

Supplementary Information

Enhanced electrocatalytic oxygen reduction reaction for Fe-N₄-C by incorporation of Co nanoparticles

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SI0 Supporting formula for the calculation of n, H₂O₂%

The electron transfer number, n, was calculated using the Koutecky-Levich equations:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K} \quad (1)$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

$$j_K = nFkC_0 \quad (3)$$

where j, j_L, and j_K are the measured, diffusion-limiting and kinetic current densities, respectively, ω is the rotating rate of the RRDE (rpm), C₀ is the bulk concentration of O₂, F is the Faraday constant, D₀ is the diffusion coefficient of O₂, and ν is the kinematic viscosity of the 0.1 M KOH solution. The value of n and the yield of H₂O₂ can be calculated as following equations:

$$n = \frac{4I_{\text{disk}}}{\frac{I_{\text{ring}}}{N} + I_{\text{disk}}} \quad (4)$$

$$\%H_2O_2 = \frac{200\frac{I_{\text{ring}}}{N}}{\frac{I_{\text{ring}}}{N} + I_{\text{disk}}} \quad (5)$$

where I_{disk} and I_{ring} are the current density of disk and ring of the RRDE, respectively, and N is the collection efficiency (0.39) of the ring electrode measured in 1 M potassium ferricyanide (K₃Fe(CN)₆) and 0.1 M KCl solution. Note that the ring electrode potential was set at 1.48 V (vs. RHE).

SI1. Compositional and morphological characterization

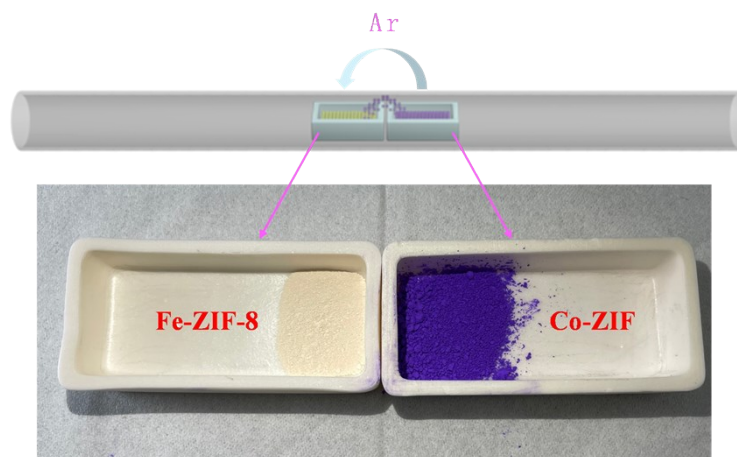


Figure S1. Scheme of assisted thermal loading method in the quartz tube.

Table S1. Preparation of samples

Sample	Boat 1	Boat 2
Co@Fe-N-C	Fe-ZIF-8	Co-ZIF
Co@N-C	ZIF-8	Co-ZIF
Fe-N-C	Fe-ZIF-8	
N-C	ZIF-8	

Note: The red arrow indicates the direction of the Ar flow (see **Figure S1**). For Co@Fe-N-C and Co@N-C, Co-ZIF is placed toward the inlet of Ar, Fe-ZIF-8 and ZIF-8 are placed toward the outlet of Ar, respectively. Fe-N-C and N-C are obtained by directly pyrolyzing Fe-ZIF and ZIF-8, respectively.

Figure S2 shows representative SEM images of ZIF-8, Fe-ZIF-8 and Co@Fe-N-C. Typical polyhedral structure characteristic for ZIF-8 is observed and for control sample and after doping with Fe. High graphitization degree is found is observed for Co@Fe-N-C. The XRD patterns of ZIF-8 and Fe-ZIF-8 reveled the same crystal structure before and after doping with Fe (**Figure S3**), indicating that Fe ions are

introduced into the pores of ZIF-8.

The XRD peaks at 24-26 degree are characteristic of (100) plane of graphitic carbon, and peaks at 43-44 degree correspond to (110) plane of graphitic carbon for Co@Fe-N-C, Fe-N-C, Co@N-C and N-C. The N₂ adsorption-desorption curves and corresponding pore size distribution of ZIF-8 and Fe-ZIF-8 (**Figure S4**) indicate a decrease in pore volume, which further confirmed that Fe-ions are adsorbed into the micropores of ZIF-8.

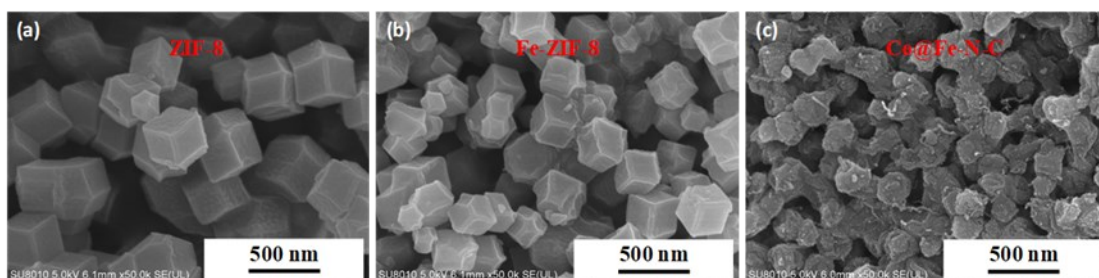


Figure S2. SEM images of (a) ZIF-8, (b) Fe-ZIF-8 and (c) Co@Fe-N-C.

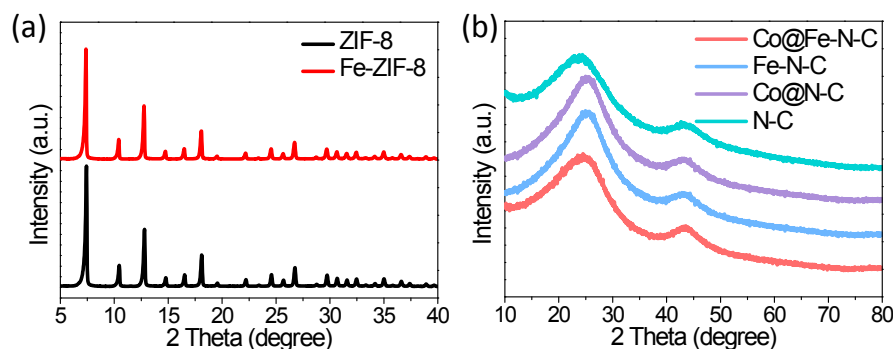


Figure S3. (a) XRD patterns of ZIF-8 and Fe-ZIF-8. (b) XRD patterns of Co@Fe-N-C, Fe-N-C, Co@N-C and N-C.

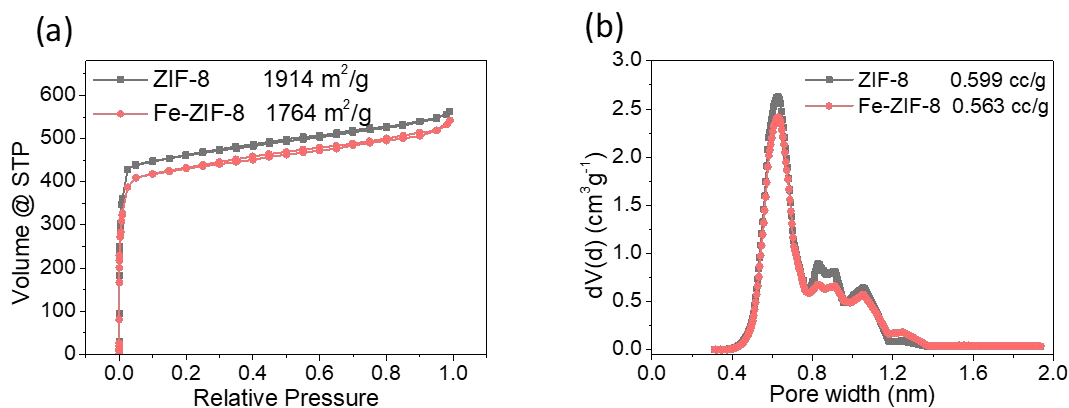


Figure S4. (a) N₂ adsorption and desorption curves and (b) corresponding pore

size distribution of ZIF-8 and Fe-ZIF-8.

The SEM images of Fe-N-C, Co@N-C and N-C. Fe-N-C (**Figure S5**) also shows high degree of graphitization, similar to Co@Fe-N-C, which could be attributed to the catalytic effect of Fe. Higher degree of graphitization in Co@N-C than in N-C is also observed and could be attributed to the catalytic effect of Co. Representative TEM and HRTEM images of Fe-N-C, Co@N-C and N-C (**Figure S6**) revealed no nanoparticles in these samples, indicating that Fe plays significant role in formation of Co nanoparticles. **Figure S7** indicated the EDS results, on the surface of Co@Fe-N-C.

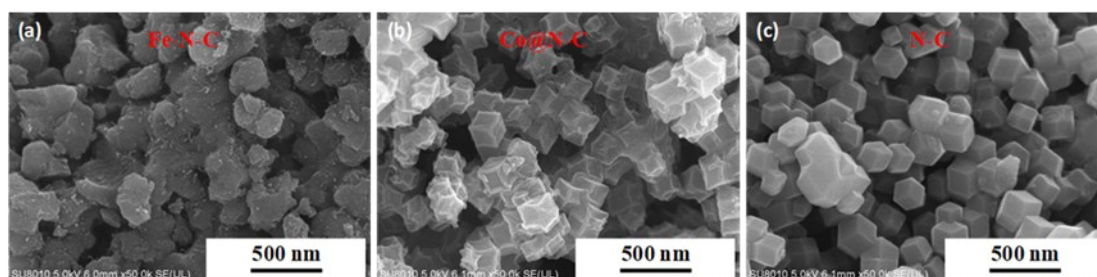


Figure S5. SEM images of (a) Fe-N-C, (b) Co@N-C and (c) N-C.

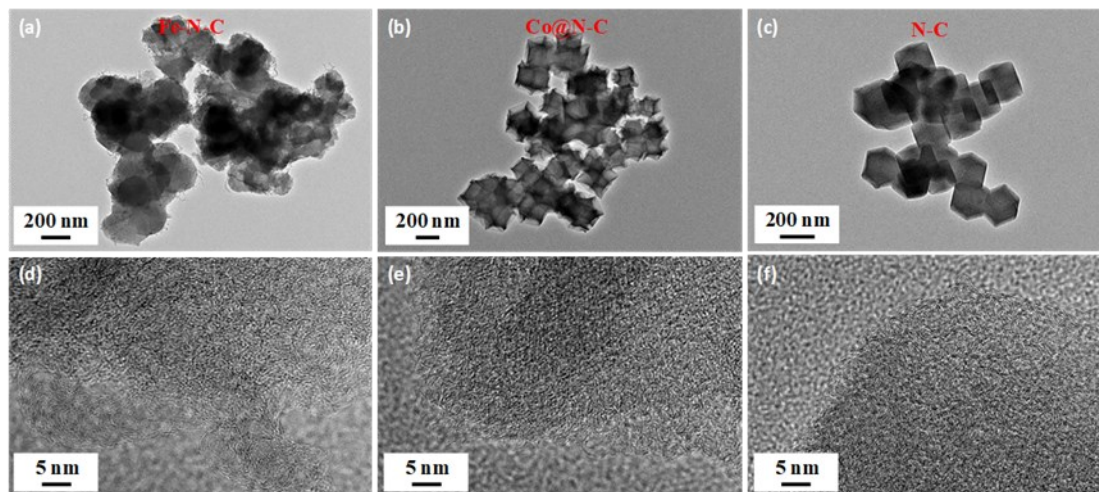


Figure S6. Representative TEM and HR TEM images of (a, d) Fe-N-C, (b, e) Co@N-C and (c, f) N-C.

Table S2. ICP results of samples

Sample	Metal	Contents (wt.%)
Co@Fe-N-C	Fe	1.2

	Co	0.1
Fe-N-C	Fe	1.22
Co@N-C	Co	0.07

Note: Table S2 showed ICP results of Co@Fe-N-C and reference samples, higher Fe contents of Co@Fe-N-C than Fe-N-C and higher Co content of Co@Fe-N-C than Co@N-C further confirmed there probably be an effect between Fe and Co, like anchoring.

Figure S7 indicated HR-XPS C 1s, Fe 2p and Co 2p spectrums of samples. C 1s spectrum is divided into three coordination C-C (C1, 284.6 eV), C=N (C2, 286.2 eV) and O-C=O (C3, 288.2 eV). The percentage of C1, C2, C3 is 87%, 10%, 3% for Co@Fe-N-C. 88%, 10%, 2% for Fe-N-C; 92%, 6%, 2% for Co@N-C; 80%, 13%, 7% for N-C, respectively. As the contents of Fe and Co in samples are too low, it is difficult to analyze the chemical states of Fe and Co. Thus, the chemical states of Fe (1.7 wt.%, see Table S1) are analyzed using XAFS (**Figure S8**), however, the contents for Co are 0.01 wt.% in Co@Fe-N-C which is too low to be tested with both XPS and XAFS.

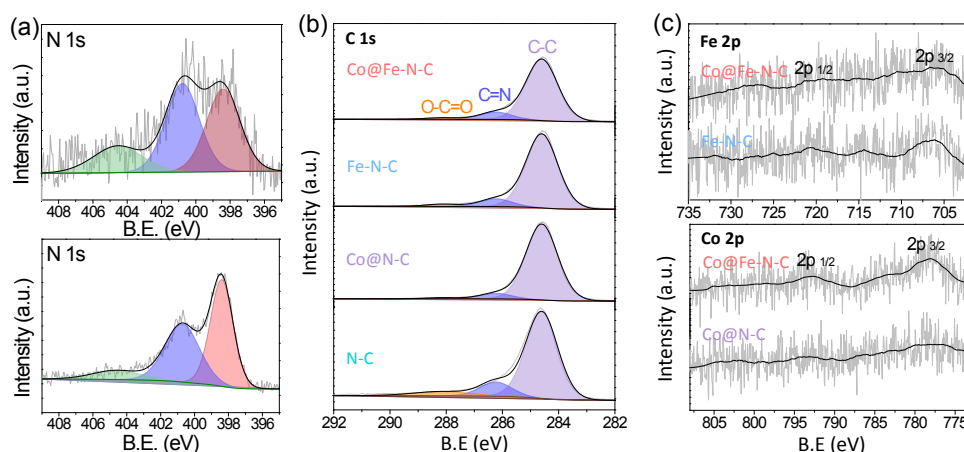


Figure S7. HR-XPS (a) N 1s of Co@Fe-N-C and Co@N-C. (b) C 1s spectrums, (c) Fe 2p of Co@Fe-N-C and Fe-N-C; and Co 2p spectrums Co@Fe-N-C and Co@N-C.

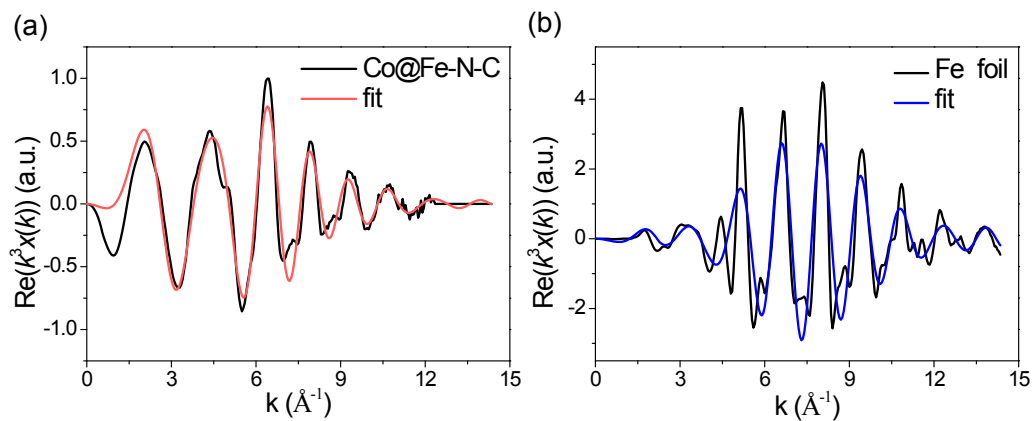


Figure S8. Corresponding Fe K-edge EXAFS fitting curves of **(a)** Co@Fe-N-C and **(b)** Fe foil.

Table S3. EXAFS data fitting results of Co@Fe-N-C.

Sample	Path	N	R(Å)	σ^2 ($10^{-3}\text{\AA}^2$)	R factor
Co@Fe-N-C	Fe-N	3.7 ± 0.6	1.99(0.02)	9.7(3.4)	0.012
	Fe-Fe1	2.1 ± 0.5	2.46(0.02)	8.0(2.1)	
	Fe-Fe2	1.6 ± 0.4	2.82(0.02)	8.0(2.1)	

Note: N, coordination number; R, distance between absorber and backscatter atoms; σ^2 , the Debye-Waller factor value. Table S3 showed the fitting results of EXAFS of Co@Fe-N-C, indicating a coordination of Fe-N₄ that was generally act as active center in ORR. Besides, metallic Fe-Fe coordination was also found in this sample.

S12. Assessment of catalytic activity

Figure S9 indicated the LSV curves of samples in 0.1 M KOH, the reference electrode was Ag/AgCl, in all the electrochemical tests of this work, the potential vs. RHE was calculated as the potential vs. Ag/AgCl + 0.97 V. **Figure S10** shows the TEM image of Co@Fe-N-C-A (remove CoNPs), indicating some pores formation because of the remove of CoNPs. The corresponding LSV and Tafel plot are shown in **Figure S11**, indicating obvious decrease in $E_{1/2}$ and Tafel slope which further confirms the positive role of CoNPs in Co@Fe-N-C. **Figure S12** refers to the LSV curves tested with different rotating speed from 400 to 2500 rpm, current density increases as the increase of rotating speed, indicating a potential of good kinetics. **Figure S13** exhibited the Tafel curves of samples, indicating Co@Fe-N-C had the lowest Tafel slope ($109.34 \text{ mV dec}^{-1}$) compared to other samples. **Figure S14** showed the TEM image of Co@Fe-N-C after 60,000 s long-term durability test, the presence of Co nanoparticles was observed.

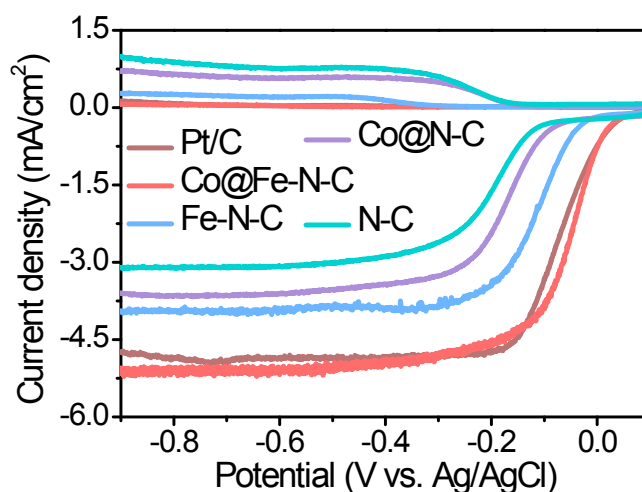


Figure S9. LSV curves for samples in 0.1M KOH (potential vs. Ag/AgCl, over saturated KCl solution)

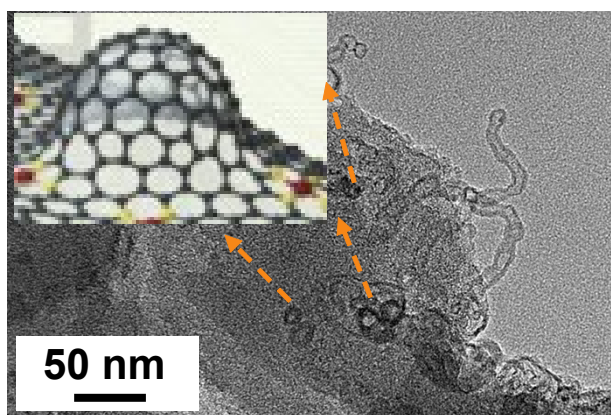


Figure S10. TEM image of Co@Fe-N-C-A (remove CoNPs).

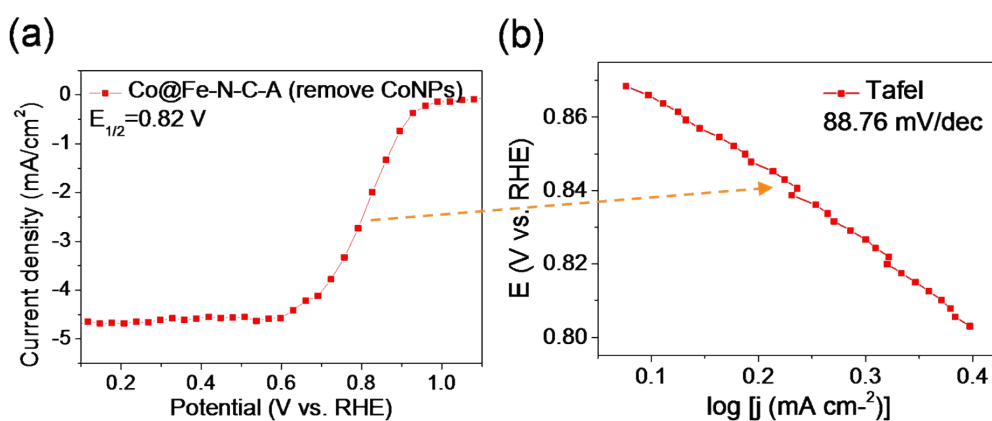


Figure S11. LSV curve and corresponding Tafel plot of Co@Fe-N-C-A (remove CoNPs).

Table S4. Summary of ORR performance parameters for Co@Fe-N-C, Co@Fe-N-C-A and Fe-N-C.

	Co@Fe-N-C	Co@Fe-N-C-A-	Fe-N-C
$E_{1/2}$	0.92 V	0.82 V	0.85 V
Tafel slope	80.26 mV/dec	88.76 mV/dec	95.05 mV/dec
Transfer electron number (n)	3.95	/	3.70
$H_2O_2\%$	3%	/	15%

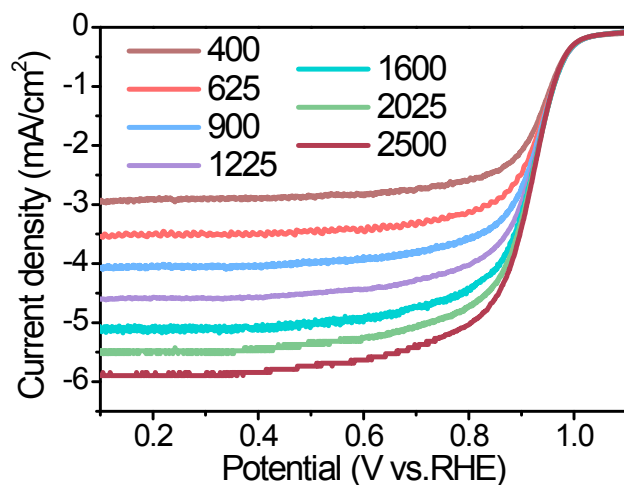


Figure S12. LSV curves of Co@Fe-N-C at various rotating rate from 400 to 2500 rpm in alkaline electrolyte.

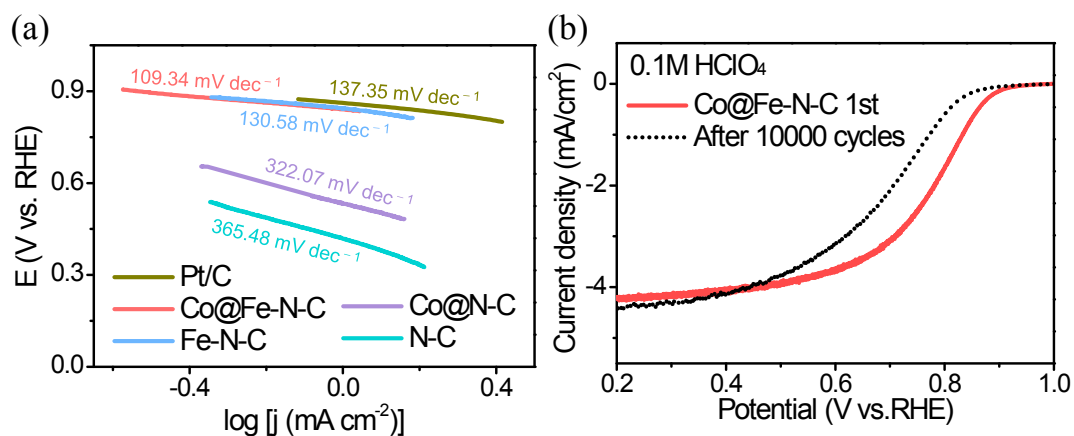


Figure S13. (a) Tafel curves of samples and (b) stability test of Co@Fe-N-C in 0.1 M HClO_4

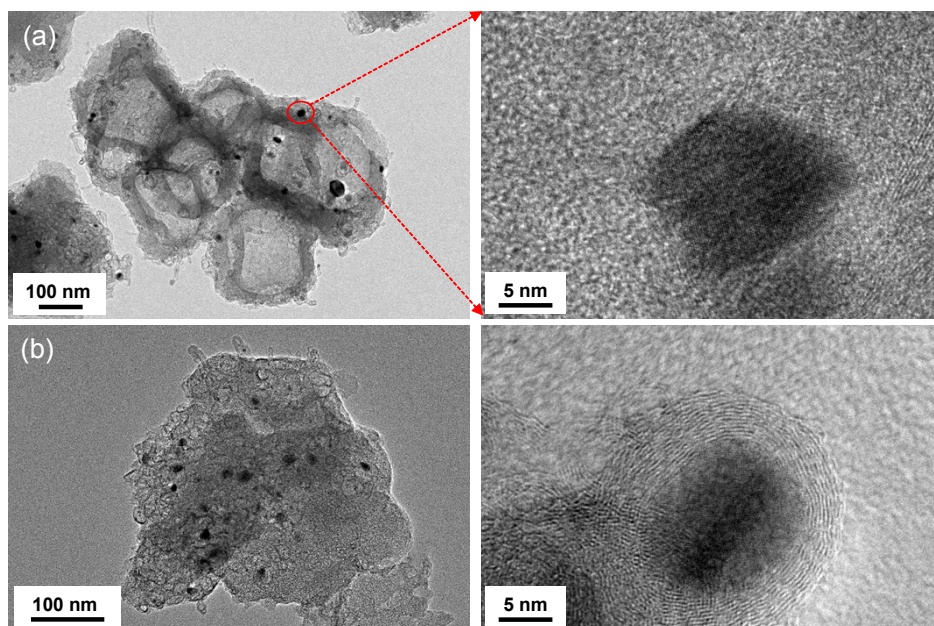


Figure S14. TEM images of Co@Fe-N-C after the (a) stability (10000 cycles) and (b) long-term durability tests.

Table S5. ORR performance of samples in other reported literature (alkaline electrolyte: 0.1 M KOH or 0.1 M NaOH)

Sample	Loading (mg cm ⁻²)	Eonset (V vs. RHE)	E _{half} (V vs. RHE)	References
FexN/N-CNT-GR	0.5	1.0	0.89	[1]
Fe _{0.5} Co _{0.5} Pc-CP	0.16	0.937	0.848	[2]
FeCo@N-GCNT-FD	0.48	0.96	0.88	[3]
Fe SAC/N-C	0.3	0.96	0.89	[4]
Fe-N ₄ SAs/NPC	0.5	0.972	0.885	[5]
Fe _{SA} -N-C	0.28	0.97	0.891	[6]
Fe-ISAs/CN	0.408	0.97	0.900	[7]
FeNCNs-800	0.36	0.95	0.89	[8]
FeCo-IA/NC	0.86	1.03	0.88	[9]
Fe2-Z8-C	0.4	0.902	0.871	[10]
Zn ₆ Co_Fe	0.5	1.01	0.89	[11]

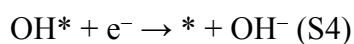
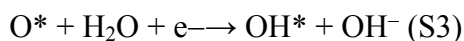
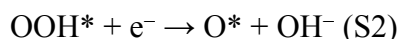
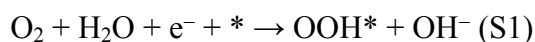
m-FePhen-C	0.816	0.98	0.901	[12]
Co@Co-N-C-A	0.204	0.90	0.85	[13]
Co@Fe-N-C	0.2	1.03	0.92	This work

Note: The catalyst loading that not given by literature are calculated values from their electrochemical testing parts. The onset potential that not given by literature are the approximate values that we observe from their LSV curves at the current density around 0.1 mA cm^{-2} .

SI3. DFT calculation

All density functional theory (DFT) calculations were performed using the Vienna *ab-initio* simulation package (VASP).^[14, 15] The interactions between valence electrons and ion cores were treated by Blöchl's all-electron-like projector augmented plane wave (PAW) method.^[16, 17] The generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) functional was adopted.^[18] The wave functions at each k -point were expanded. The plane-wave cutoff energy of 400 eV and Fermi-level smearing of 0.1 eV were applied throughout all the computations. Brillouin zone integration was approximated by a sum over special selected k -points using the $3 \times 3 \times 1$ Monkhorst-Pack sampling.^[19] The energy and the force were converged to 10^{-6} eV/atom and 10^{-2} eV/Å as the criterions of geometries optimization, respectively. The harmonic vibrational frequency calculations were performed to obtain the Zero Point Energy (ZPE) corrections. To consider the van der Waals (vdW) interaction, the DFT-D3 force-field approach was employed. A vacuum space of 15 Å is built to avoid the periodic interaction. The spin polarization was considered throughout the calculations due to the existence of magnetic atoms of Fe and Co. **Figure S15-S16** and **Figure S17** show the geometrical structures of the active center of Co@Fe-N-C and Fe-N-C, respectively, the single-atom active center is realized by embedding FeN₄-moiety into a carbon nanosheet (44 C atoms). To avoid the lattice mismatch as far as possible, the Co(100) plane was chosen as the exposed part for Co@Fe-N-C. A 4×4 supercell and three layers of Co(100) slab was constructed, where the most bottom layer of Co are fixed during the structure optimization.

In alkaline medium, the ORR may involve the following 4-electron steps:



According to the method developed by Nørskov et al.,^[20] the free energy change from initial states to final states of the reaction is calculated as follows:

$$\Delta G = \Delta E + \Delta ZEP - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_{field}$$

where ΔE is the total energy change obtained from DFT calculations, ΔZPE is the change in zero-point energy, T is room temperature (298.15 K), and the ΔS is the change in entropy. $\Delta G = -eU$, where U is the electrode potential with respect to standard hydrogen electrode, and e is the transferred charge. $\Delta G_{pH} = k_B T \ln 10 \times pH$, where k_B is the Boltzmann constant, and pH=14 for alkaline medium. ΔG_{field} is the free energy correction due to the electrochemical double layer and is neglected as in previous studies.^[21, 22] Gas-phase H₂O at 0.035 bar was used as the reference state, since at this pressure, the gas-phase H₂O is in equilibrium with liquid water at 298.15 K. The free energy of O₂ is obtained from the free energy change of the reaction $O_2 + 2H_2 \rightarrow 2H_2O$, which is -4.92 eV at 298.15 K and a pressure of 0.035 bar. The free energy of OH⁻ in solution is estimated by $\Delta G(H_2O) - 1/2\Delta G(H_2)$.

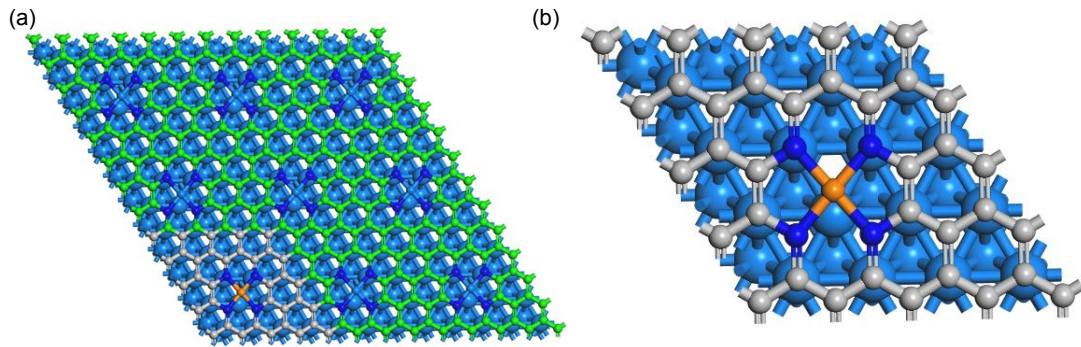
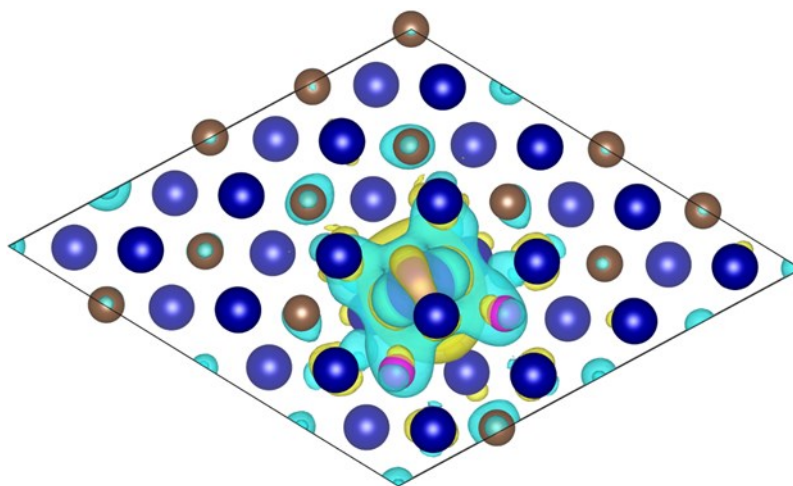
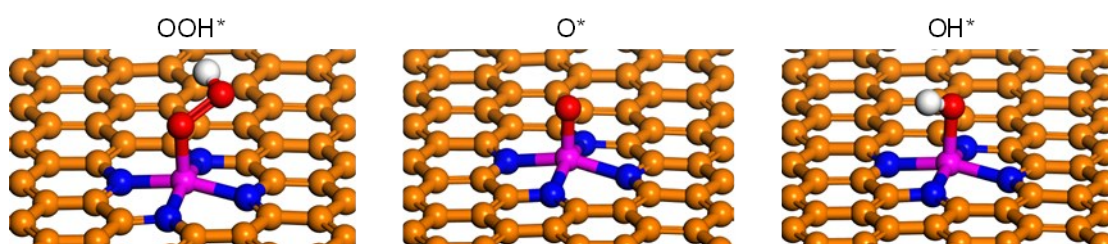
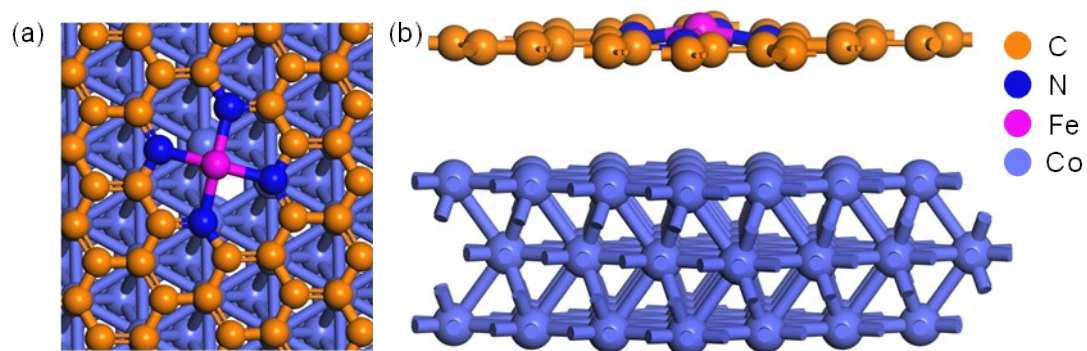


Figure S15 The (a) scheme and (b) magnified field of Co@Fe-N-C



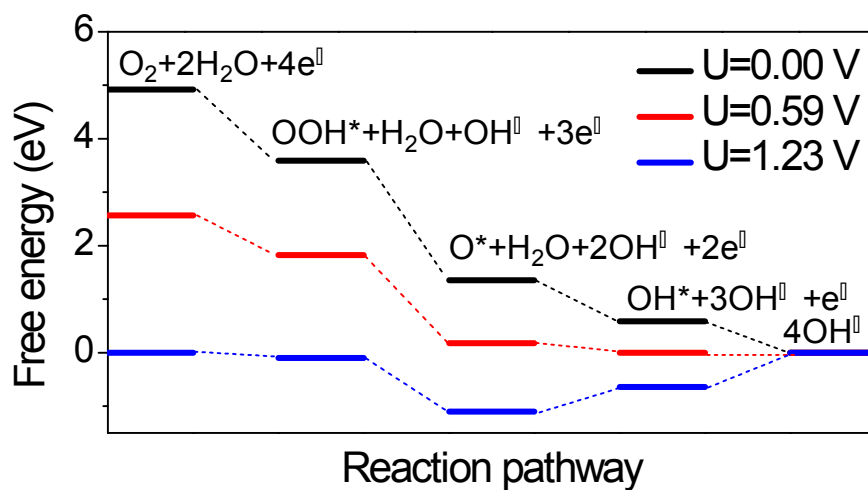


Figure S19. Free energy diagram of Fe-N-C.

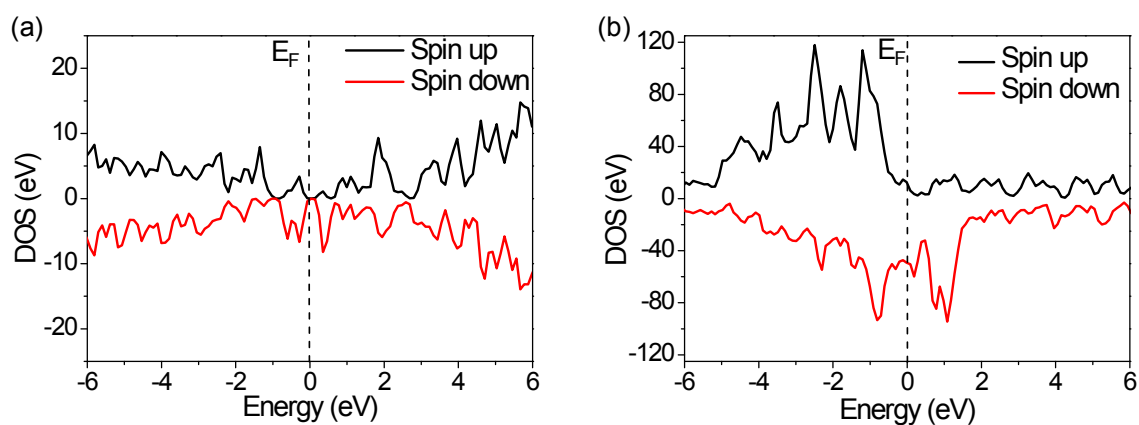


Figure S20. Fermi energy diagram of (a) Fe-N-C and (b) Co@Fe-N-C.

Table S6. Zero-point energy, and entropy contribution, and the total free energy correction of the molecules and ORR absorbates.

Species	E_{ZPE} (eV)	$-TS$ (eV)	$G-E_{\text{DFT}}$ (eV)
H_2	0.27	-0.41	-0.14
H_2O	0.56	-0.67	-0.11
OOH* on Fe-N-C	0.42	-0.25	0.17
OH* on Fe-N-C	0.33	-0.17	0.16
O* on Fe-N-C	0.06	-0.12	-0.06
OOH* on Co@ Fe-N-C	0.43	-0.18	0.25

OH* on Co@ Fe-N-C	0.35	-0.10	0.25
O* on Co@ Fe-N-C	0.07	-0.06	0.01

SI4. Effect of growth conditions on Co nanoparticles formation and catalytic activity

Co content should have significant impact on the performance of Co@Fe-N-C, samples of Co@Fe-N-C prepared with different Fe-ZIF: Co-ZIF ratio were investigated. Co@Fe-N-C that prepared with different mass ratios of Fe-ZIF-8 (100 mg) to Co-ZIF (50 mg, 100 mg, 200 mg, 300 mg) were used to investigate the impact of Co content on ORR activity. **Figure S21** showed hollow morphologies were observed for the samples formed with ratios of 2:1 and 1:1 and were not observed for 1:2 and 1:3 samples. And the optimal ratio of 1:2 had the most uniform Co nanoparticles and best ORR activity (**Figure S22**).

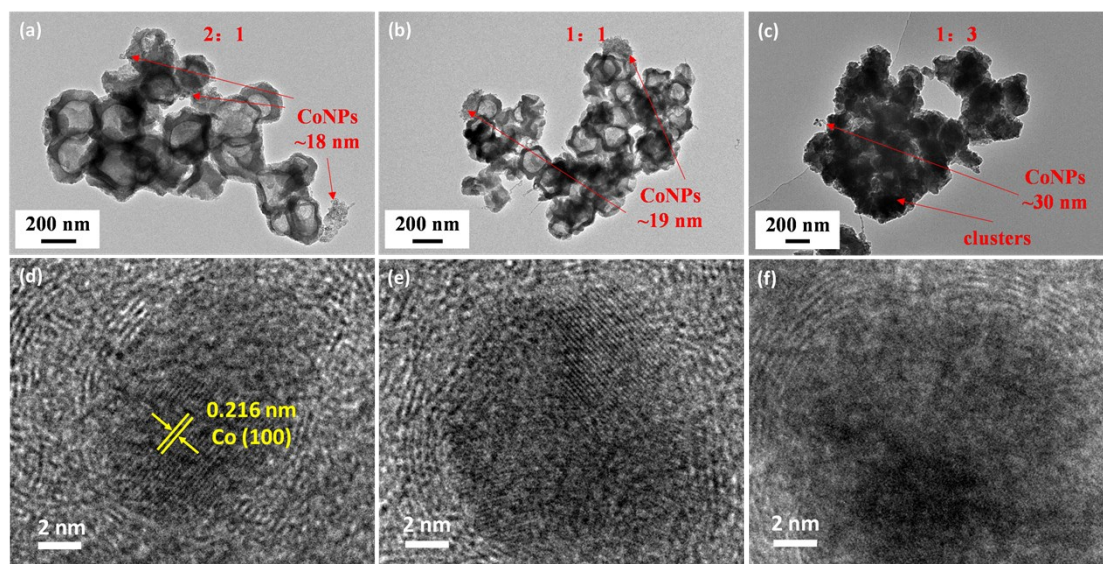


Figure S21. TEM and HRTEM of Co@Fe-N-C with different proportion of Fe-ZIF-8 to Co-ZIF, (a, d) 2:1 (b, e) 1:1 and (c, f) 1:3.

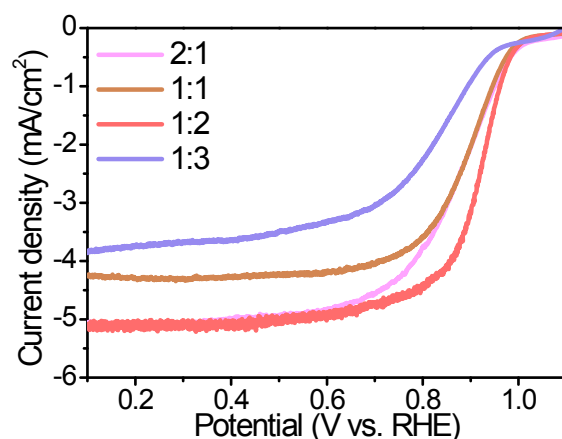


Figure S22. RDE LSV curves of Co@Fe-N-C with different proportion of Fe-ZIF-8 to Co-ZIF.

Table S7. ICP results of Co@Fe-N-C treated under different conditions.

Conditions	Metal	Contents (wt.%)
Fe: Co=2: 1	Fe	1.88
	Co	0.04
Fe: Co=1: 1	Fe	1.58
	Co	0.08
Fe: Co=1: 3	Fe	1.76
	Co	0.14
700 °C	Fe	0.79
	Co	0.04
800 °C	Fe	1.15
	Co	0.06
1000 °C	Fe	2.35
	Co	0.06
Low Ar flow	Fe	1.66
	Co	0.04
High Ar flow	Fe	1.22
	Co	0.01

Note: Table S5 showed the ICP results of Co@Fe-N-C treated under different conditions including Ar gas flow rate, mass ratio of Fe-ZIF to Co-ZIF, Fe contents. Fe and Co contents decreased at higher Ar gas flow rate which might increase the volatilization of Fe and Co. Proper mass ratio of Fe-ZIF to Co-ZIF did significant influence on the morphologies and catalytic performance of Co@Fe-N-C as discussed in manuscript.

The Co@Fe-N-C samples are prepared at different temperatures and are analyzed using TEM (**Figure S23**) and Raman spectroscopy (**Figure S24**). Raman spectroscopy reveals that I_G/I_D value increases from 0.97, 0.99, 1.16 to 1.22 as the temperature increases from 700, 800, 900 to 1000 °C, indicating higher heating temperature corresponded to higher graphitization degree. ORR catalytic activity results show the optimal Ar flow rate is 50 mL min⁻¹ (**Figure S25**).

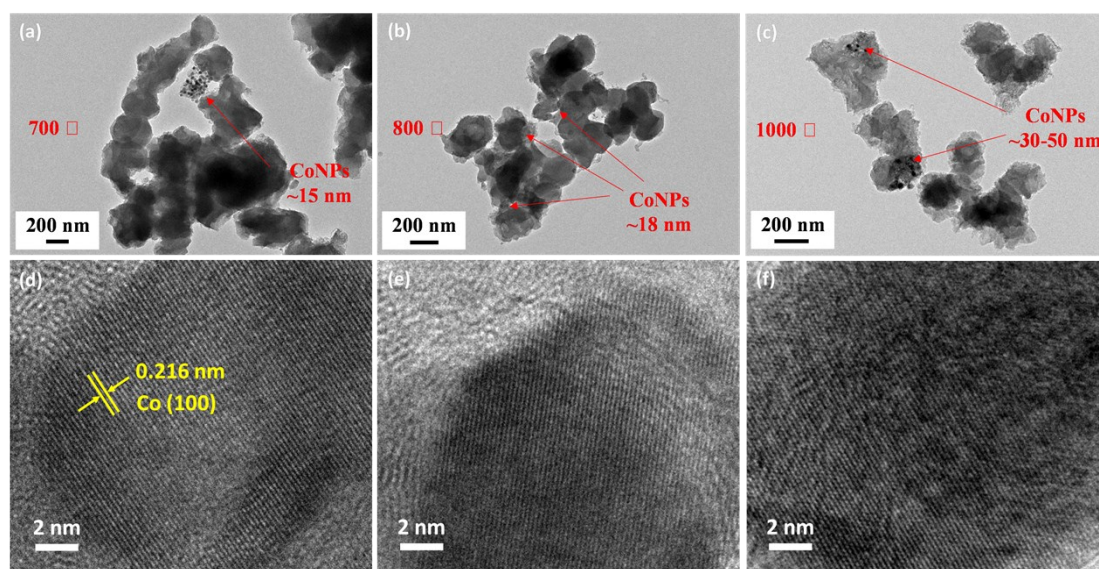


Figure S23. TEM and HRTEM of Co@Fe-N-C at different heating temperature, (a, d) 700 °C (b, e) 800 °C and (c, f) 1000 °C.

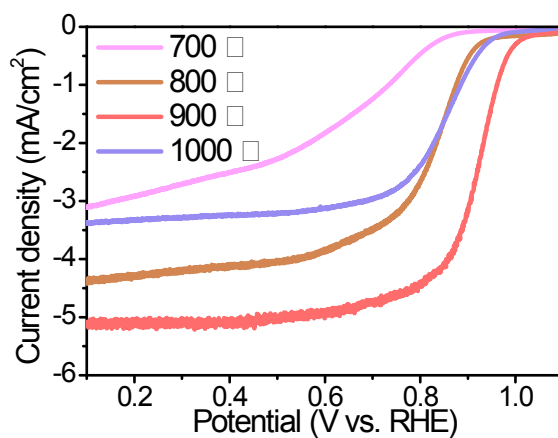


Figure S24. RDE LSV curves of Co@Fe-N-C at different treatment temperature from 700 to 1000 °C.

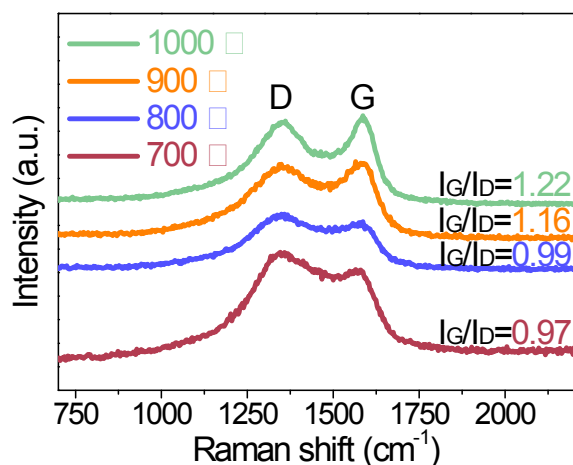


Figure S25. Raman curves of Co@Fe-N-C at different heating temperature from 700 to 1000 °C.

Samples of Co@Fe-N-C that prepared with different Ar flow rates are investigated. **Figure S26** showed a lot of black clusters (Co clusters) are observed on the surface of low flow rate (10 mL min⁻¹) one. However, no Co species were found in the high flow rate sample. As the Ar flow rate definitely affect the possibility of Co nanoparticles being loaded on the surface of Fe-N-C. Thus, the optimal Ar flow rate 50 mL min⁻¹ sample had the most uniform distribution of Co nanoparticles and enjoyed the best ORR activity (**Figure S27**).

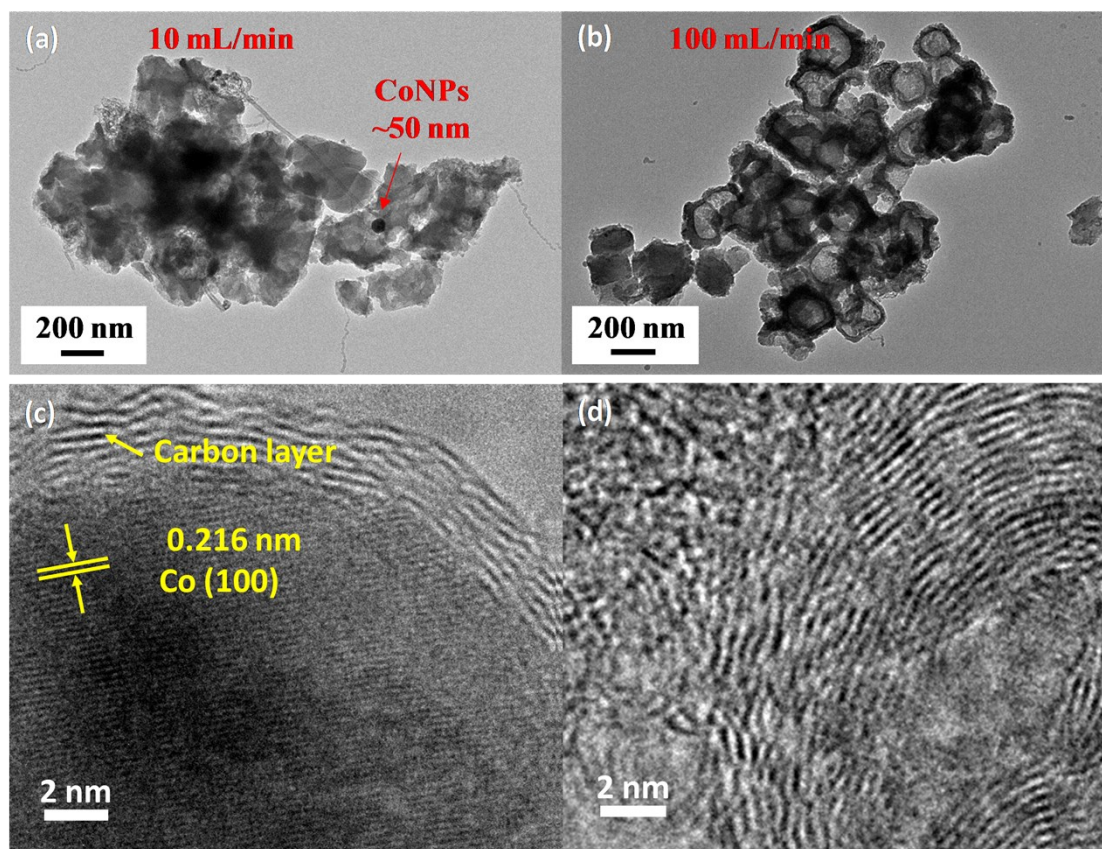


Figure S26. TEM and HRTEM of Co@Fe-N-C prepared with Ar flow rate of (a, c) 10 mL/min, (b, d) 100 mL/min.

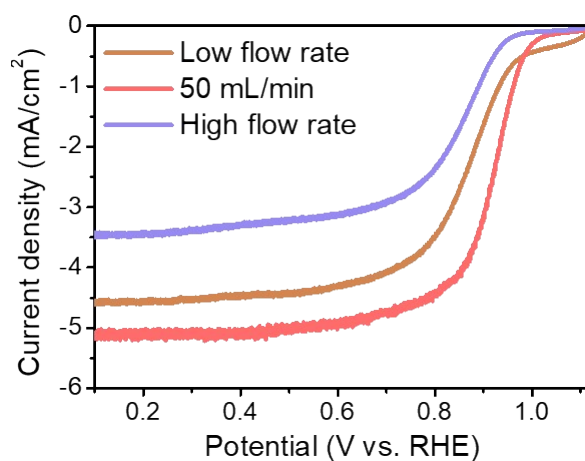


Figure S27. RDE LSV curves of Co@Fe-N-C with different Ar flow rate.

Table S8. The CoNPs density, sizes and corresponding ORR activity of Co@Fe-N-C treated at different condition

Sample	CoNPs density	CoNPs size	$E_{1/2}$ in 0.1 M KOH
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900 °C, Ar 50 mL/min, 1 : 2, Fe conten 1.20 wt. %	Optimal / high	~20 nm	0.92 V
700 °C	isolated	~ 15 nm	0.67 V
800 °C	low	~18 nm	0.82 V
1000 °C	general	~30-50 nm	0.84 V
Ar 10 mL/min	general	~20-50 nm	0.86 V
Ar 100 mL/min	none		0.82 V
2 : 1	low	~18 nm	0.85 V
1 : 1	general	~19 nm	0.86 V
1 : 3	agglomerates		0.82 V

Note: the CoNPs density ranges follows: agglomerates > high > general > low > isolated > none.

References

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