Supporting information

Fe, Co, Ni co-doped nitrogen-doped carbon nanotubes for electrocatalytic oxygen reduction reaction

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Experimental Section

1. Chemical regents.

Nickel nitrate hexahydrate and Zinc acetate were purchased from Sinopharm Chemical Regent., Ltd. 2-methylimidazole, Tris(hydroxymethyl)aminomethane (Tris), 1,10-Phenanthroline (Phen) were purchased from Admas-Beta. Iron nitrate nonahydrate, Cobalt nitrate hexahydrate and Dopamine hydrochloride were purchased from Aladdin. Pt/C (20wt%) was purchased from Shanghai Hesen Electrical Co. All the chemicals were purified for direct use.

2. The preparation of ZIF precursors.

16 mmol of Zinc acetate was dissolved in 80 mL deionized water, which donated as solution A. 64 mmol 2-methylimidazole were dissolved in 80 mL deionized water, which donated as solution B. solution B poured into vigorously stirred solution A. The mixed solution was stirred vigorously at 60°C for 24 hours, then collected by centrifugation, washed with deionized water and dried in a vacuum oven at 60°C overnight, the obtained white powder was donated at ZIF.

3. The preparation of FeCoNi@CNTs-NC

1 g of ZIF precursor and 0.6 g of Tris were dispersed in 50 mL deionized water and 50 mL ethanol mix solttion, and stirred for 20 min. Then, 2 mL of 50 mg mL^{-1} of M-Phen were added dropwise to the mixture solution, where the M-phen (M= Fe, Co, Ni, n_{M}:n_{Phen}=1:3). After stirred 24 h, Centrifugation, drying in a vacuum oven at 60°C overnight, the obtained brown powder was named FeCoNi-PMPDA. 0.4 g FeCoNi-

PMPDA powder was heated under Ar flow at 920°C for 2 h, the obtained black powder donated as FeCoNi@CNTs-NC. The FeCoNi@CNTs-NC powder was immersed in 0.5 M H_2SO_4 solution at 80°C for 5 h, after cooling down to room temperature, centrifugation and DI water wash three times, dry at 60°C overnight. After that, the FeCoNi@CNTs-NC-2 obtained by the secondary carbonization under the same condition.

As a comparison, P-NC without only dopamine hydrochloride, and FeCoNi/NC without dopamine hydrochloride and single NC were prepared under the same preparation conditions.

4. Characterization

Powder X-ray diffraction (MiniFlex-600, Rigaku, Japan) was applied to analyzed the crystal structure of catalysts. The specific surface area and porosity adsorbent nalyzer (ASAP 2460, US) is used to analyze the specific surface area and porosity of catalysts. a XploRA PLUS Raman spectrometer ((HORIBA, France) is used to analyze the degree of graphitization and defects in catalysts. The field emission scanning electron microscope (FESEM, FEI, NANO SEM430, 15 kV) was applied to analyze the morphology of prepared catalysts. The transmission electron microscope (TEM, JEM-2100, Japan) was applied to characterization the morphology of catalysts. The X-ray photoelectron spectrometer (XPS, Thermo Scientific ESCALAB Xi+, Al kα, hv = 1486.6 eV) which calibrated the binding energy with C1s (284.8 eV) was applied to analyze the chemical states of elements on the surface of prepared catalysts. The Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Fisher ICP-OES, USA) was applied to analyze the contents of the metal element of the catalysts.

The TGA contents was calculated by the follow chemical equation:

$$FeCoNi@CN + xO_2 \rightarrow ZnFe_2O_4 + NO_2\uparrow + CO_2\uparrow \#(S1)$$

$$N + O_2 = NO_2\uparrow \#(S2)$$

$$C + O_2 = CO_2\uparrow \#(S3)$$

5. Electrochemical measurement

All electrochemical properties were measured on the electrochemical workstation (CHI 760E) by using a typical three electrode system which the platinum network as a counter electrode and Hg/HgO as a reference electrode. A 3 mm rotating disk electrode (RDE) and a 5 mm rotating ring disk electrode (RRDE) was used as work electrode for

ORR study. All the measurement potentials were converted in the reversible hydrogen electrode (RHE) by the following equation:

$$E_{vs.RHE} = E^{\theta}_{Hg/HgO} + E + 0.059 \times pH\# \ (S4)$$

Where E is the tested potential, and $E^{\theta}_{Hg/HgO}$ is the standard potential of Hg/HgO reference electrode.

The working electrode were prepared as follow: 5 mg of catalysts powders were dispersed in a 1 mL mixture solution (V_{Nafion}: V_{water}: $V_{ethanol}$ = 1:9:10) to form a homogeneous black ink. 8 μL of catalysts ink was pipetted to a RDE as well as 22 μL for RRDE to form the catalysts loaded at 0.57 mg cm^{-2} for ORR test. The cyclic voltametric (CV) and liner sweep voltametric (LSV) curves were tested in a 0.1 M KOH solution saturated with O_2 and Ar under various rotating speeds from 625 rpm to 2500 rpm. The electron transfer was obtained by fitting Koutecky-Levich (K–L) equation:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_d} = \frac{1}{nFkC_{O_2}} + \frac{1}{B\omega^{1/2}}\#(S5)$$

$$B = 0.62nFAC_O D_O^{2/3} v^{-1/6}\#(S6)$$

Where the J_K and J_d were presented as kinetic current density and limit diffusion current density. n is the overall number of electron transfer number. F is Faraday constant (F=96485 C mol^{-1}). A is the area of electrode. C_O is the bulk phase concentrations of O_2 in electrolyte solution (1.2 *10^{-3} mol cm^{-3}, 0.1 mol L^{-1} KOH). N is the kinematic viscosity of the electrolyte (0.01 cm^2, 0.1 mol L^{-1} KOH). D_O is the diffusion coefficient of O_2 in the electrolyte (1.9 *10^{-5} cm^2 s^{-1}, 0.1 mol L^{-1} KOH). ω is the angular velocity of the disk (ω = 2πN, N is the linear rotation speed). When the rotating speed is expressed in rpm, the formula (S3) can be expressed (S4):

$$B = 0.2nFAC_O D_O^{2/3} v^{-1/6}\#(S7)$$

The yield of hydrogen peroxide and corresponding electron transfer number was test by RRDE measurement, which calculated by the following equation:

$$H_2H_2\% = \frac{I_R/N}{I_R/N + I_D} \times 200\%\#(S8)$$

$$n = 4 \times \frac{I_D}{I_D + I_R/N} \#(S9)$$

where I_R and I_D were the current density of ring and disk. N is the collection efficiency (0.38) of the Pt ring of RRDE.

The Tafel plot is derived by fitting the following equation:

$$E = a \times \log j + b \#(S10)$$

Where E and j were the potential (V vs. RHE) and current density ($mAcm^{-2}$).

The electrochemical double layer capacitance (C_{dl}) for evaluating electrochemical surface area (ECSA) was measured by non-Faradaic capacitive current with cyclic voltammograms (CV). The CV curves were used to evaluate the bilayer capacitance by testing the CV curves with different scan rates in an Ar-saturated 0.1 M KOH solution and in the non-Faraday potential interval of 1.1-1.2 V (*vs*.RHE). The ECSA was fitted as follow:

$$ECSA = \frac{C_{dl}}{C_s} \#(S11)$$

Where C_s is 60 μF cm^{-2}.

6. Home-made Zn-air battery prepared and measurement.

A home-made Zn-air batteries (ZABs) were used to study the performance of catalysts in the field of ZABs. In a simple apparatus, a 3 mm thick zinc plate was used as the metal anode and a carbon paper loaded with catalyst acts as the air cathode, 6.0 mol L^{-1} KOH containing 0.20 mol L^{-1} Zinc acetate as electrolyte solution. The charge and discharge cycle and rate test were measured in a Neware test sysem.

Figures

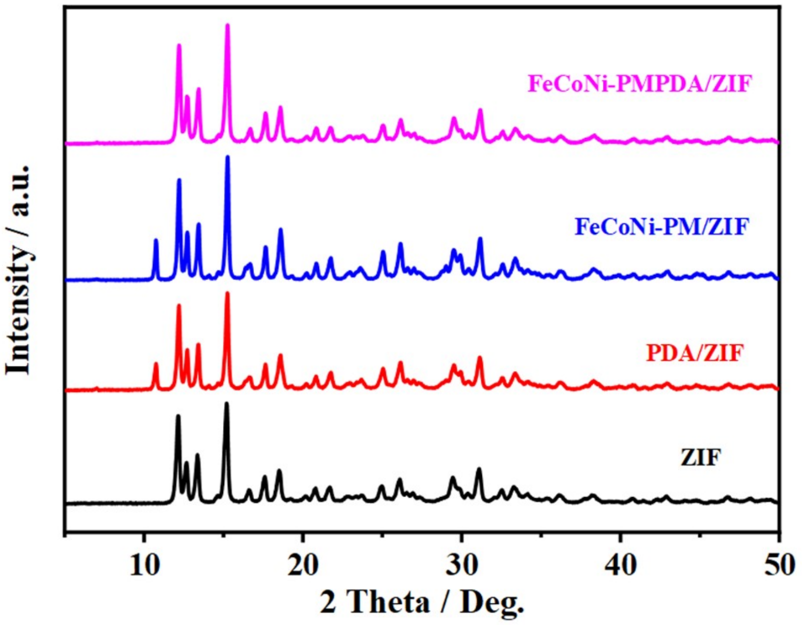

Figure S1 XRD pattern of ZIF, PDA/ZIF, FeCoNi-PM/ZIF and FeCoNi-PMPDA/ZIF.

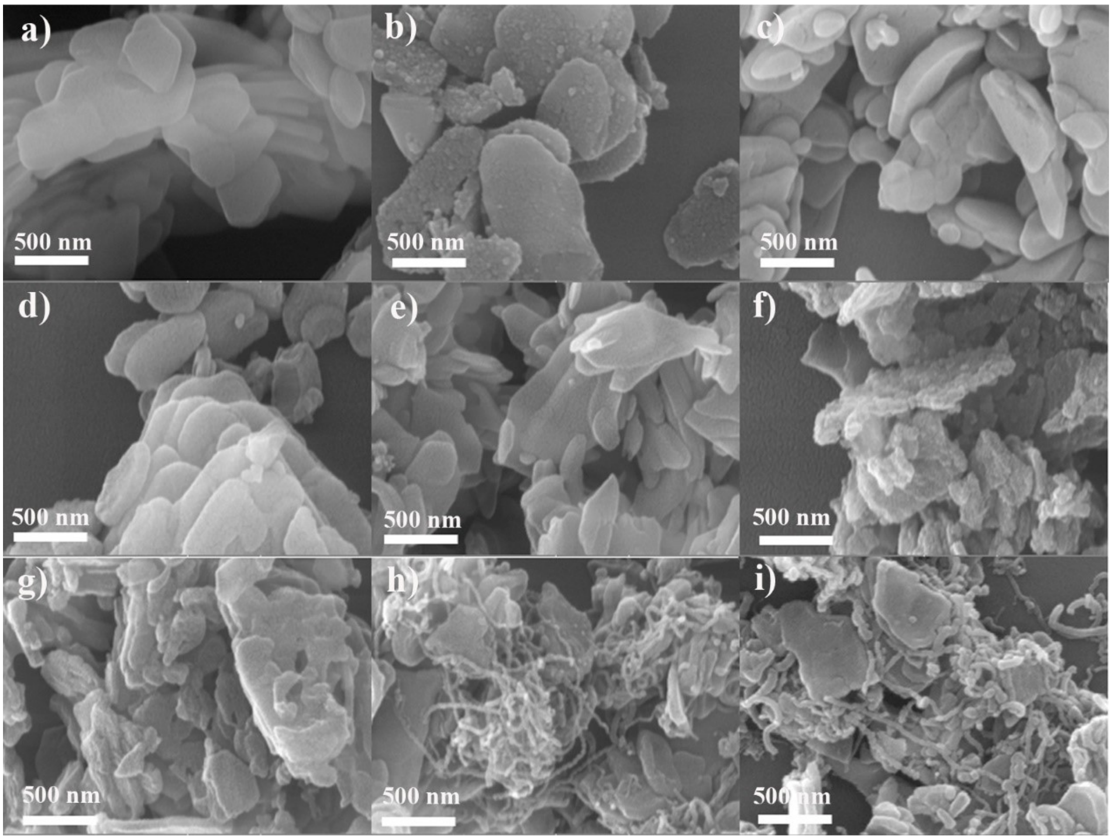

Figure S2 SEM images of ZIF (a), PDA/ZIF (b), FeCoNi-PM/ZIF (c), FeCoNi-PMPDA/ZIF (d), NC (e), P-NC (f), FeCoNi/NC (g), FeCoNi@CNTs-NC (h), FeCoNi@CNTs-NC-2 (i), respectively.

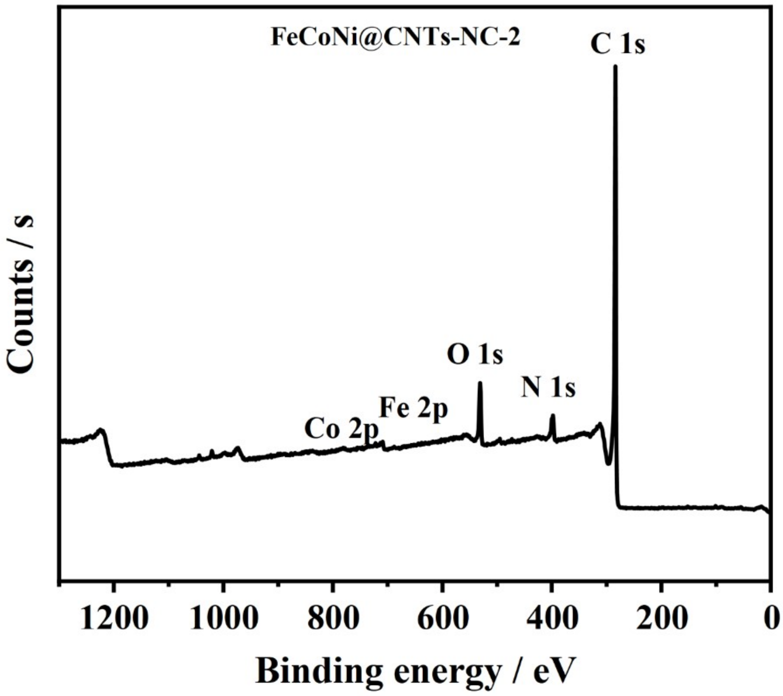

Figure S3 the survey XPS spectrum of FeCoNi@CNTs-NC-2.

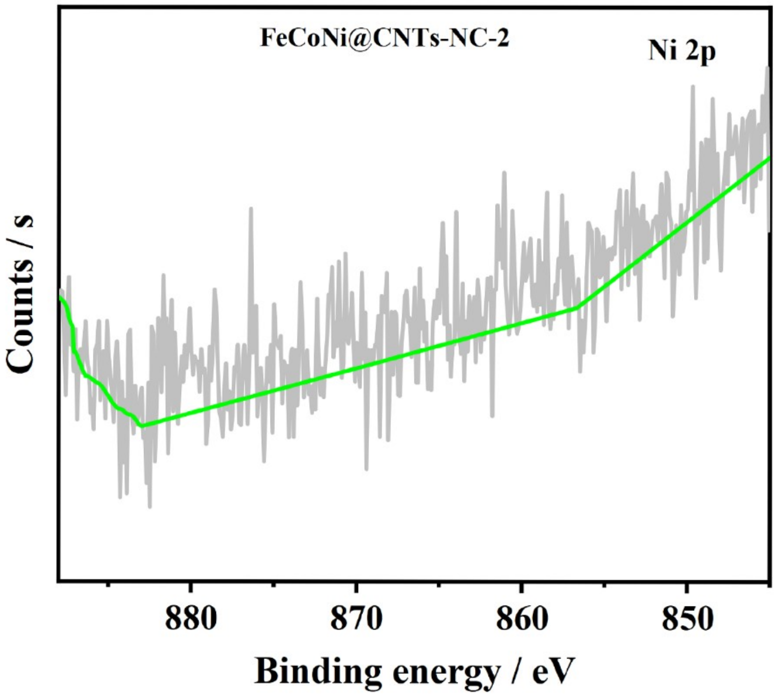

Figure S4 the Ni 2p spectrum of FeCoNi@CNTs-NC-2.

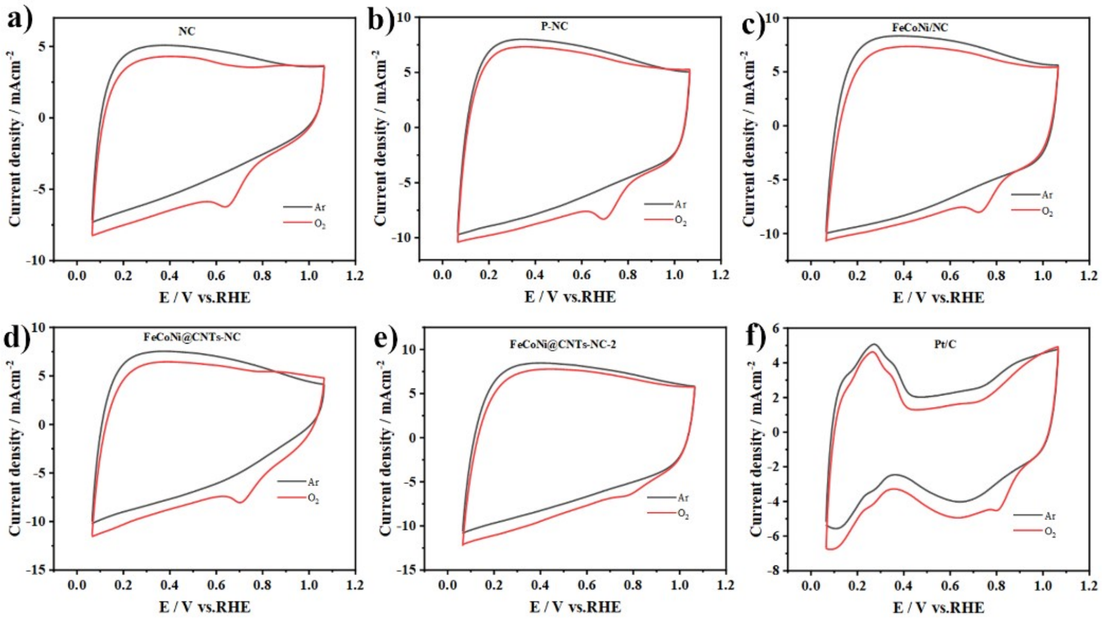

Figure S5 the CV curves of NC (a), P-NC (b), FeCoNi/NC (c), FeCoNi@CNTs-NC (d), FeCoNi@CNTs-NC-2 (e), Pt/C (f), respectively.

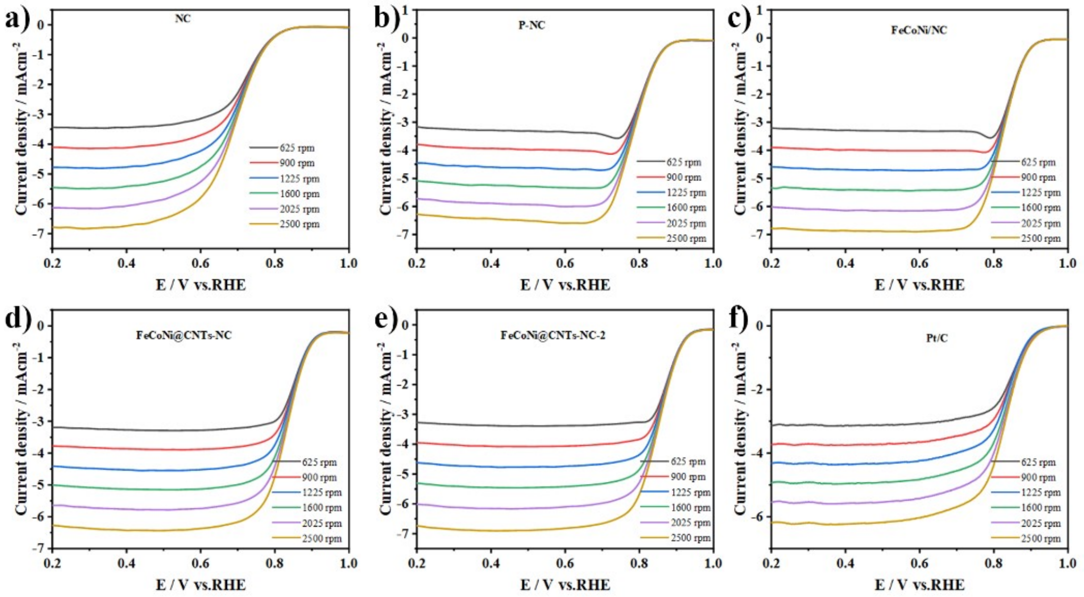

Figure S6 the LSV curves of NC (a), P-NC (b), FeCoNi/NC (c), FeCoNi@CNTs-NC (d), FeCoNi@CNTs-NC-2 (e), Pt/C (f) with different rotate speeds, respectively.

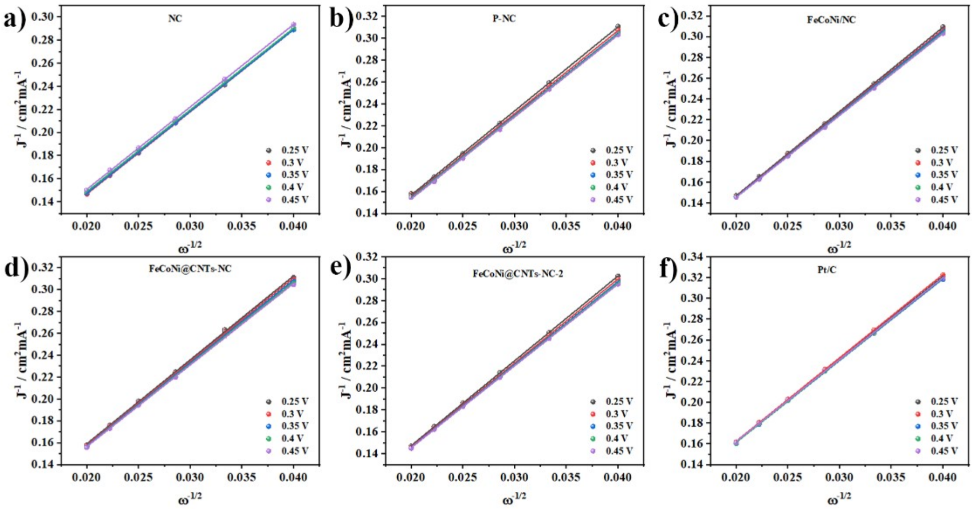

Figure S7 the K-L plot curves of NC (a), P-NC (b), FeCoNi/NC (c), FeCoNi@CNTs-NC (d), FeCoNi@CNTs-NC-2 (e), Pt/C (f), respectively.

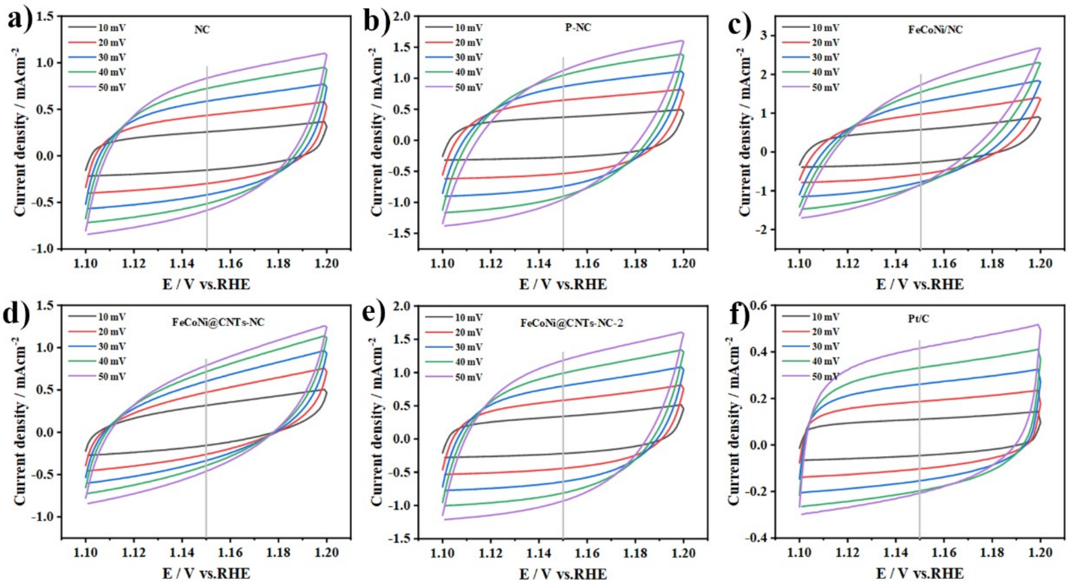

Figure S8 CV curves of NC (a), P-NC (b), FeCoNi/NC (c), FeCoNi@CNTs-NC (d), FeCoNi@CNTs-NC-2 (e), Pt/C (f), respectively.

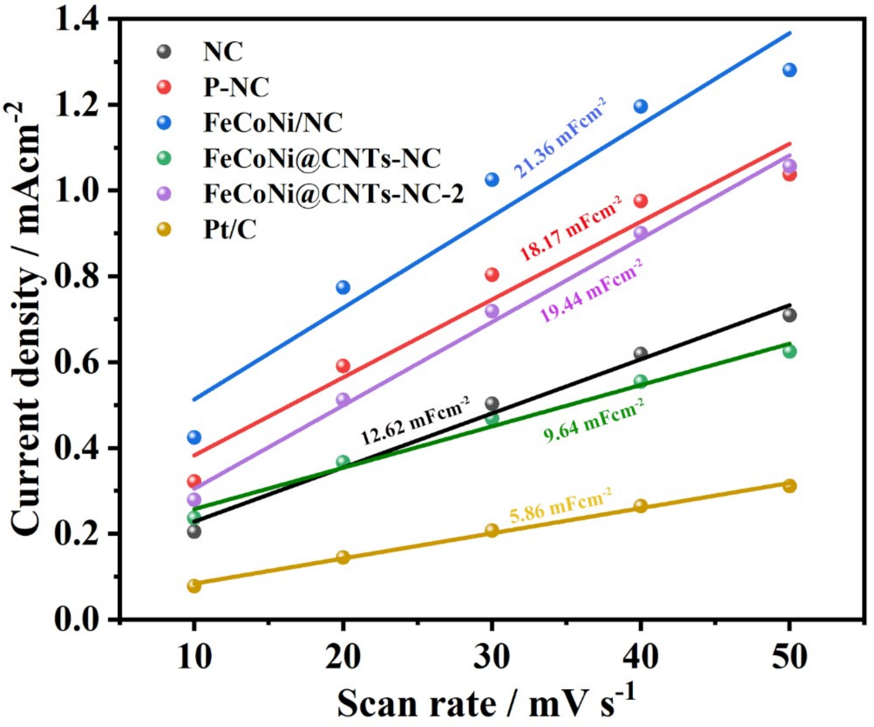

Figure S9 C_{dl} curves of NC, P-NC, FeCoNi/NC, FeCoNi@CNTs-NC, FeCoNi@CNTs-NC-2 and Pt/C, respectively.

Table S1 BET surface area, pore volume and average pore size of prepared catalysts.

Sample	BET surface area $m^2\ g^{-1}$	Pore volume $cm^3\ g^{-1}$
FeCoNi@CNTs-NC	450.47	0.23
FeCoNi@CNTs-NC-2	526.36	0.32

Table S2 the N species contents of FeCoNi@CNTs-NC-2 fitted by N 1s spectrum.

Sample	Pyrrolic-N (Atomic %)	Pyridinc-N (Atomic %)	Graphitic-N (Atomic %)	Oxidized-N (Atomic %)	M-N (Atomic %)
FeCoNi@CNTs -NC-2	14.77	20.02	44.88	19.41	1.4

Table S3 the metal contents of FeCoNi@CNTs-NC-2 by ICP-OES.

Sample	Fe (wt%)	Co (wt%)	Ni (wt%)	Zn (wt%)
FeCoNi@CNTs-NC	2.515	0.387	0.032	4.345
FeCoNi@CNTs-NC-2	2.109	0.380	0.031	0.747

Table S4 The E_o and $E_{1/2}$ of prepared catalysts by the LSV curves.

Sample	E_o (V vs.RHE)	$E_{1/2}$ (V vs.RHE)
NC	0.88	0.71
P-NC	0.92	0.80
FeCoNi/NC	0.94	0.83
FeCoNi@CNTs-NC	0.95	0.84
FeCoNi@CNTs-NC-2	0.98	0.87
Pt/C	0.97	0.84

Table S5 ORR and ZAB performance comparison tables reported in previous paper.

Catalysts	ORR		ZABs			Ref.
	$E_{1/2}$	electrolyte	V_{OCP}	Power density	electrolyte	
FeCoNi@CNTs-NC-2	0.85 V (vs. RHE)	0.1 M KOH	1.51 V	197.1 mW cm^{-2}	6M KOH +0.2 M Zn(ac)$_2$	This work
FeCo/FeCoNi@NCNTs-HF	0.85 V (vs. RHE)	0.1 M KOH	1.481 V	156.22 mW cm^{-2}	6M KOH +0.2 M Zn(ac)$_2$	1
FeCoNi@HNC	0.805 V (vs. RHE)	0.1 M KOH	1.53 V	109.3 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	2
NiFeCo-NC2	0.620 V (vs. RHE)	0.1 M KOH	1.44 V	——	6 M KOH + 4 % ZnO electrolyte (2 mL)	3
FeCoNi-CNTs-2	0.82 V (vs. RHE)	1 M KOH	1.49 V	210.5 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	4
Fe-Co-Ni@NDC	0.902 V (vs. RHE)	0.1 M KOH	1.496 V	247 mW cm^{-2}	gel electrolyte	5
FeCoNi/NCHNs	0.885 V (vs. RHE)	0.1 M KOH	1.48 V	160 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	6
Co-FeNi-342	0.86 V (vs. RHE)	0.1 M KOH	1.32 V	77 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	7
FeCoNi-N-CS	0.871 V (vs. RHE)	0.1 M KOH	1.52 V	140 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	8
Fe$_{1.2}$(CoNi)$_{1.8}$S$_6$	0.81 V (vs. RHE)	0.1 M KOH	1.45 V	158.4 mW cm^{-2}	6M KOH + 0.2 M ZnCl$_2$	9
FeCoNi/NC	0.84 V (vs. RHE)	0.1 M KOH	1.5 V	161 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	10
FeCoNi-NC	0.838 (vs.RHE)	0.1 M KOH	——	231 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	11
FeCoNi FCNFs	0.92 (vs.RHE)	0.1 M KOH	1.5 V	121 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	12
Commercial Pt/C	0.84 (vs.RHE)	0.1 M KOH	1.47 V	107 mW cm^{-2}	6M KOH + 0.2 M Zn(ac)$_2$	This work

Reference

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