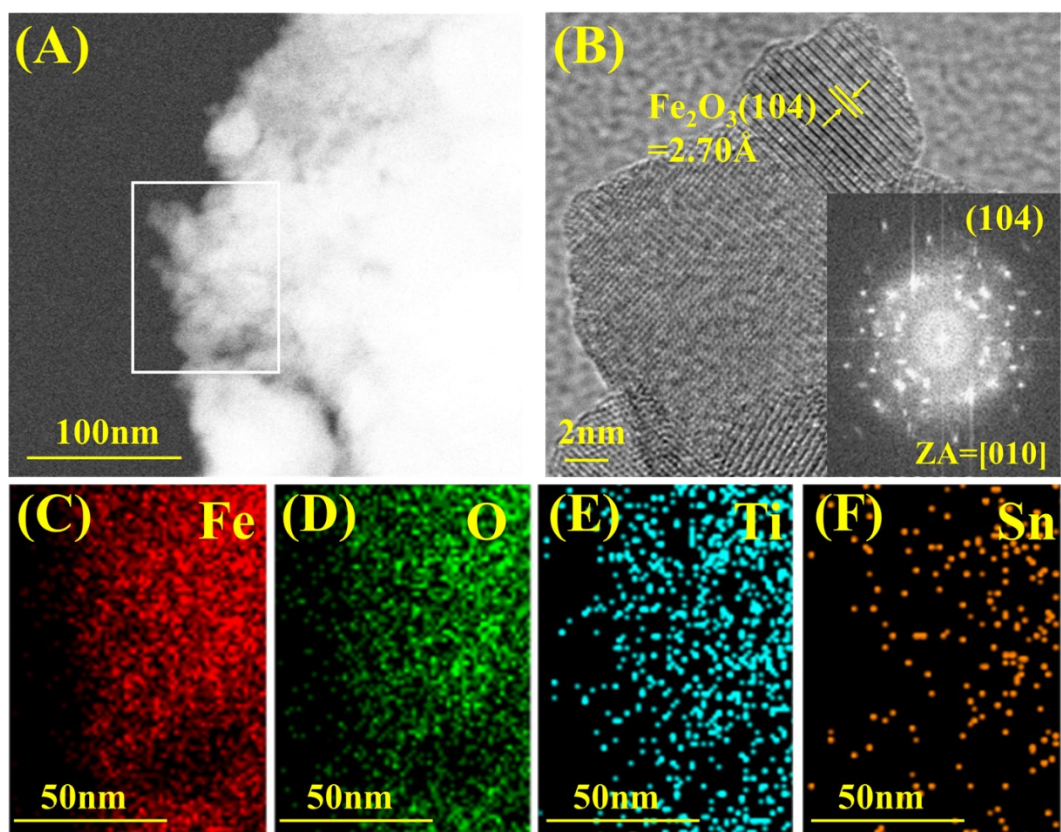


Fig. S11. (A) Low-magnification HR-TEM images, (B) ADF-STEM images and (insets) corresponding fast Fourier patterns and (C-F) EDS elemental mapping images for Ti(4%):Fe₂O₃ photoanode.

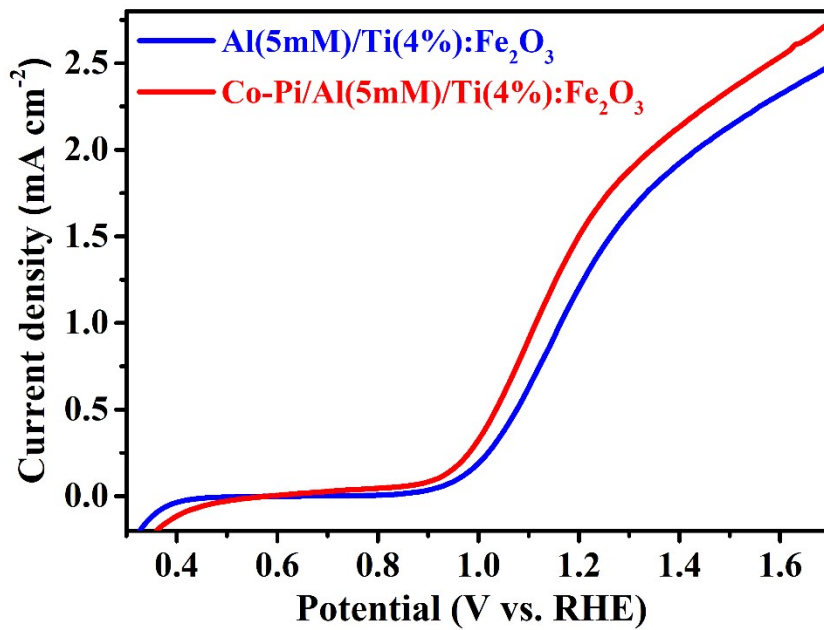


Fig. S12. Photocurrent-potential ($J-V$) curves of Al(5mM)/Ti(4%):Fe₂O₃ and Co-Pi/Al(5mM)/Ti(4%):Fe₂O₃ photoanodes using 1 M NaOH electrolyte under 1-sun standard illumination conditions.

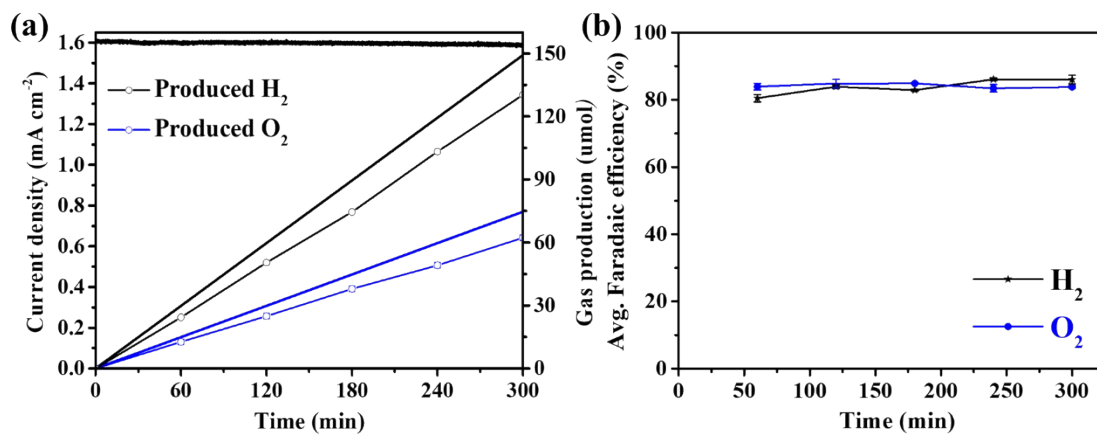


Fig. S13. (a) Photocurrent profiles and corresponding time-profiled evolution of O₂ and H₂ using Co-Pi/Al(5mM)/Ti(4%):Fe₂O₃ electrode, (solid line represents theoretical values), (b) Average faradaic efficiency under simulated solar light illumination (100 mW cm⁻²) in 1 M NaOH over Co-Pi/Al(5mM)/Ti(4%):Fe₂O₃ photoelectrode.

Reference

- [1] A. Subramanian, E. Gracia-Espino, A. Annamalai, H. H. Lee, S. Y. Lee, S. H. Choi and J. S. Jang, *Appl. Surf. Sci.*, 2018, **427**, 1203–1212.