Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Facile synthesis of multiphases cobalt-iron spinel with enriched oxygen vacancies for bifunctional oxygen electrocatalyst

Jianan Zhang,[a] Luyu Ji, [a] Junbo Gong [a] and Zhao Wang*[a]

Experimental Section

Preparation of CoO_x/C-D, CoO_x/C-C catalysts. The preparation of the precursor was similar to the description in the article. Specifically, $Fe(NO_3)_3 \cdot 9H_2O$ was replaced by $Co(NO_3)_2 \cdot 6H_2O$, and a total of 0.004 mol $Co(NO_3)_2 \cdot 6H_2O$ (1.16 g) was dissolved in the deionized water. And the subsequent process (the cold plasma and calcination methods) was same with the previous work. The catalysts were designed as CoO_x/C-D and CoO_x/C-C, respectively.

Information about the cold plasma method. Dielectric barrier discharge plasma was used in our cold plasma method. The plasma power was from Corona. lab (CTR-2000K). Before processing the samples in the reactor, made sure to put the same mass of precursor in the reactor (200 mg), which was sufficiently grinding. DBD plasma method was a gentle treatment, and the temperature in the reactor was displayed by an infrared camera, which was below 50 °C (Fig. S3).

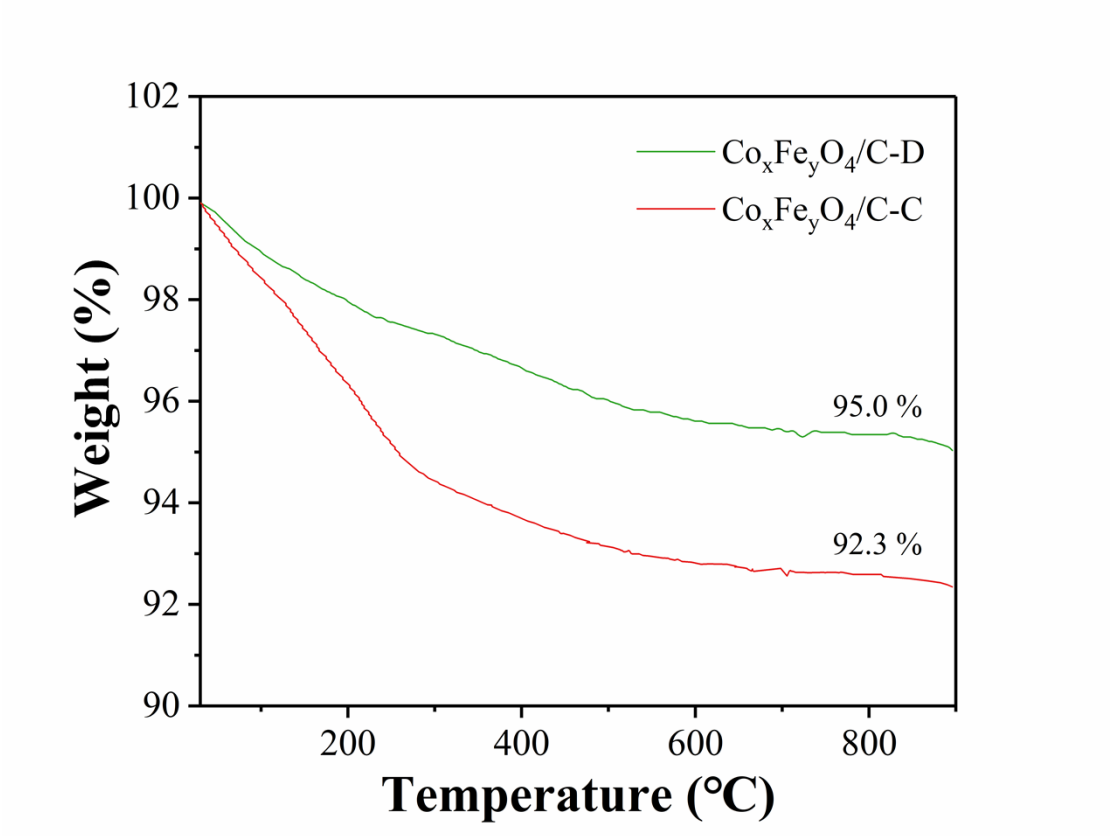

Fig. S1 TGA curves of $Co_xFe_yO_4$/C-D and $Co_xFe_yO_4$/C-C.

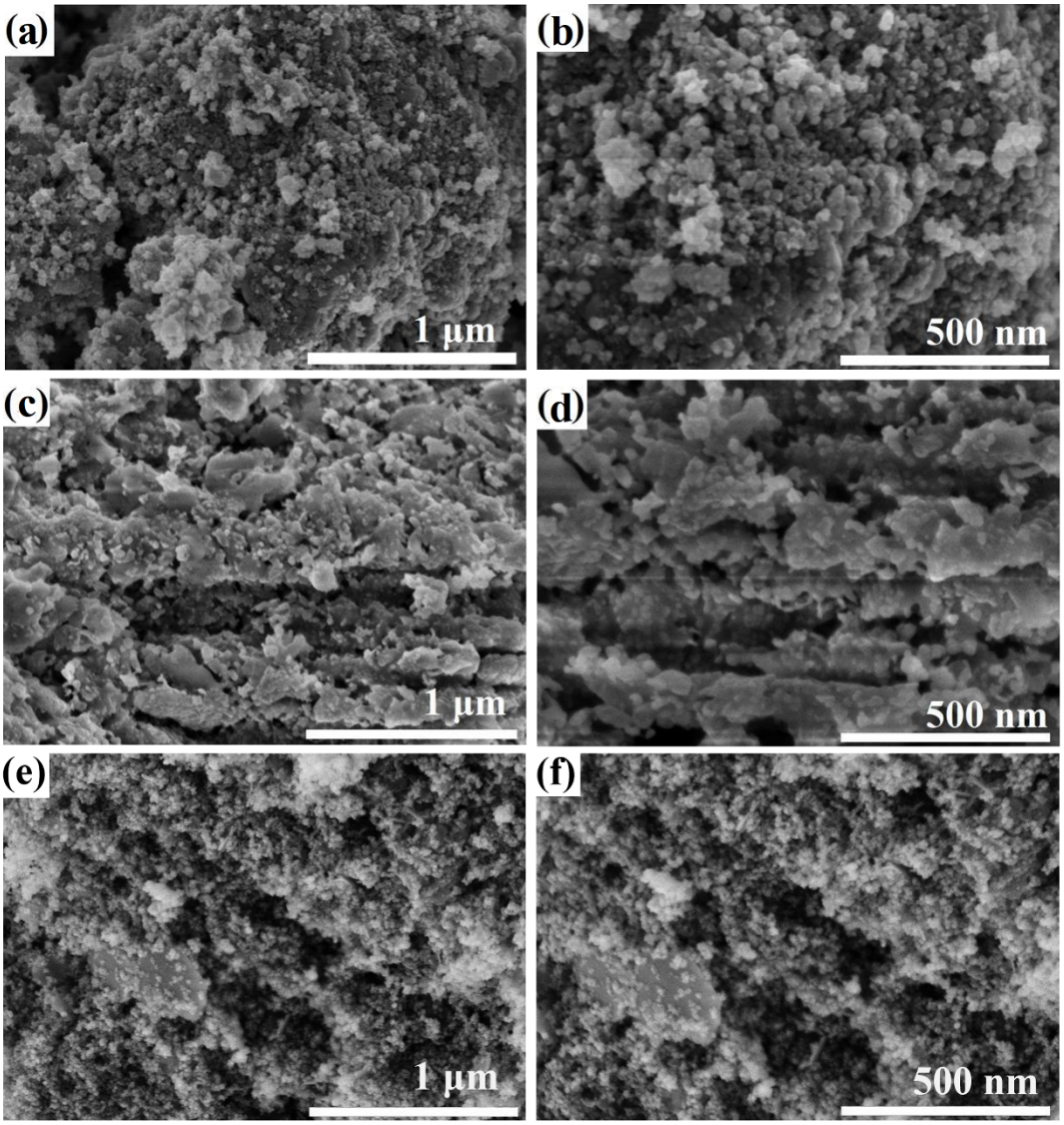

Fig. S2 SEM images at different scales of (a, b) $Co_xFe_yO_4$/C-D, (c, d) $Co_xFe_yO_4$/C-C, (e, f) $Co_xFe_yO_4$/C-P.

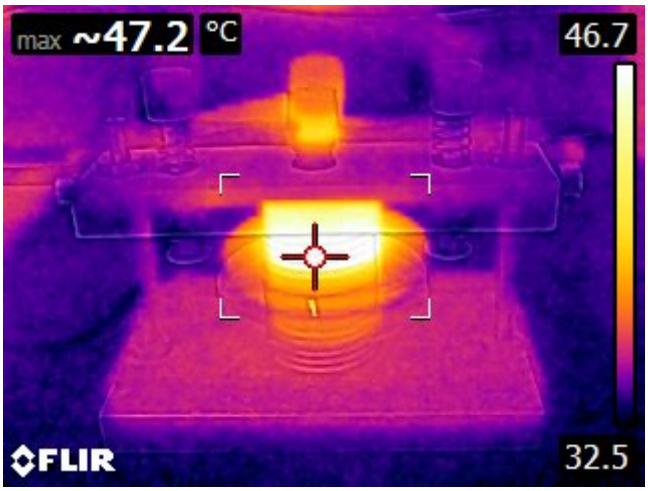

Fig. S3 Infrared image about the reactor of the DBD plasma.

Table S1 Molar ratios of Co, Fe, O, C and N in the samples determined by XPS

	Co (wt.%)	Fe (wt.%)	O (wt.%)	C (wt.%)	N (wt.%)
$Co_xFe_yO_4$/C-D	2.80	1.08	15.96	77.58	2.58
$Co_xFe_yO_4$/C-C	1.18	0.81	5.94	91.35	0.71
$Co_xFe_yO_4$/C-P	20.18	9.31	46.89	25.63	0.10

Table S2 The ratio of different types of oxygen of catalysts in XPS spectra.

Sample	O1 (Lattice oxygen)	O2 (Defect-oxygen)	O3 (Physically adsorbed water/C-O)	O2 / O1
	Peak area (%)	Peak area (%)	Peak area (%)	Peak area radio
$Co_xFe_yO_4$/C-D	19.9	39.9	40.2	2.01
$Co_xFe_yO_4$/C-C	32.1	42.2	25.7	1.32
$Co_xFe_yO_4$/C-P	64.9	22.1	13.0	0.34

Table S3 Ratios of Co^{3+}/Co^{2+} of as-obtained catalysts in Co $2p_{3/2}$ peaks spectra

	Species	Location	Co^{3+}/Co^{2+}
$Co_xFe_yO_4$/C-D	Co^{3+}	780.50	1.23
	Co^{2+}	782.57	
$Co_xFe_yO_4$/C-C	Co^{3+}	780.72	0.66
	Co^{2+}	782.25	
$Co_xFe_yO_4$/C-P	Co^{3+}	779.88	1.13
	Co^{2+}	781.30	

Table S4 Ratios of Fe^{3+}/Fe^{2+} of as-obtained catalysts in Fe $2p_{3/2}$ spectra

	Species	Location	Fe^{3+}/Fe^{2+}
$Co_xFe_yO_4$/C-D	Fe^{2+}	711.10	0.83
	Fe^{3+}	713.20	
$Co_xFe_yO_4$/C-C	Fe^{2+}	710.58	0.75
	Fe^{3+}	713.31	
$Co_xFe_yO_4$/C-P	Fe^{2+}	710.27	1.05
	Fe^{3+}	712.93	

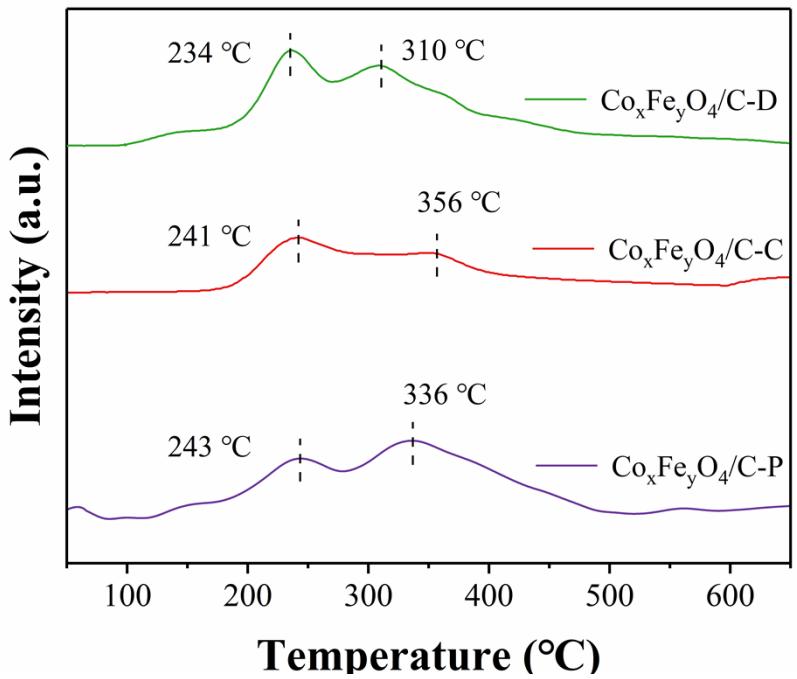

Fig. S4 O_2-TPD profiles of $Co_xFe_yO_4$/C-D, $Co_xFe_yO_4$/C-C and $Co_xFe_yO_4$/C-P.

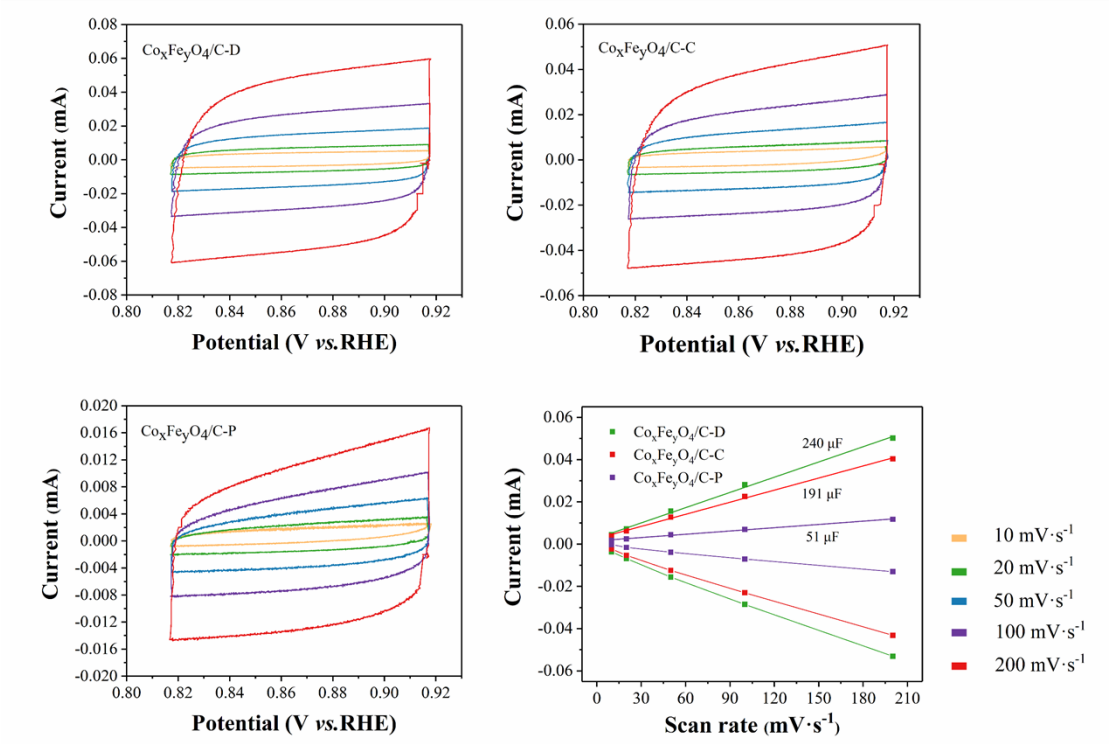

Fig. S5 CV curves of a) $Co_xFe_yO_4$/C-D, b) $Co_xFe_yO_4$/C-C and c) $Co_xFe_yO_4$/C-P at different scan rates, d) The fitted currents against the scan rates of catalysts.

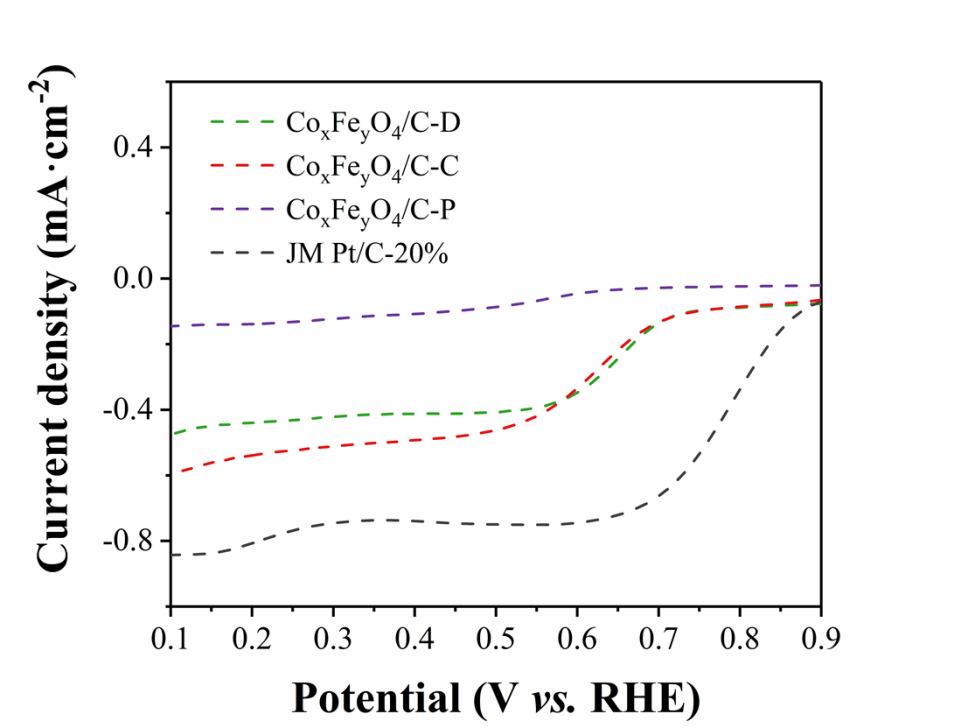

Fig. S6 LSV at 1600 rpm in N_2-saturated 0.1 M KOH solution.

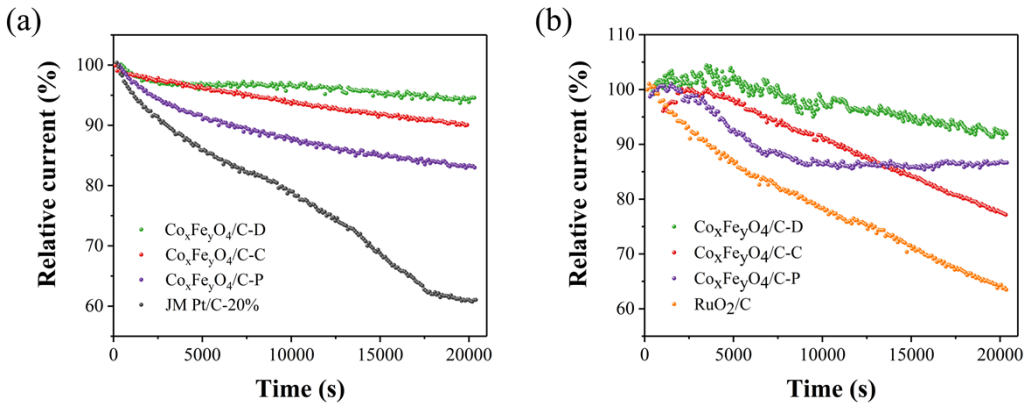

Fig. S7 Relative current-time (i-t) chronoamperometric responses for (a) the ORR and (b) the OER on oxides $Co_xFe_yO_4$/C prepared by the cold plasma, calculation and coprecipitation methods and commercial Pt/C or RuO_2/C at a potential of -0.6 V (*vs.* Hg/HgO) for ORR and 0.75 V (*vs.* Hg/HgO) for OER in O_2-saturated 0.1 M KOH at a rotating speed of 1600 rpm.

Table S5 The electronic conductivity at room temperature of the $Co_xFe_yO_4$/C-D, $Co_xFe_yO_4$/C-C and $Co_xFe_yO_4$/C-P samples.

	electrical resistivity (Ω·cm)	electronic conductivity ($S \cdot cm^{-1}$)
$Co_xFe_yO_4$/C-D	0.0926	10.80
$Co_xFe_yO_4$/C-C	0.2930	3.41
$Co_xFe_yO_4$/C-P	0.4518	2.21

Table S6 Comparison of the synthesis methods of $(Co, Fe)_3O_4$ catalysts and their electrocatalytic performance.

Catalysts	Preparation methods	Temperature / Time	E_{10} OER (V *vs.* RHE)	$E_{1/2}$ ORR (V *vs.* RHE)	ΔE (V) $=E_{OER}$-E_{ORR}	Ref.
multiphase cobalt-iron spinel	cold plasma method	~50 ℃ for 1h	1.53	0.64	0.89	this work
$CoFe_2O_4$/ N/S co-doped mesoporous carbon	hydrothermal	180 ℃ for 3h	1.7096	0.7846	0.925	[12]
$CoFe_2O_4$ /carbon nanotube	solvothermal & calcination method	180 °C for 12 h and annealed at 500 °C for 2 h	1.620	0.808	0.812	[13]
Co- and Fe-containing mixed oxides	vapor deposition	~ 520 K for 5 min in an O_2 (6–8 × 10^{-6} mbar) and ~770 K for 60 min in UHV	1.550	0.520	1.030	[14]
$CoFe_2O_4$ hexagonal nanoplates	hydrothermal& calcination method	180 °C for 4 h and was calcinated in air at 300 °C for 3 h	1.620	0.580	1.040	[15]

Table S6 Comparison of the synthesis methods of (Co, Fe)$_3$O$_4$ catalysts and their electrocatalytic performance. (continued)

Catalysts	Preparation methods	Temperature / Time	E_{10} OER (V *vs.* RHE)	$E_{1/2}$ ORR (V *vs.* RHE)	ΔE (V) $=E_{OER}$-E_{ORR}	Ref.
(Co, Fe)$_3$O$_4$/N-CNT	a mixing process and an impregnation technique	sonicate for 5 h; gas diffusion layer (GDL) substrates were annealed for 0.5 h at 300 °C	1.5548	0.6268	0.928	[16]
oxygen-vacancy-rich $CoFe_2O_4$ anchored on cage-like carbon	solvothermal approach	180 °C for 24 h	1.590	0.765	0.825	[17]
$Co_xFe_{3-x}O_4$ / acetylene black	hydrothermal method	200 °C for 20 h	1.7066	0.5766	1.13	[18]
Co/$CoFe_2O_4$ / N-doped graphene	solution-polymerization & pyrolysis	pyrolysis at 800 °C in Ar for 3h	1.630	0.670	0.960	[19]

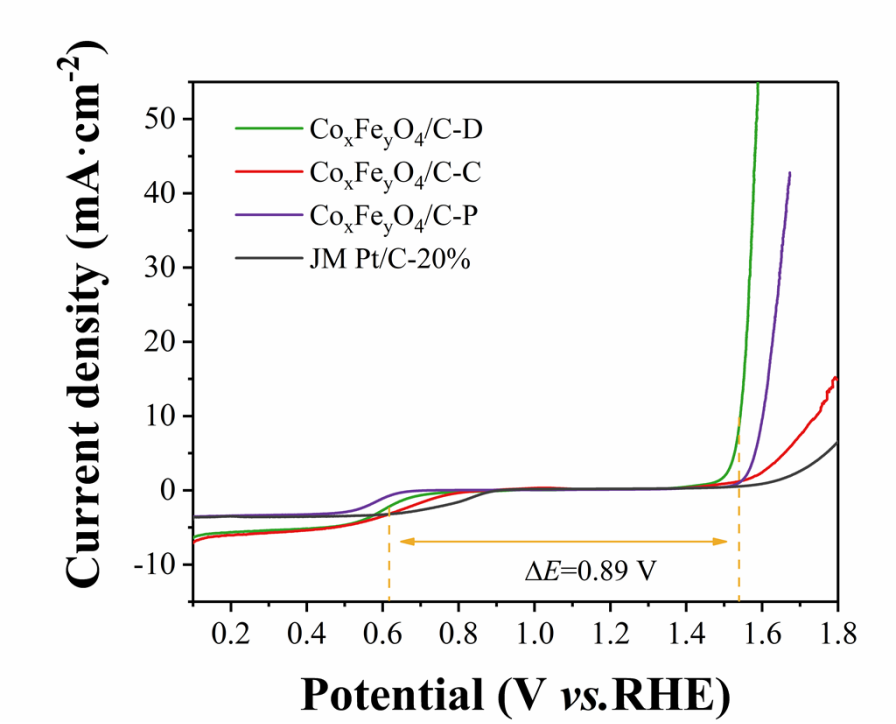

Fig. S8 Overall polarization curves of $Co_xFe_yO_4$/C-D, $Co_xFe_yO_4$/C-C, $Co_xFe_yO_4$/C-P and the commercial Pt/C catalysts at 1600 rpm in O_2-saturated 0.1 M KOH solution.

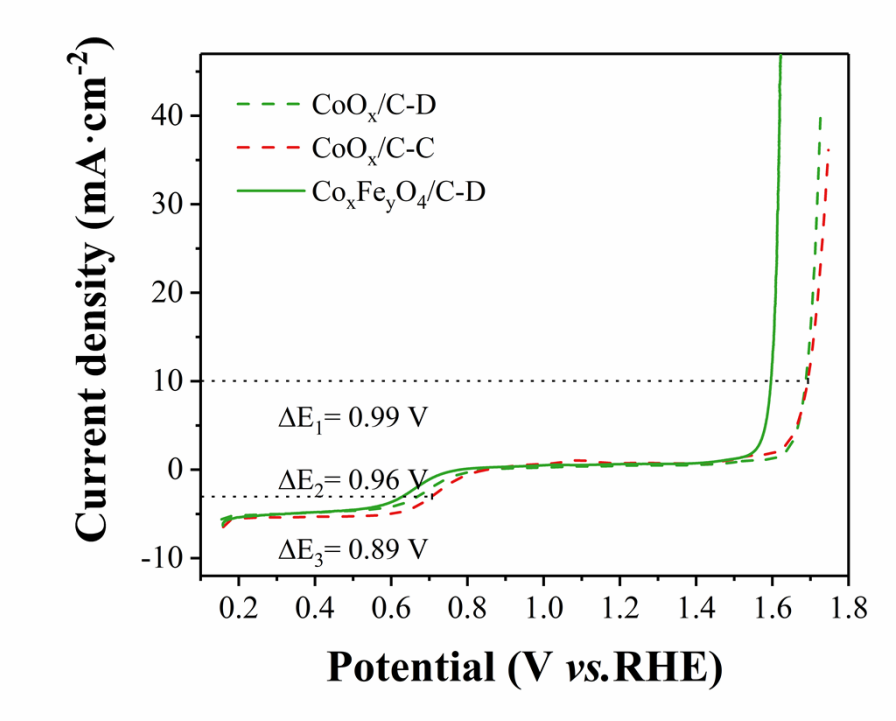

Fig. S9 Overall polarization curves of CoO_x/C-D, CoO_x/C-C and $Co_xFe_yO_4$/C-D at 1600 rpm in O_2-saturated 0.1 M KOH solution.