Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

A Fe-doped Co-oxide Electrocatalyst Synthesized Through Post-Modification Method Toward Advanced Water Oxidation

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Chemical reaction processes of catalysts

In a facile experiment, 0.8 mmol $Co(SO_4)_2 \cdot 7H_2O$, 0.8 mmol urea and 0.8 mmol NH_4F were dispersed in 40 mL of ultrapure water in an ultrasonication bath to form homogeneous solution. Subsequently the above solution was transferred to a Teflon-lined stainless-steel autoclave (50 mL). The whole system was sealed and then heated to 120 ℃ for 6 h. After being taken out and left to cool to room temperature, the product (i.e. Co(OH)F precursor) was washed several times with ultrapure water and ethanol, and dried at 80 ℃ overnight. Then, in a secondary hydrothermal process, 50 mg of Co(OH)F precursor synthesized before were put into a 50 mL Teflon-lined stainless-steel autoclave containing a uniform solution of a certain amount of $FeCl_3 \cdot 6H_2O$ and 40 mL of N,N-Dimethylformamide. Immediately after, the autoclaves were maintained at 100℃ for 4 h. After the reaction is complete, the products (i.e. CoFe(OH)F-α) were washed several times with ethanol by centrifugation and dried at 80 ℃. Finally, the prepared CoFe(OH)F-α were put in quartz tube and then filled the entire system with nitrogen. After a further calcination at 300 °C for 30 min, $Co_{3-x}Fe_xO_4$-α were obtained. As a control, Co(OH)F that had not been treated with $FeCl_3 \cdot 6H_2O$ was also calcined under the same conditions, which was marked as Co_3O_4 according to the XRD pattern.

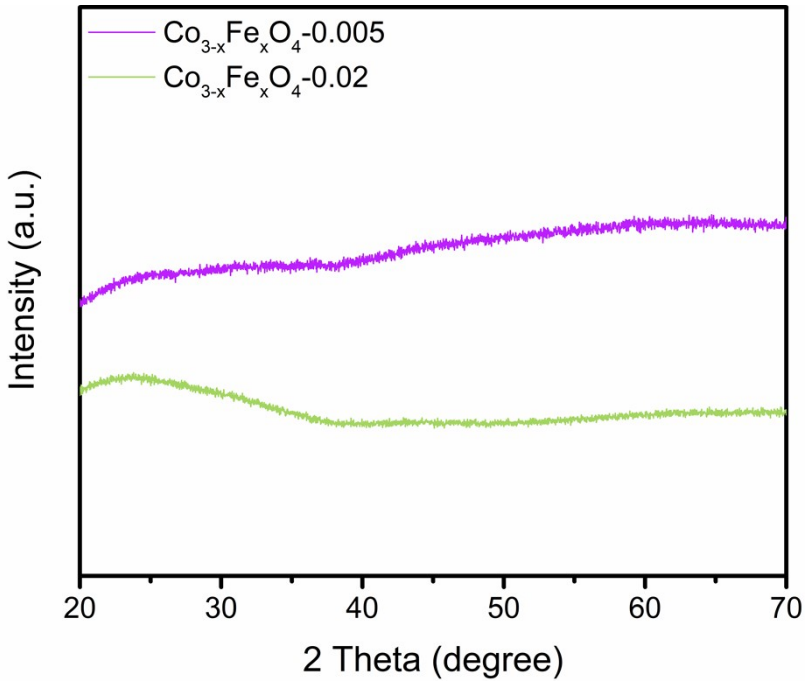

Figure S1. XRD patterns of $Co_{3-x}Fe_xO_4$-0.005 and $Co_{3-x}Fe_xO_4$-0.02.

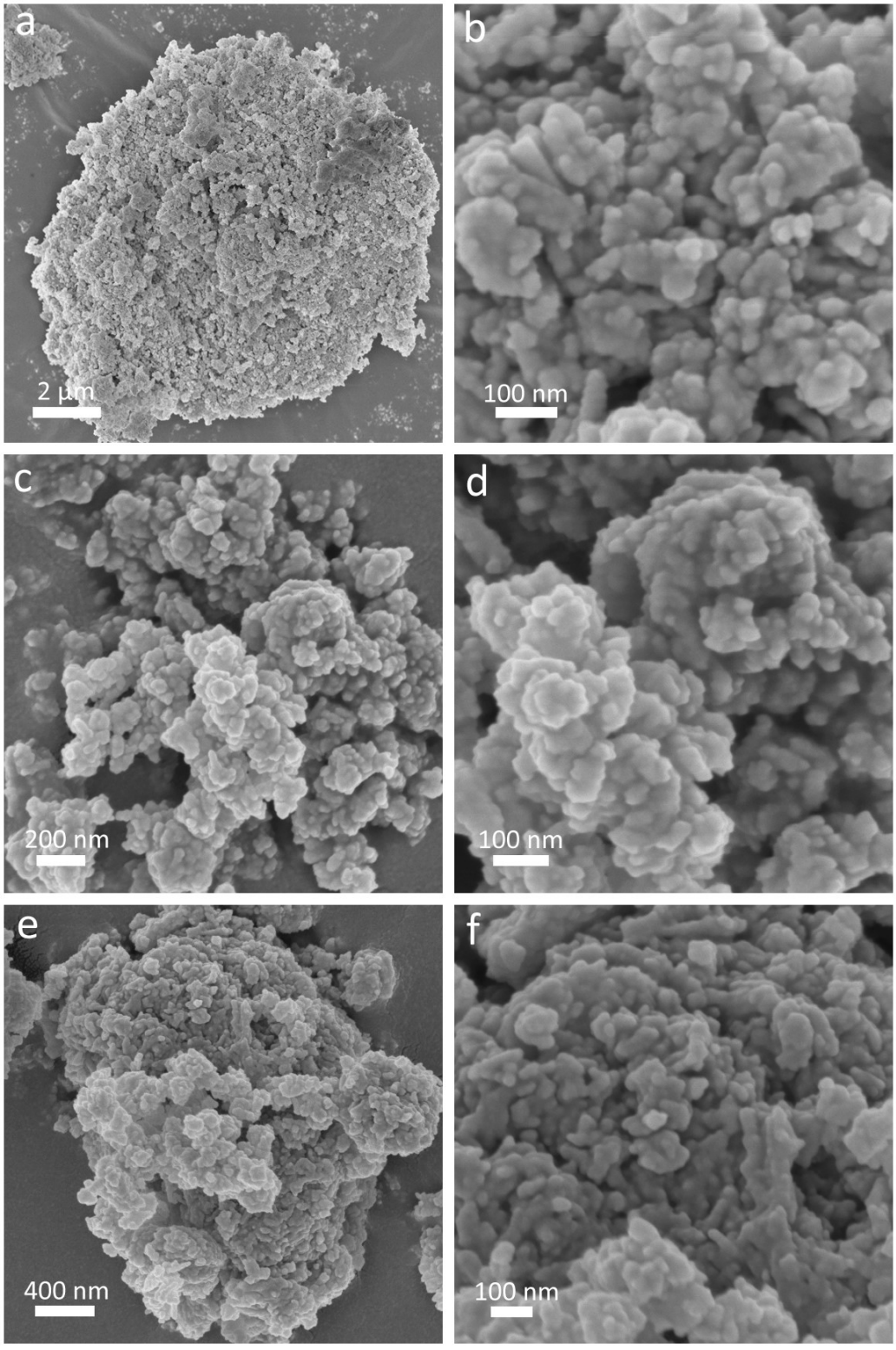

Figure S2. FESEM images of (a) and (b) CoFe(OH)F-0.005, (c) and (d) CoFe(OH)F-0.01, (e) and (f) CoFe(OH)F-0.02.

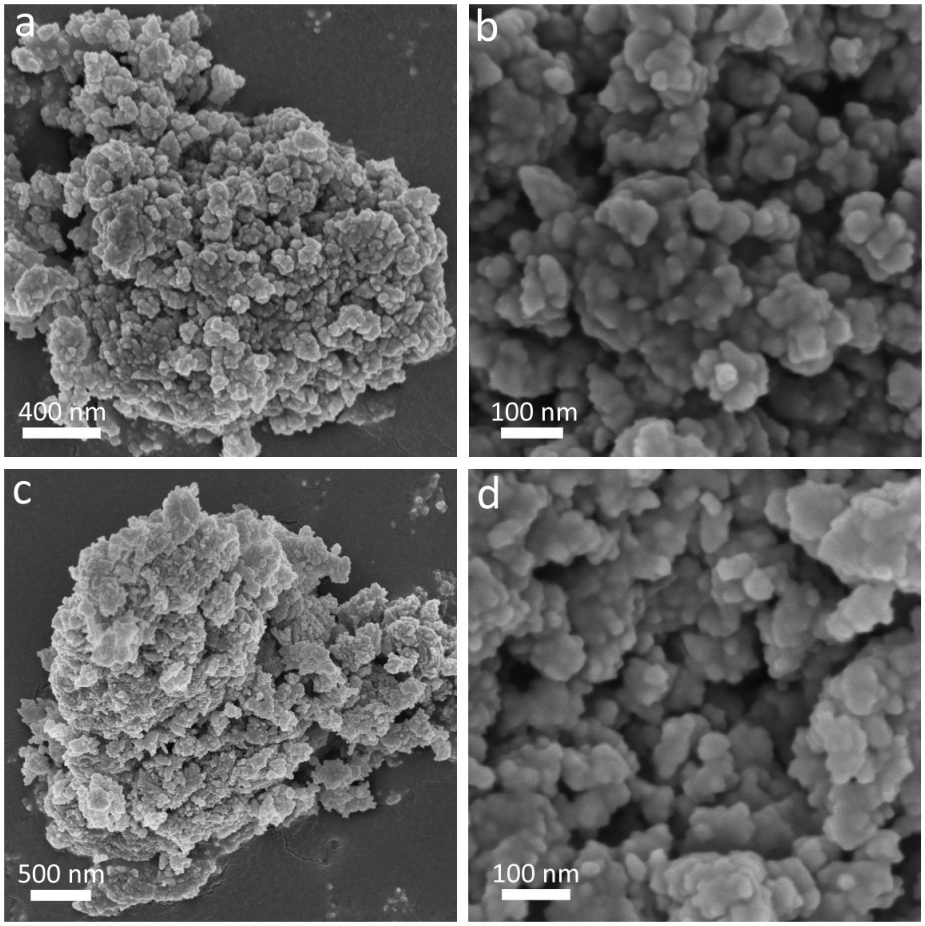

Figure S3. FESEM images of (a) and (b) $Co_{3-x}Fe_xO_4$-0.005, (c) and (d) $Co_{3-x}Fe_xO_4$-0.02.

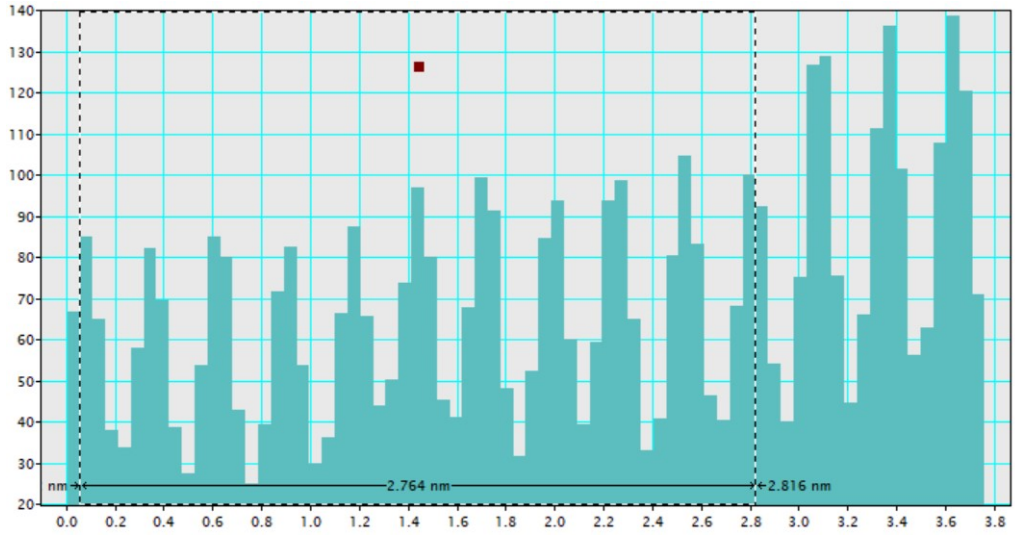

Figure S4. The corresponding crystal lattice analysis of $Co_{3-x}Fe_xO_4$-0.01.

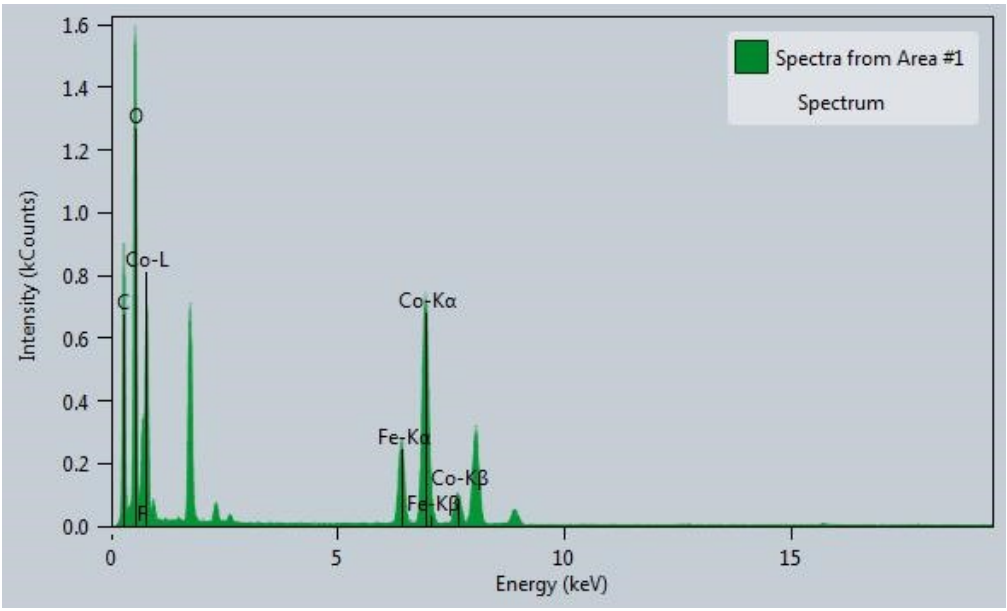

Figure S5. EDX spectrum of $Co_{3-x}Fe_xO_4$-0.01.

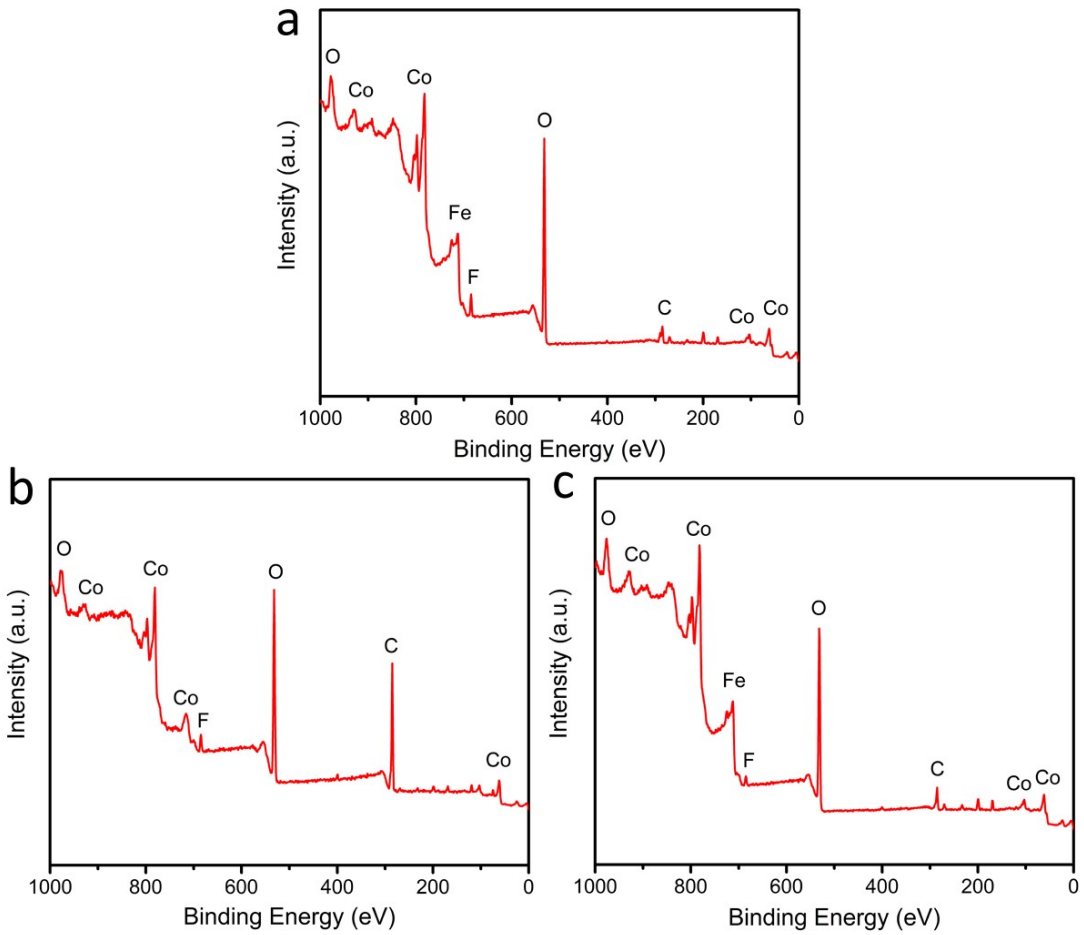

Figure S6. XPS survey spectrum of (a) CoFe(OH)F-0.01, (b) Co_3O_4 and (c) $Co_{3-x}Fe_xO_4$-0.01.

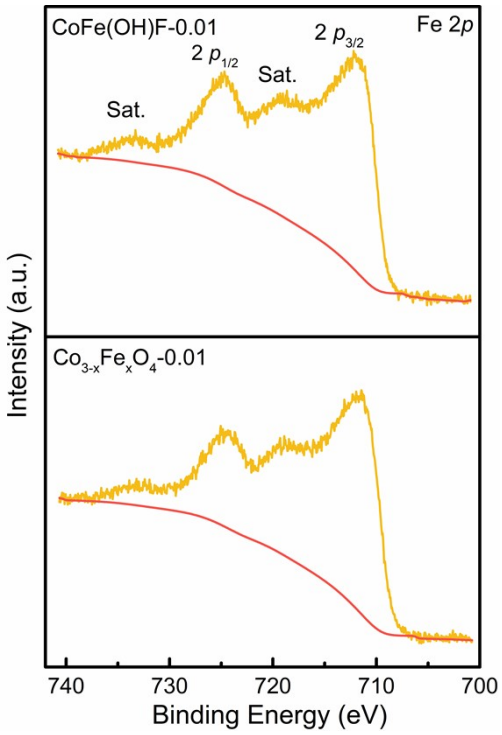

Figure S7. XPS high-resolution spectra of Fe 2*p* of (a) CoFe(OH)F-0.01 and (b) $Co_{3-x}Fe_xO_4$-0.01.

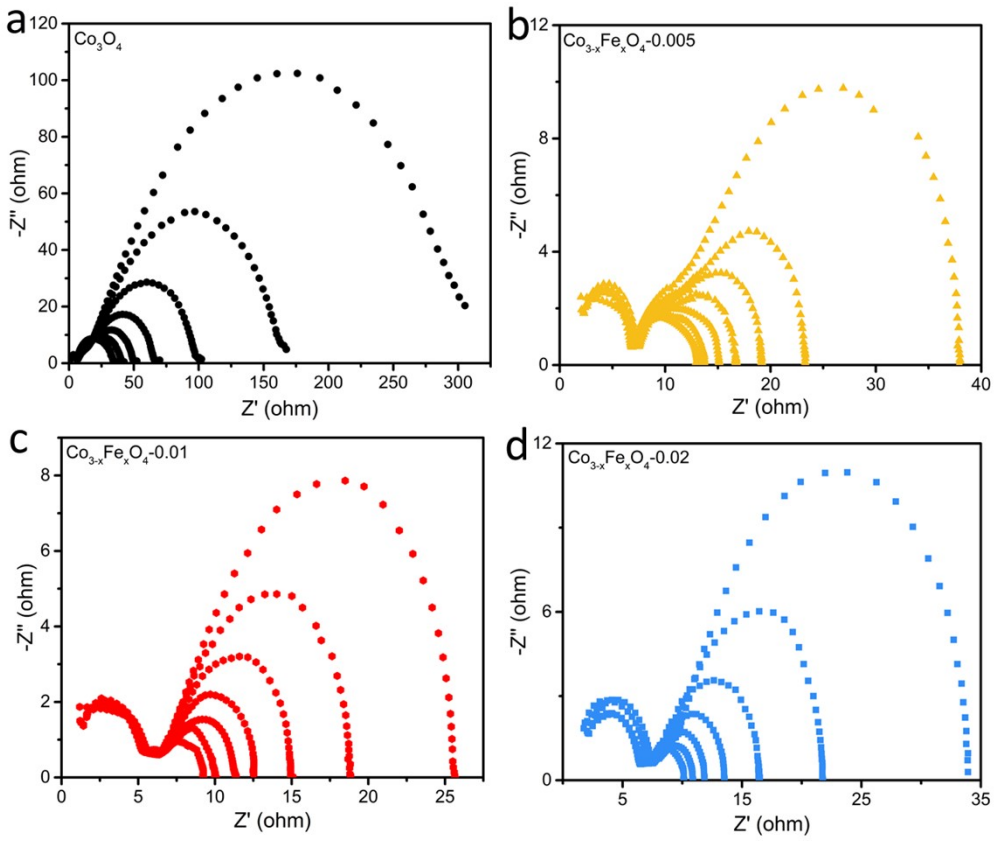

Figure S8. EIS plots at the potential from 1.52 to 1.67 V vs. RHE of (a) Co_3O_4, (b) $Co_{3-x}Fe_xO_4$-0.005, (c) $Co_{3-x}Fe_xO_4$-0.01 and (d) $Co_{3-x}Fe_xO_4$-0.02.

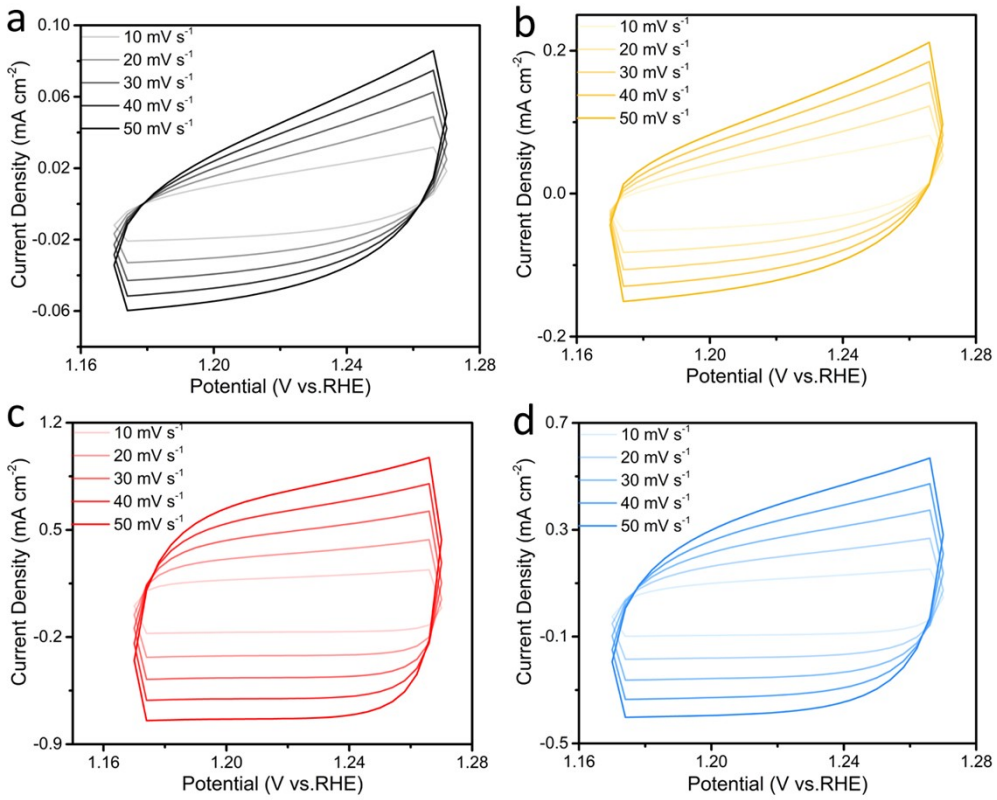

Figure S9. CV curves of (a) Co_3O_4, (b) $Co_{3-x}Fe_xO_4$-0.005, (c) $Co_{3-x}Fe_xO_4$-0.01 and (d) $Co_{3-x}Fe_xO_4$-0.02 under potential of 1.17-1.27 V vs RHE with different scan rate from 10 to 50 mV s^{-1}.

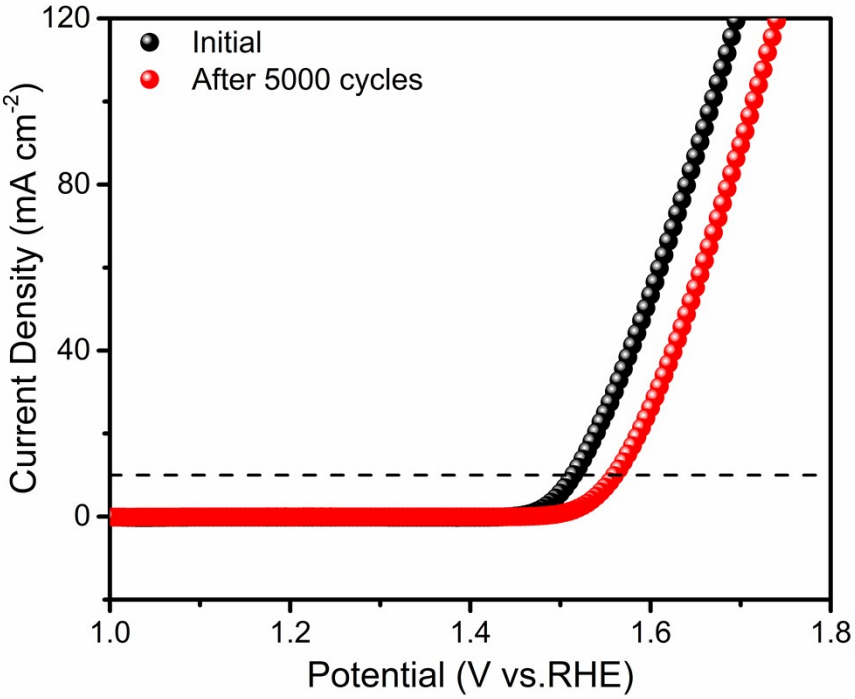

Figure S10. LSV curve of CoFe(OH)F-0.01 before and after 5000 cycles of CV.

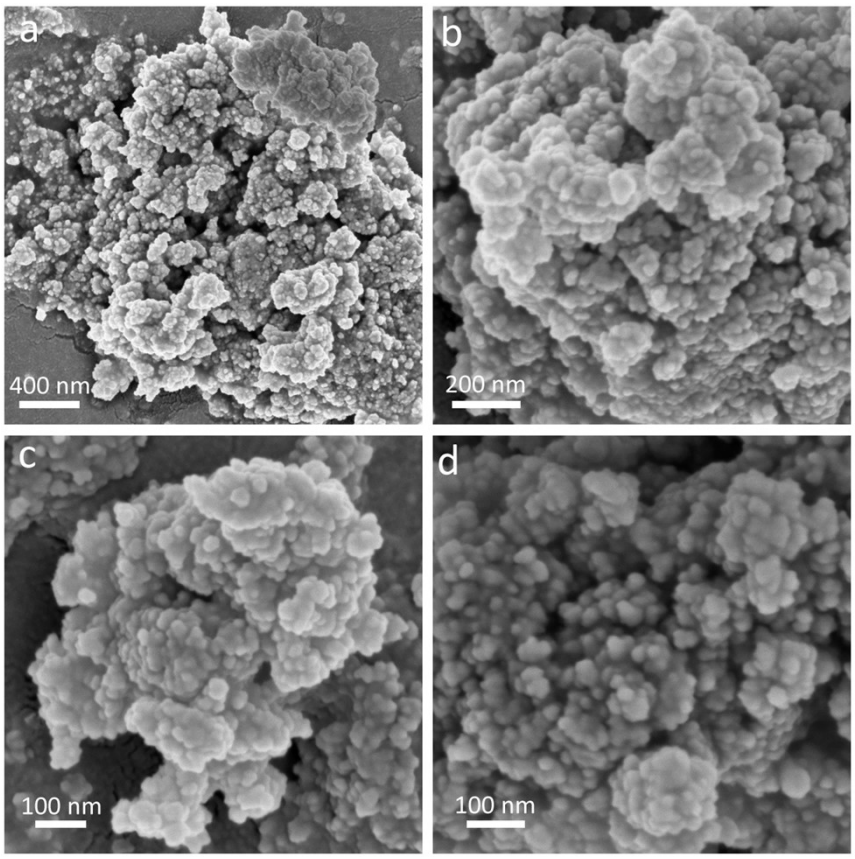

Figure S11. FESEM images of $Co_{3-x}Fe_xO_4$-0.01 after OER tests.

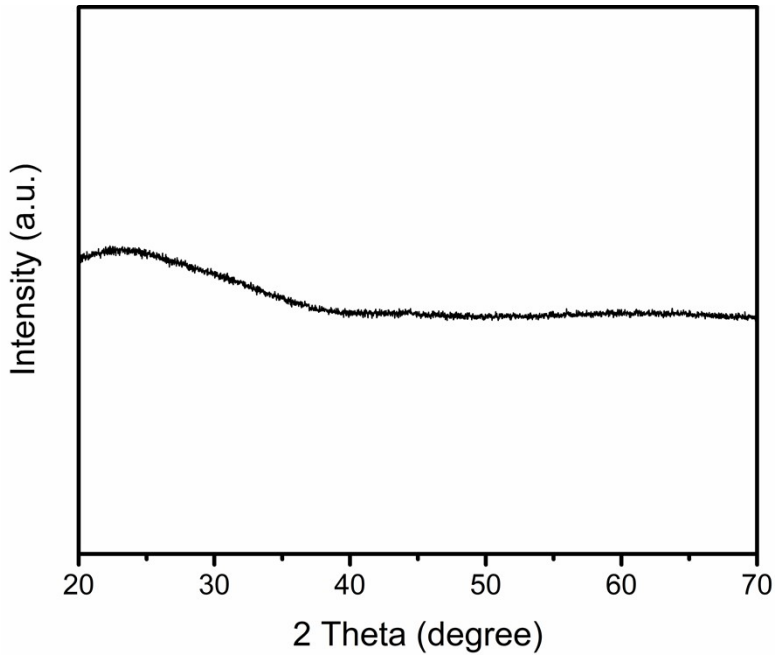

Figure S12. XRD pattern of $Co_{3-x}Fe_xO_4$-0.01 after OER tests.

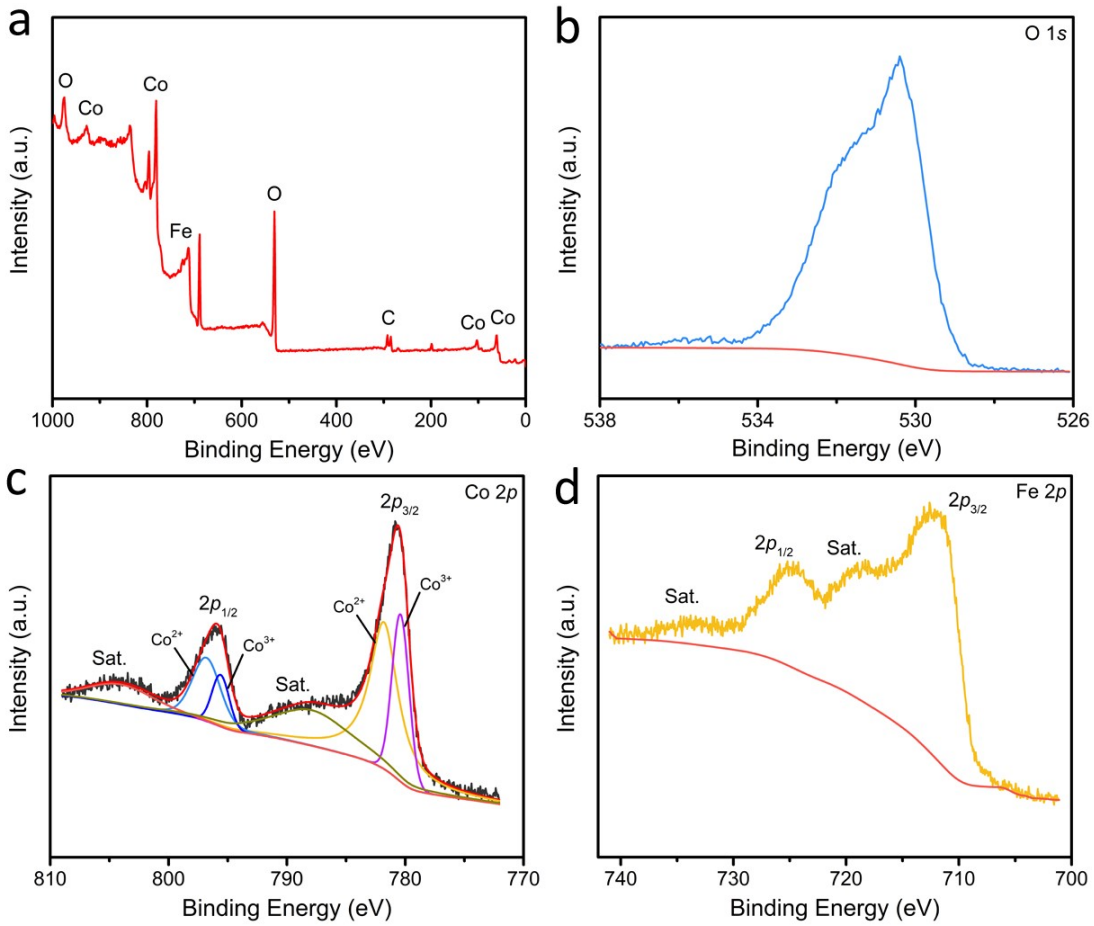

Figure S13. (a) XPS survey spectrum, XPS high-resolution spectra of (b) O 1*s*, (c) Co 2*p* and (d) Fe 2*p* of $Co_{3-x}Fe_xO_4$-0.01 after OER tests.

Table S1. Percentage of elements corresponding to EDX spectrum of $Co_{3-x}Fe_xO_4$-0.01.

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
6	C	K	39.08	5.57	20.39	1.69	2.67
8	O	K	40.56	9.93	28.19	6.08	1.77
26	Fe	K	5.24	1.01	12.70	1.96	0.17
27	Co	K	15.12	2.92	38.72	5.99	0.16

Table S2. The quantitative information of the samples of Co-O, CoFe-OH-0.01 and $Co_{3-x}Fe_xO_4$-0.01 based on the XPS results in Figure 5b.

Sample	Co^{2+} $2p_{3/2}$ (eV)	Co^{2+} (%)	Co^{3+} $2p_{3/2}$ (eV)	Co^{3+} (%)
CoFe(OH)F-0.01	781.8	77.7	780.5	22.3
Co_3O_4	781.8	67.5	780.4	32.5
$Co_{3-x}Fe_xO_4$-0.01	781.9	66.3	780.5	33.7

Table S3. Comparison of OER performance between $Co_{3-x}Fe_xO_4$-0.01 and CoFe bimetal base electrocatalysts reported in recent years.

Catalyst	Overpotential at 10 mA cm^{-2} (mV)	Tafel Slope (mV dec^{-1})	Electrolyte	Reference
$Co_{3-x}Fe_xO_4$-0.01	294	47.3	1.0 M KOH	This work
CoFe-LDH/MWCNT/rGO	430	77.73	1.0 M KOH	1
CoFe-200	316	49.6	1.0 M KOH	2
CoFe-LDH/MXene	352	50	1.0 M KOH	3
25%La-CoFe LDH	317	125	1.0 M KOH	4
CoFe–$CoFe_2O_4$/N-CNTs	334	80	1.0 M KOH	5
CoFe@N–C-700°C	292	64	1.0 M KOH	6
CoFe LDH/Co_3O_4(6:4)	290	77	1.0 M KOH	7
$CoFe(OH)_x$-2	293	67.4	1.0 M KOH	8
CoFe//LDH – pulsed 0.1	286	48	1.0 M KOH	9
CoFe-H	280	28	1.0 M KOH	10
CoFe@NC-700	380	110	0.1 M KOH	11
CoFe/Co_8FeS_8/CNT	290	38	1.0 M KOH	12
CoFe@HNSs	371	69.5	0.1 M KOH	13
NPMC/CoFe	310	50.6	1.0 M KOH	14
CoFe-PYZ	300	44	0.1 M KOH	15
CoFe@N-CNWF	320	71.4	1.0 M KOH	16
CoFe LDH-F	300	40	1.0 M KOH	17
CoFe@N-C/MNGF	330	130.6	0.1 M KOH	18
CoFe-Co@PNC-12	320	82	0.1 M KOH	19
CoFeP NSs	305	49.6	1.0 M KOH	20

Reference

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