

## Electronic Supplementary Information

### ***In situ* controllably self-assembled amorphous Co-TDPAT MOFs as superior cocatalysts of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheet arrays for highly efficient and ultrastable photoelectrochemical oxygen evolution**

Weiguang Hu <sup>a,b,c</sup>, Qinghua Xia <sup>c</sup>, Lian Ying Zhang <sup>d</sup>, Jianguo Lu <sup>e</sup>, Qinggang He <sup>b</sup>,  
Weiyong Yuan <sup>b,c,\*</sup>

<sup>a</sup> *School of Biological and Chemical Engineering, NingboTech University, Ningbo 315100, China*

<sup>b</sup> *College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China*

<sup>c</sup> *Ningbo Innovation Centre, Zhejiang University, Ningbo 315100, China*

<sup>d</sup> *College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China*

<sup>e</sup> *State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*

\* *Corresponding author. E-mail address: wyyuan@zju.edu.cn*

#### **Contents**

1. Calculation of photoconversion efficiency.
2. Calculation of donor density.
3. Calculation of Debye length.
4. Calculation of depletion layer width.
5. FESEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA before the hydrothermal reaction and after hydrothermal reactions with only H<sub>6</sub>TDPAT and with only Co<sup>2+</sup> in solution (Figure S1).
6. EDX spectrum, HADDF-STEM image, and EDS mapping images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT (Figure S2).
7. XRD pattern and enlarged XRD pattern of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA (the growth time is 60 min) (Figure S3).
8. FESEM images of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA at 80 °C, 120 °C, and 160 °C (Figure S4).
9. FESEM images of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA using Co<sup>2+</sup> concentrations of 2, 10, and 50 mM (Figure S5).
10. Linear sweep voltammograms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA, Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT (S), Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT (L) (Figure S6).

11. XRD patterns of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA for 20, 40, and 60 min (Figure S7).
12. High-resolution Co 2p XPS spectra of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA for 20, 40, and 60 min (Figure S8).
13. Photocurrent densities and maximum photoconversion efficiencies of representative FTO supported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA-based photoanodes for water splitting (Table S1).
14. Onset potentials and stability of representative FTO supported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-based photoanodes in 1 M NaOH/KOH (Table S2).
15. High-resolution Fe 2p XPS spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA before and after growth of Co-TDPAT (Figure S9).
16. Valence band and the secondary electron onset position of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT (Figure S10).
17. FESEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT before and after the stability test (Figure S11).
18. XRD patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT before and after the stability test (Figure S12).
19. High-resolution Co 2p XPS spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT before and after the stability test (Figure S13).

### 1. Calculation of photoconversion efficiency

The photoconversion efficiency of a photoanode was calculated according to the following formula [1,2]:

$$\eta\% = \frac{J(1.23 - V)}{P} \times 100$$

Where J is the current density under simulated sunlight irradiation, V is the applied voltage versus RHE, and P is the light intensity (100 mW cm<sup>-2</sup>).

### 2. Calculation of donor density

$N_d$  can be estimated from the slope of the M-S plots according to the following equation [1,3]:

$$N_d = \frac{2}{e_0 \varepsilon \varepsilon_0} \left[ \frac{d \frac{1}{C^2}}{dV} \right]^{-1}$$

where  $e_0$  is the electron charge,  $\varepsilon$  the dielectric constant of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\varepsilon_0$  the permittivity of vacuum ( $8.85 \times 10^{-12}$  N<sup>-1</sup> C<sup>2</sup> m<sup>-2</sup>).

### 3. Calculation of Debye length

The charge carrier diffusion lengths (Debye length,  $L_D$ ) for both electrodes were also calculated according to the following equation [1,4]:

$$L_D = \left( \frac{\varepsilon \varepsilon_0 k T}{e^2 N_D} \right)^{\frac{1}{2}}$$

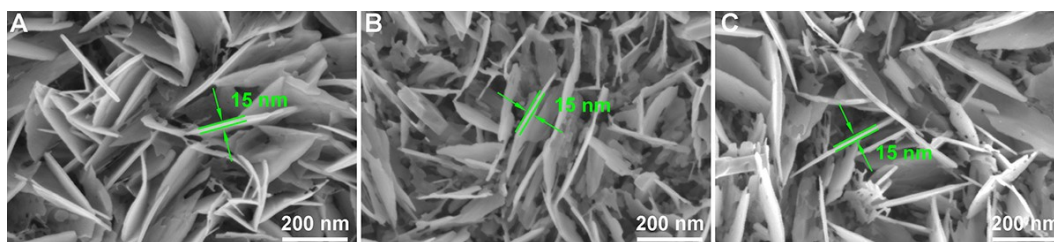
where  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J K<sup>-1</sup>) and  $T$  is the absolute temperature (K).

### 4. Calculation of depletion layer width

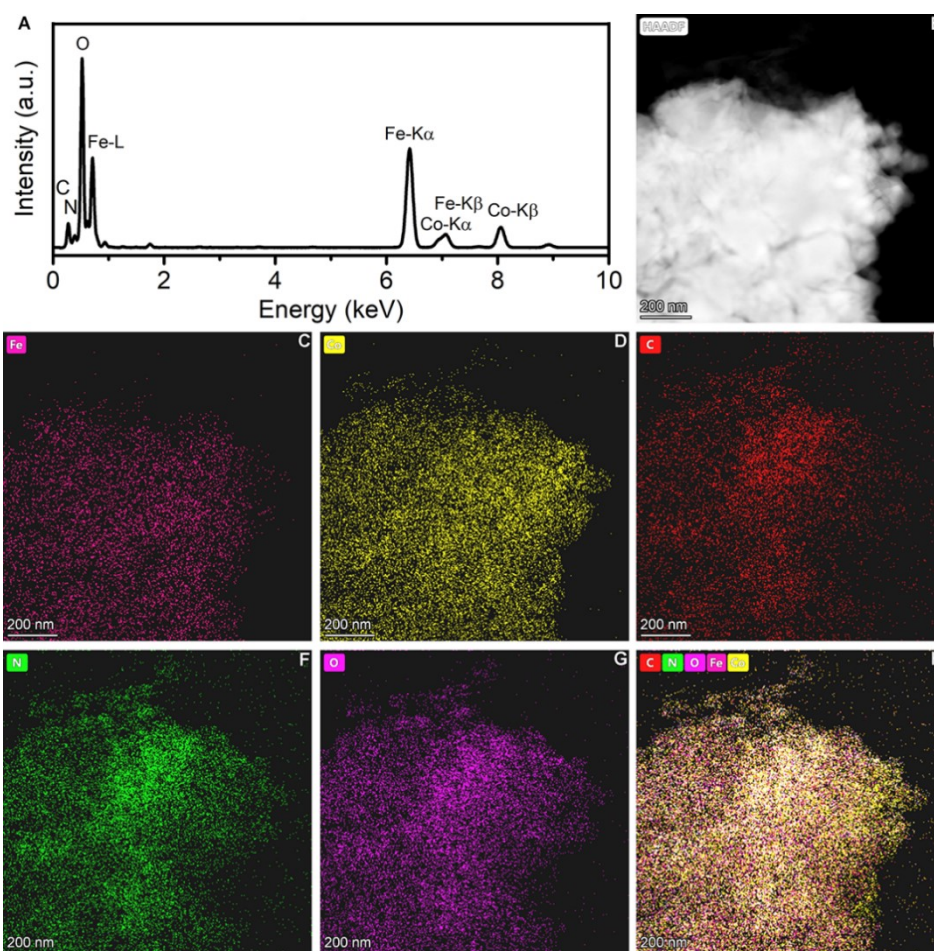
The depletion layer width ( $W$ ) at 1.0 V vs. RHE can be calculated via the following equation [1,4]:

$$W = \left( \frac{2 \varepsilon \varepsilon_0 \phi}{e^2 N_D} \right)^{\frac{1}{2}}$$

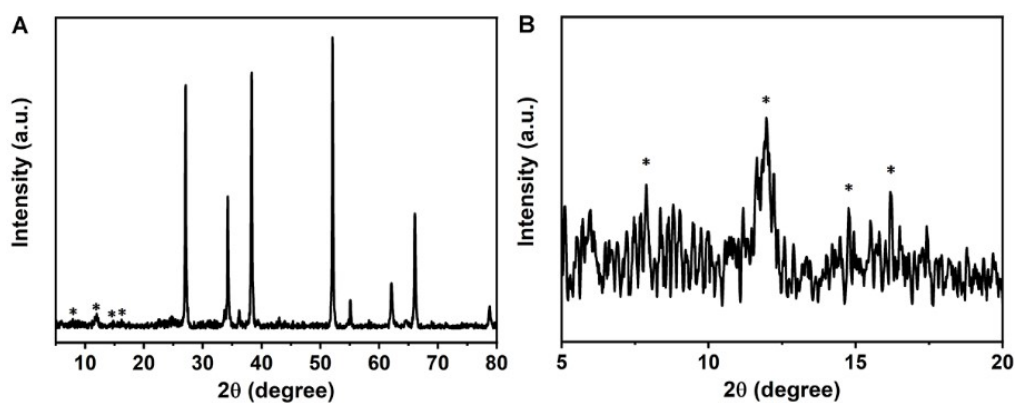
where  $\phi = V - V_{FB}$  is the maximum potential drop in the depletion layer.



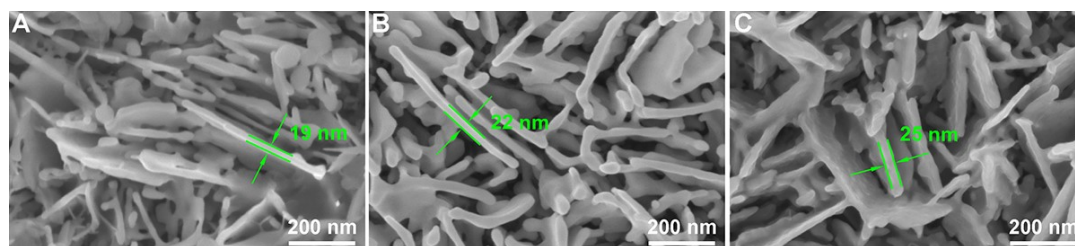
**Figure S1.** FESEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA before the hydrothermal reaction (A) and after hydrothermal reactions with only H<sub>6</sub>TDPAT (B) and with only Co<sup>2+</sup> (C) in solution.



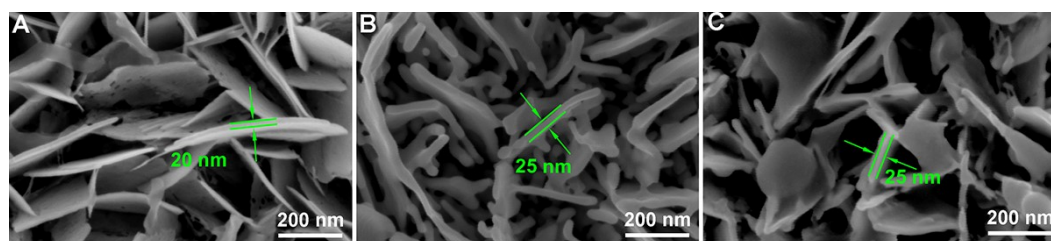
**Figure S2.** EDX spectrum (A), HADDF-STEM image (B), and EDS mapping images (C-H) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT. (C), (D), (E), (F), and (G) show the distribution of Fe, Co, C, N, and O, respectively, and (H) shows the overlapping image of C, N, O, Fe, and Co.



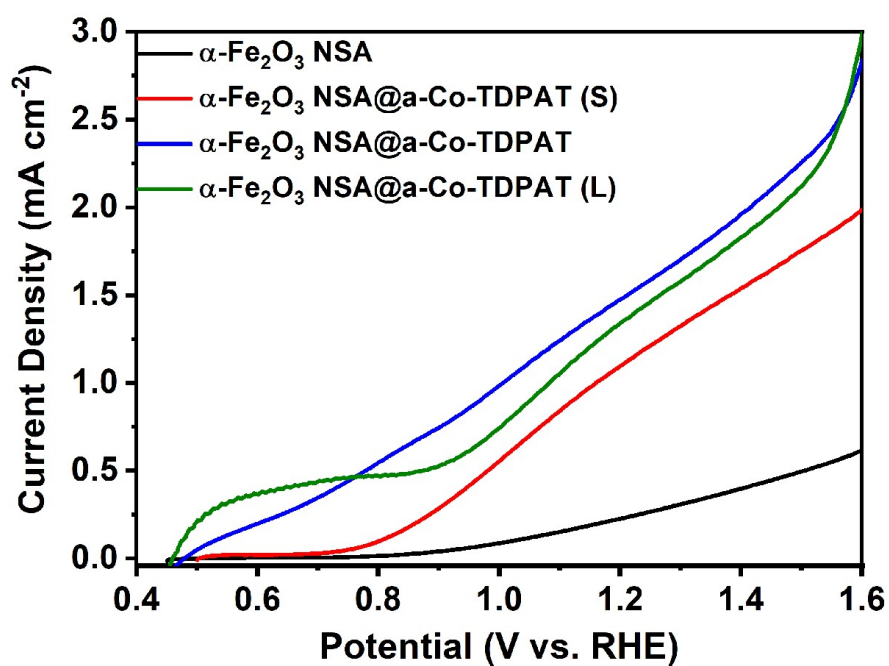
**Figure S3.** XRD pattern (A) and enlarged XRD pattern (B) of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA (the growth time is 60 min).



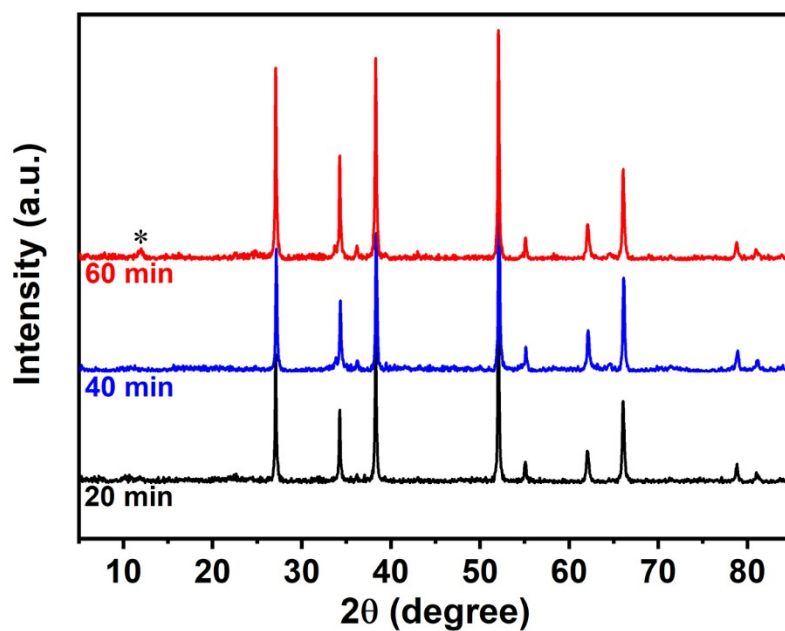
**Figure S4.** FESEM images of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA at 80 °C (A), 120 °C (B), and 160 °C (C).



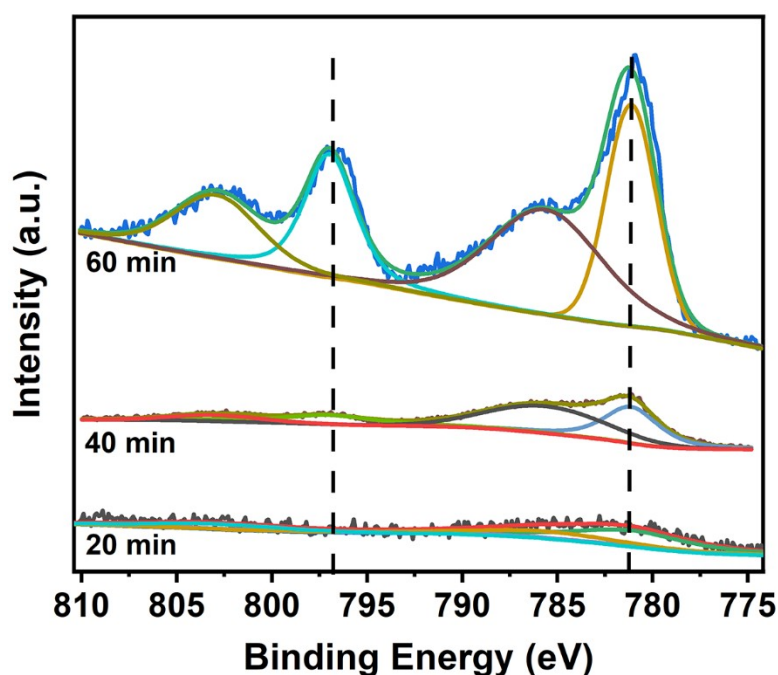
**Figure S5.** FESEM images of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA using Co<sup>2+</sup> concentrations of 2 (A), 10 (B), and 50 (C) mM.



**Figure S6.** Linear sweep voltammograms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA, Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT (S), Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT (L).



**Figure S7.** XRD patterns of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA for 20, 40, and 60 min. The peak labeled with “\*” is due to crystallization of the Co-TDPAT MOF.



**Figure S8.** High-resolution Co 2p XPS spectra of Co-TDPAT grown on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA for 20, 40, and 60 min.

**Table S1.** Photocurrent densities and maximum photoconversion efficiencies of representative FTO-supported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA-based photoanodes for water splitting in 1.0 M NaOH/KOH (Light source used: AM 1.5 G, 100 mW cm<sup>-2</sup>).

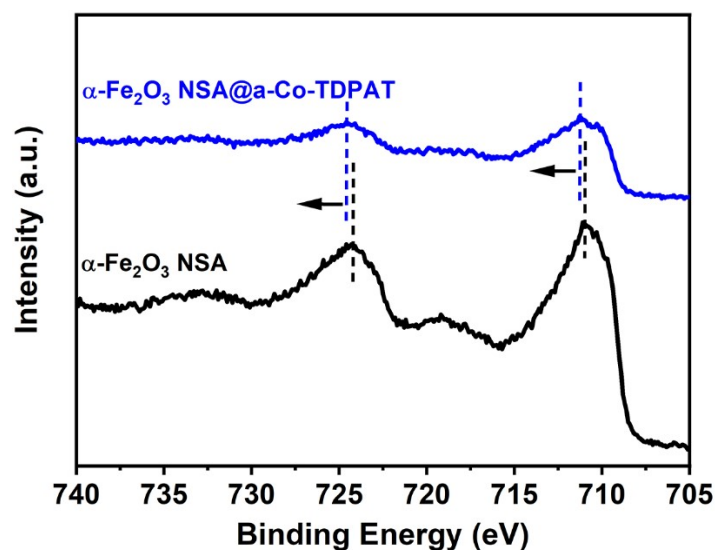
Photoanode	Photocurrent density (V vs. RHE)	Maximum photoconversion efficiency	Reference
Zr-doped $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> 16 h synthesis	0.52 (1.5V)	N.A.	5
Fe <sub>2</sub> O <sub>3</sub> nanoplates	~0.0567 (1.23)	N.A.	6
P-Fe <sub>2</sub> O <sub>3</sub>	0.78 (1.23)	0.085%	7
P-Fe <sub>2</sub> O <sub>3</sub> /Ce-Pi	1.24 (1.23)	N.A.	7
Fe <sub>2</sub> O <sub>3</sub> /C <sub>3</sub> N <sub>4</sub> /CoO <sub>x</sub>	1.50 (1.23)	0.17%	8
In treated $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.65 (1.23)	~0.055%	9
In treated $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Co-Pi	~1 (1.23)	N.A.	9
Sn-Fe <sub>2</sub> O <sub>3</sub> /CoPi	0.6 (1.23)	N.A.	10
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> NSA-Ti	0.77 (1.23)	N.A.	11
Ge-doped $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanosheet arrays (500)	1.4 (1.23)	N.A.	12
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.53 (1.23)	N.A.	13
Sn-doped hematite (5%)	1.51 (1.23)	N.A.	14
Ge-doped hematite (6%)	0.42 (1.23)	N.A.	14
2at.%Co-Fe-1 at.%Ca	0.095 (1.23)	N.A.	15

**Table S2.** Onset potentials and stability of representative FTO-supported  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-based photoanodes in 1 M NaOH/KOH (Light source used: AM 1.5 G, 100 mW cm<sup>-2</sup>).

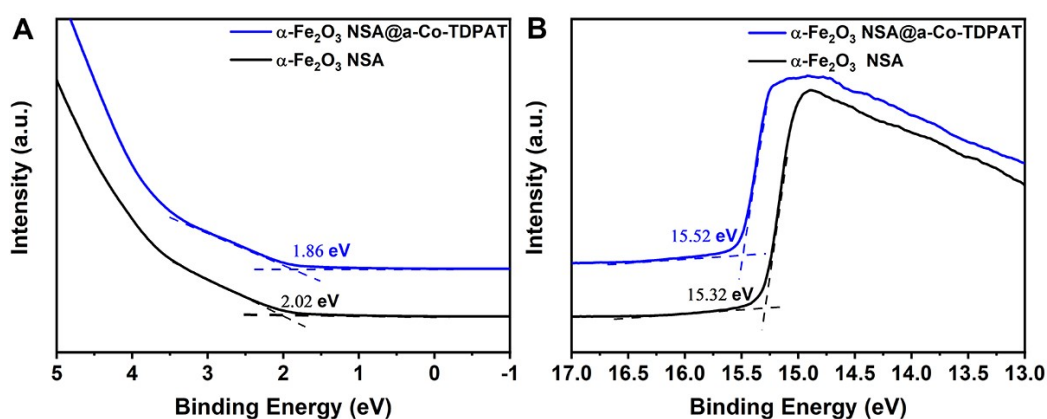
Photoanode	Onset potential (V vs. RHE)	Stability (1.23V vs. RHE)	Reference
P-Fe <sub>2</sub> O <sub>3</sub> /Ce-Pi	0.72	5.5	7
Fe <sub>2</sub> O <sub>3</sub> /C <sub>3</sub> N <sub>4</sub> /CoO <sub>x</sub>	0.62	5	8
Sn-Fe <sub>2</sub> O <sub>3</sub> /CoPi	0.65	0.167	10
Ge-doped hematite (6%)	~0.67	N.A.	14
2at.%Co-Fe-1 at.%Ca	0.6	N.A.	15
Ni-MOF/Fe <sub>2</sub> O <sub>3</sub> -24h	0.61	2	16
Cu@ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> -Vo-pn-1mM-4h	0.736	3	17
NiCo(OH) <sub>x</sub> /BCN/F	0.6	5	18
S-FeOOH@Fe <sub>2</sub> O <sub>3</sub>	0.58	5	19
0.02 M Li@ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.6	N.A.	20
Co-Pi/Co <sub>3</sub> O <sub>4</sub> /Ti:Fe <sub>2</sub> O <sub>3</sub>	0.64	0.1	21
FTO/p-Fe <sub>2</sub> O <sub>3</sub> /Fe-Pi/ZnFe <sub>2</sub> O <sub>3</sub>	0.7	N.A.	22
Ni(OH) <sub>2</sub> QDs/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.71	2	23
Fe <sub>2</sub> O <sub>3</sub> @ZIF-67-0.75	0.74	2	24
Co-Pi/Fe <sub>2</sub> O <sub>3</sub> -NaBH <sub>4</sub>	0.7	12	25
CoP/SnO <sub>2</sub> :Fe <sub>2</sub> O <sub>3</sub>	0.81	5	26
3-Si/Ti:HT	0.8	8	27
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /rGO/NiFe-LDH	0.65	2	28
Ni <sub>2</sub> P/Ta: $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.68	24	29
Pristine $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.7	N.A.	30
CoO <sub>x</sub> @C/Ti-Fe <sub>2</sub> O <sub>3</sub>	0.611	2	31
Ce-Fe <sub>2</sub> O <sub>3</sub> /ZIF-67	0.639	3	32
2h FeOOH/Fe <sub>2</sub> O <sub>3</sub>	0.582	5	33
Grey hematite	0.61	N.A.	34
WN- $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @Co <sub>3</sub> O <sub>4</sub> /GQD	0.72	2	35
Ti-Fe <sub>2</sub> O <sub>3</sub> /NiFeS <sub>x</sub>	0.79	N.A.	36
Ti <sub>1</sub> -Pt <sub>1</sub>	0.7	N.A.	37
WN- $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @Co <sub>3</sub> O <sub>4</sub>	0.62	2	38
Co-Ci/Zr-Fe <sub>2</sub> O <sub>3</sub> (LV)	0.85	20	39
Fe <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> TiO <sub>5</sub> /LDH	~0.84	20	40
Ta:Fe <sub>2</sub> O <sub>3</sub> @CaFe <sub>2</sub> O <sub>4</sub> /FeNiO <sub>x</sub>	0.63	50	41
FeCo-MOF/F	0.8	5	42
Zn-doped $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.6	2.3	43
HEDP-Fe <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> TiO <sub>5</sub> /FeNiOOH	0.64	N.A.	44
Ti-Fe <sub>2</sub> O <sub>3</sub>	~0.8	4	45
0FeP/Ti-Fe <sub>2</sub> O <sub>3</sub>	0.88	N.A.	46
FTO/TiO <sub>2</sub> /Sn@ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Co-Pi	0.71	10	47
CoOOH/Fe <sub>2</sub> O <sub>3</sub>	0.75	2	48
HfFe-NP	0.67	10	49
Co-MOF/Ti:Fe <sub>2</sub> O <sub>3</sub>	0.61	6	50
Mo/Sn codoped $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.68	N.A.	51



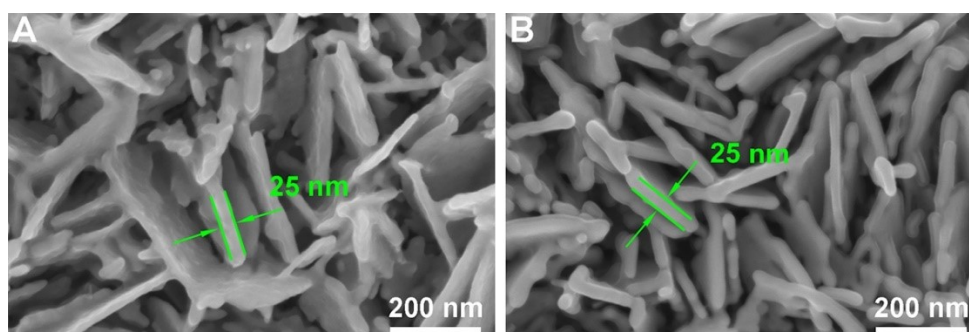
F-Ti-Fe <sub>2</sub> O <sub>3</sub> /FeNiOOH	0.57	N.A.	52
ATO-Fe <sub>2</sub> O <sub>3</sub>	~0.86	N.A.	53
NiFeO <sub>x</sub> /P,Ti-Fe <sub>2</sub> O <sub>3</sub>	~0.73	20	54
Co-Pi/MNs/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.57	20	55
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Co(salen)-250	0.6	3	56
W-Zr-Fe <sub>2</sub> O <sub>3</sub>	0.61	N.A.	57
exfLDH/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.55	N.A.	58
Co-Sil/F-Fe <sub>2</sub> O <sub>3</sub>	0.7	5	59
Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> /FeNiOOH	0.61	N.A.	60
2D SnO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	~0.65	0.083	61
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /CoPi	0.65	12	62
Ni-Bi/Ti-Fe <sub>2</sub> O <sub>3</sub>	0.85	6	63
1ZnFe-H	0.98	1	64
Fe <sub>2</sub> O <sub>3</sub> /Sn-10/NiO <sub>x</sub>	0.65	24	65
FeFx/Zr-Fe <sub>2</sub> O <sub>3</sub>	0.77	3	66
PC-Fe <sub>2</sub> O <sub>3</sub>	0.55	N.A.	67
6W-TiO <sub>2</sub> /Ti-Fe <sub>2</sub> O <sub>3</sub>	0.88	N.A.	68
Fe <sub>2</sub> O <sub>3</sub> NT-FeOOH/NiOOH	~0.66	4	69
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> -2c-Fe(II) LA	0.58	3	70
FTO/Sn@ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /NiOOH-Ar	0.71	10	71
Fe <sub>2</sub> O <sub>3</sub> -Co(OH) <sub>2</sub>	0.85	6	72
CoMo-Fe <sub>2</sub> O <sub>3</sub> (LV)	0.72	1	73
Ti-Fe <sub>2</sub> O <sub>3</sub> /In <sub>2</sub> O <sub>3</sub>	~0.8	3	74
FePO <sub>4</sub> ·2H <sub>2</sub> O	0.74	0.5	75
Hematite nanowires	0.8	N.A.	76
<b><math>\alpha</math>-Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT</b>	<b>~0.48</b>	<b>24</b>	<b>This work</b>



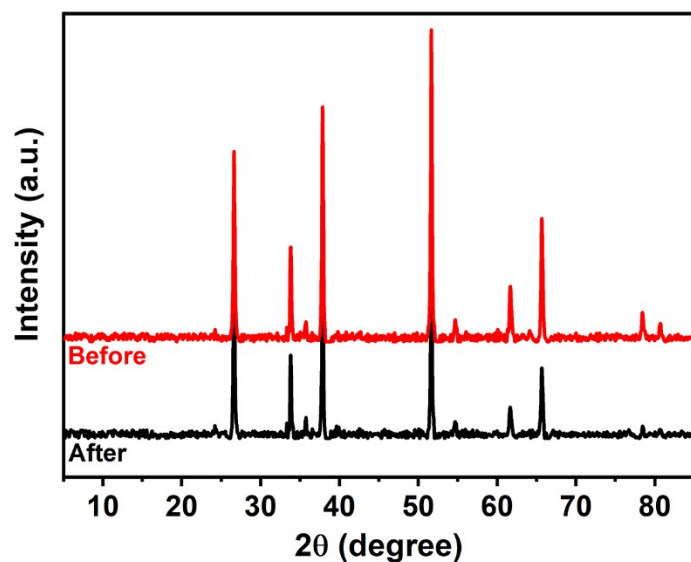
**Figure S9.** High-resolution Fe 2p XPS spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA before and after growth of Co-TDPAT.



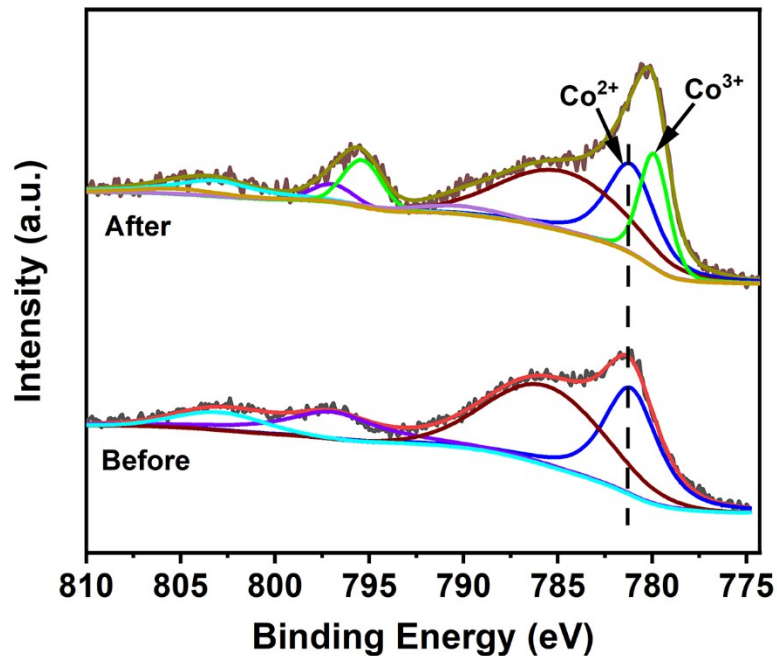
**Figure S10.** Valence band (A) and the secondary electron onset position (B) of  $\alpha\text{-Fe}_2\text{O}_3$  NSA and  $\alpha\text{-Fe}_2\text{O}_3$  NSA@a-Co-TDPAT. The valence band value of  $\alpha\text{-Fe}_2\text{O}_3$  NSA equals  $(21.2-15.32+2.02)$  eV, which is 7.9 eV and that of  $\alpha\text{-Fe}_2\text{O}_3$  NSA@a-Co-TDPAT equals  $(21.1-15.52+1.86)$  eV, which is 7.44 eV.



**Figure S11.** FESEM images of  $\alpha\text{-Fe}_2\text{O}_3$  NSA@a-Co-TDPAT before (A) and after (B) the stability test.



**Figure S12.** XRD patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT before (A) and after (B) the stability test.



**Figure S13.** High-resolution Co 2p XPS spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSA@a-Co-TDPAT before (A) and after (B) the stability test.

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