Supporting Information

Isolated Fe and Co dual active sites on nitrogen-doped carbon for highly efficient oxygen reduction reaction.

Diyang Zhang, †[a] Wenxing Chen, †[a] Zhi Li, *[a] Yuanjun Chen [a], Lirong Zheng,[b] Yue Gong [c], Qiheng Li [a], Rongan Shen [a], Yunhu Han[a], Weng-Chon Cheong [a], Lin Gu [c] and Yadong Li*[a]

1.Experimental method

Chemicals

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$,99%), 2-Methylimidazole (98%), Nafion, and commercial Pt/C (20 wt% metal) were purchased from Alfa Aesar (China). Iron(III) 2,4-pentanedionate ($Fe(acac)_3$, 99%) and Cobalt(III) 2,4-pentanedionate ($Co(acac)_3$, 99%) were obtained from Aladdin Industrial Corporation. Methanol A.R and KOH A.R were bought from Beijing Chemical Works. All the chemicals were used without further purification.

Synthesis of ZIF-8

In a common synthsis, $Zn(NO_3)_2 \cdot 6H_2O$ (21.38g) was dissovled in 300ml methanol in flask A with stirring and 2-Methylimidazole (23.22mg) was dissolved in 200ml methanol in flask B with stirring. After A and B formed clear solution, B flask was added into flask A. Subsequently, flask A was sealed with plastic wrap and stirred for 24h under room temperature. The as-prepared products were centrifuged and washed with methanol three times, then dried in vacuum at 30℃ for several hours.

Synthesis of CN support

ZIF-8 powder was placed in a ceramic boat, which was subsequently transferred in a tube furnace and heated to 900°C for 2h with a heating rate of 5 ℃/min under flowing Ar gas. After that the sample was cooled to room temperature, naturally. The as-obtained products were grinded in the pestle.

Synthesis of Fe-ISAs/CN

$Fe(acac)_3$ (12.65mg) was dissolved in 1ml methanol in test tube A. 400mg CN support was dispersed in 80ml methanol in flask A under ultrasound for 20min and vigorously stirred for 10min. Then, test tube A was added into flask A at room temperature under constant stirring for 24h. After that, the precursor ($Fe(acac)_3$@CN) was separated by centrifugation and washed with methanol three times, then dried in vacuum at 30℃ for several hours. Finally, the as-prepared $Fe(acac)_3$@CN was transferred in a tube furnace and heated to 900°C for 2h with a heating rate of 5 ℃/min under flowing Ar gas. The

sample was cooled to room temperature, naturally. The as-obtained Fe-ISAs/CN were grinded in the pestle.

Synthesis of FeCo-ISAs/CN

$Co(acac)_3$ (19.2mg) was dissovled in 2ml methanol in test tube A. 150mg Fe-ISAs/CN was dispersed in 30ml methanol in flask A under ultrasound for 20min and vigorously stirred for 10min. Then, test tube A was added into flask A at room temperature under constant stirring for 24h. After that, the precursor ($Co(acac)_3$@ Fe-ISAs/CN) was separated by centrifugation and washed with methanol three times, then dried in vacuum at 30℃ for several hours. Finally, the as-prepared $Co(acac)_3$@ Fe-ISAs/CN was transferred in a tube furnace and heated to 900°C for 2h with a heating rate of 5 ℃/min under flowing Ar gas. The sample was cooled to room temperature, naturally. The as-obtained FeCo-ISAs/CN were grinded in the pestle.

Synthesis of Co-ISAs/CN

$Co(acac)_3$ (51.2mg) was dissolved in 3ml methanol in test tube A. 400mg CN support was dispersed in 80ml methanol in flask A under ultrasound for 20min and vigorously stirred for 10min. Then, test tube A was added into flask A at room temperature under constant stirring for 24h. After that, the precursor ($Co(acac)_3$@CN) was separated by centrifugation and washed with methanol three times, then dried in vacuum at 30℃ for several hours. Finally, the as-prepared $Co(acac)_3$@CN was transferred in a tube furnace and heated to 900°C for 2h with a heating rate of 5 ℃/min under flowing Ar gas. The sample was cooled to room temperature, naturally. The as-obtained Co-ISAs/CN were grinded in the pestle.

Electrochemical Measurement

The electrochemical measurements were carried out by a CHI 660 electrochemical workstation with a traditional three-electrode system in 0.1M KOH. A rotating disk electrode (RDE) of 5mm in diameter covered by the ink was used as working electrode. A Ag/AgCl (3.5M KCl solution) electrode and a carbon rod were served as reference and counter electrode, respectively. Catalysts inks we used in the electrochemical

measurements were prepared by dispersing 5mg of catalyst powder in 1ml ethanol and 20μl 5% Nafion solution and then sonicating for 30 min to form homogeneous catalyst inks. Then, dropping the catalyst inks onto the glassy carbon (GC) disk of the rotating disk electrode (RDE) or rotating ring disk electrode (RRDE) to obtain a loading of 0.408 mg_{metal} cm^{-2} nonprecious catalyst and 0.102 mg_{Pt} cm^{-2} Pt/C. Before the tests, a O_2 flow was bubbled through the electrolyte in the cell for 20min to made sure the O_2 in the solution was saturated. Cyclic Voltammetry (CV) with a sweep rate of 100 mV s^{-1} between 0.7 V (vs RHE) to 1.1 V (vs RHE) for 5000 circles in O_2 saturated 0.1 M KOH electrolyte was used to test the durability of FeCo-ISAs/CN and Pt/C. The ORR polarization curves were obtained after 5000 cycles. All the tests were run in O_2-saturated 0.1 M KOH under room temperature with a sweep rate of 10 mV s^{-1}.

The result of electron transfer number(n) was calculated from Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K}$$

$$\mathrm{B} = 0.62\mathrm{n}FC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

In this equation, J, J_K and J_L are the measured current density, kinetic current density and limiting current density, respectively. ω is the angular velocity of the disk, n is the electron transfer number. F (96485 C mol^{-1}), C_0 (1.2×10^{-6} mol cm^{-3}) and D_0 (1.9×10^{-5} cm^2 s^{-1}) are the Faraday constant, bulk concentration of O_2 and the diffusion coefficient of O_2 in 0.1 M KOH, respectively. V (0.01 cm^2 s^{-1}) is the kinematic viscosity of the electrolyte.

The following equation was the method that we used to calculate the hydrogen peroxide yield (H_2O_2%) and the electron transfer number (n):

$$H_2O_2\,\% = 200 \times \frac{\frac{I_R}{N}}{I_D + \frac{I_R}{N}}$$

$$n = 4 \times \frac{I_D}{\frac{I_R}{N} + I_D}$$

In above equation, I_D and I_R are the disk current and ring current. The value of N is 0.4 that is the collection efficiency of the Pt ring on the rotating ring disk electrode (RRDE). The intrinsic activity data came from calculation of Turnover Frequencies (TOFs) at 0.88V (vs RHE). TOFs of the FeCo-ISAs/CN and Fe-ISAs/CN catalysts were calculated from the equations:

$$TOF\ (FeCo\text{-}ISAs/CN) = \frac{J \times S}{4 \times F \times (n_{Fe} + n_{Co})} = 0.943$$

$$TOF\ (Fe\text{-}ISAs/CN) = \frac{J' \times S}{4 \times F \times n'_{Fe}} = 0.755$$

$$n_{Fe} = 0.964\% \times \frac{0.08mg}{56g/mol} = 1.38 \times 10^{-8} mol$$

$$n_{Co} = 0.218\% \times \frac{0.08mg}{58.9g/mol} = 2.96 \times 10^{-9} mol$$

$$n'_{Fe} = 0.555\% \times \frac{0.08mg}{56g/mol} = 7.93 \times 10^{-9} mol$$

In this equation, J, J' are the current density at 0.88V (vs RHE) of catalysts, respectively. S (0.252 × π) and F (96485 C mol-1) are the area of RDE and the Faraday constant. 0.964%, 0.218% and 0.555% come from the results of ICP-OES and 0.08mg is the loading of the catalyst on the RDE.

Characterizations

TEM images were imaged by a Hitachi H-800 transmission electron microscope working at 100 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were performed on a JEOL JEM-2100F field-emission transmission electron microscope. The atomic-resolution spherical aberration corrected Scanning Transmission Electron Microscope (AC-STEM) characterization was performed using a probe aberration-corrected microscope, JEMARM200F equipped with cold emitter, operated at 200kV. The attainable spatial resolution of this microscope is 78 pm. The XRD results were record on a Rigaku RU-200b X-ray powder diffractometer (XRD) with Cu Kα radiation (λ=1.5406 Å).

X-ray photoelectron spectroscopy (XPS) results were performed by Thermo Fisher Scientific ESCALAB 250Xi XPS System in Tsinghua university material college. Fe and Co content in the samples were conducted on the inductively coupled plasma optical emission spectrometry (ICP-OES).

XAFS spectra at the Fe K-edge and Co K-edge were recorded by the beamline 1W1B station of the Beijing Synchrotron Radiation Facility, China. The Fe K-edge and Co K-edge XANES data were performed from a fluorescence mode. Fe foil, Co foil, Fe_2O_3 and Co_3O_4 were used as references.

2. Supplemental Figures and Tables

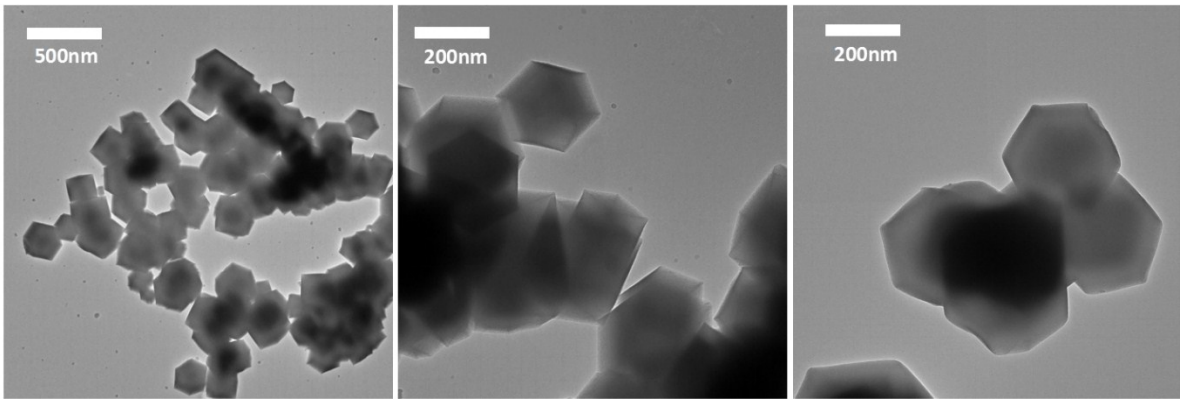


Figure S1. TEM of ZIF-8 derived CN.

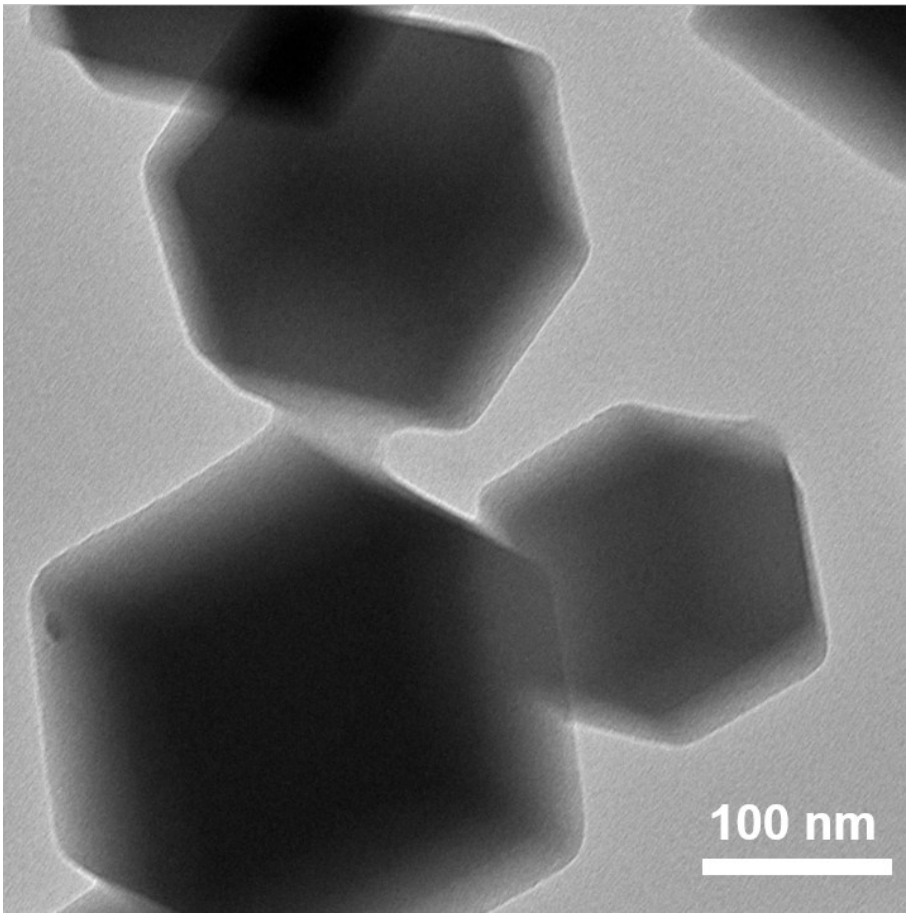


Figure S2. TEM image of ZIF-8

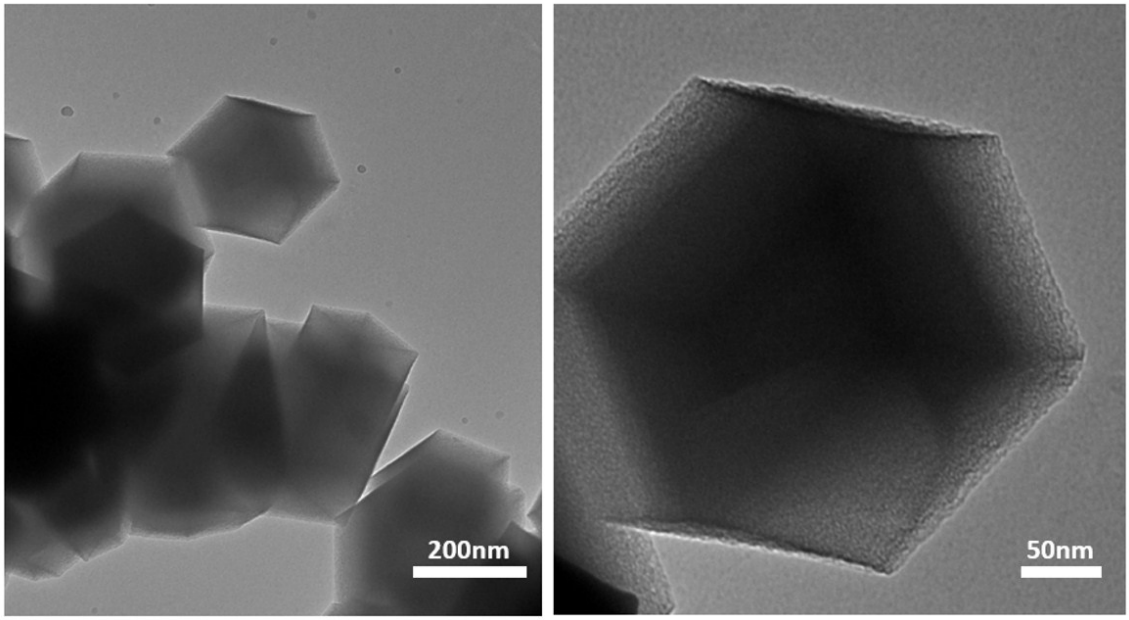


Figure S3. TEM for FeCo-ISAs/CN.

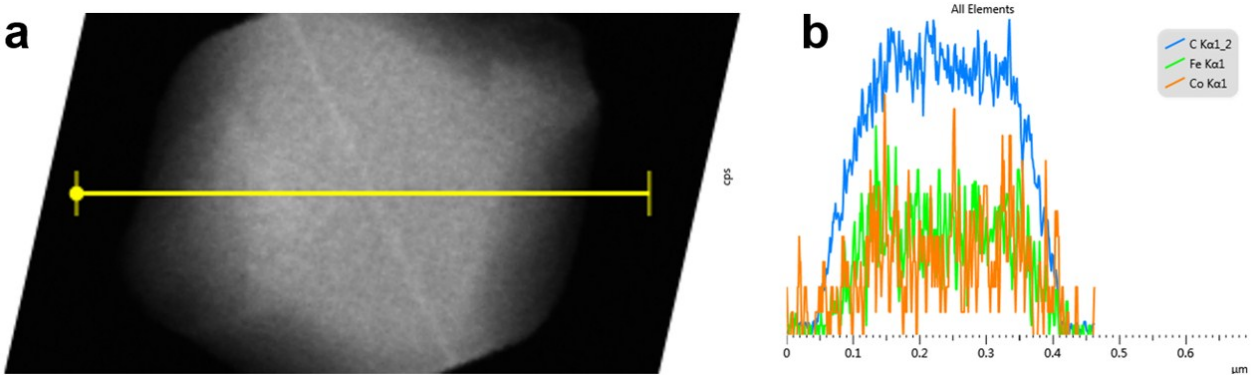


Figure S4. EDS lines scanning profile for FeCo-ISAs/CN.

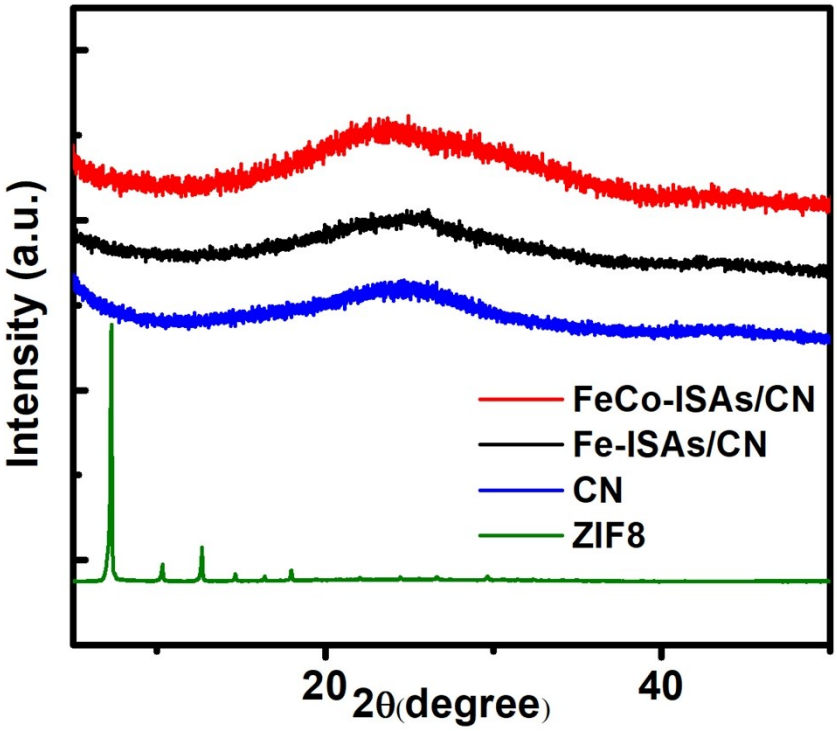


Figure S5. XRD patterns of the ZIF-8 and the samples.

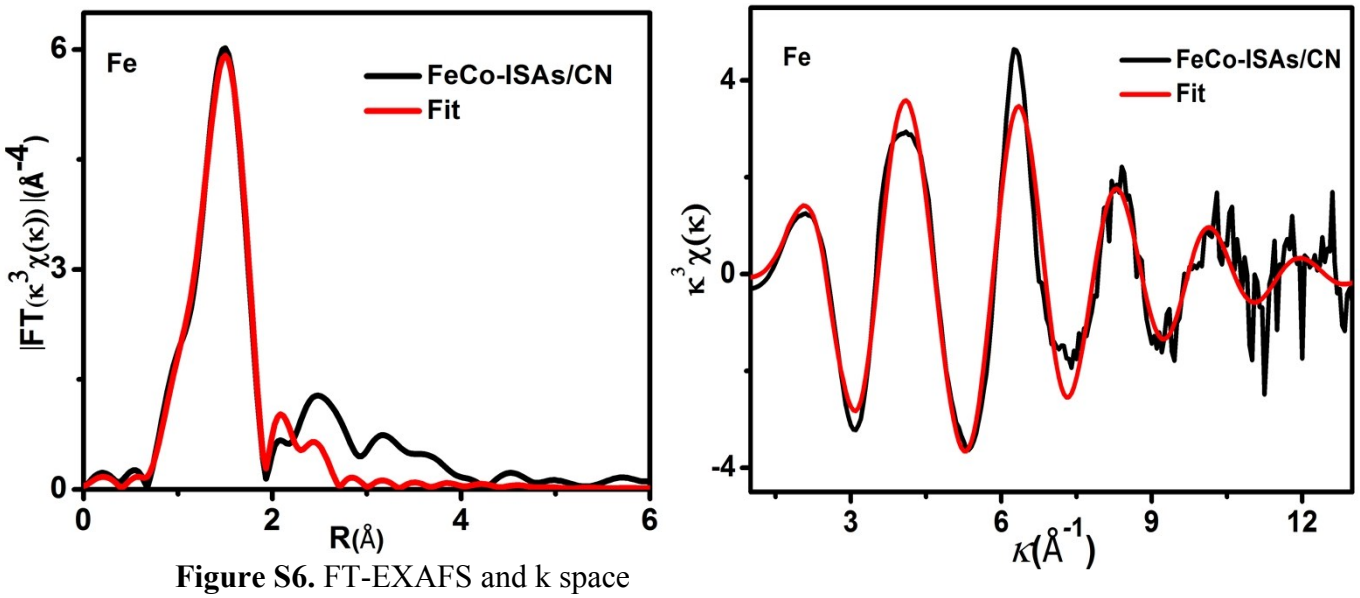


Figure S6. FT-EXAFS and k space fitting curves of the FeCo-ISAs/CN at Fe K-edge.

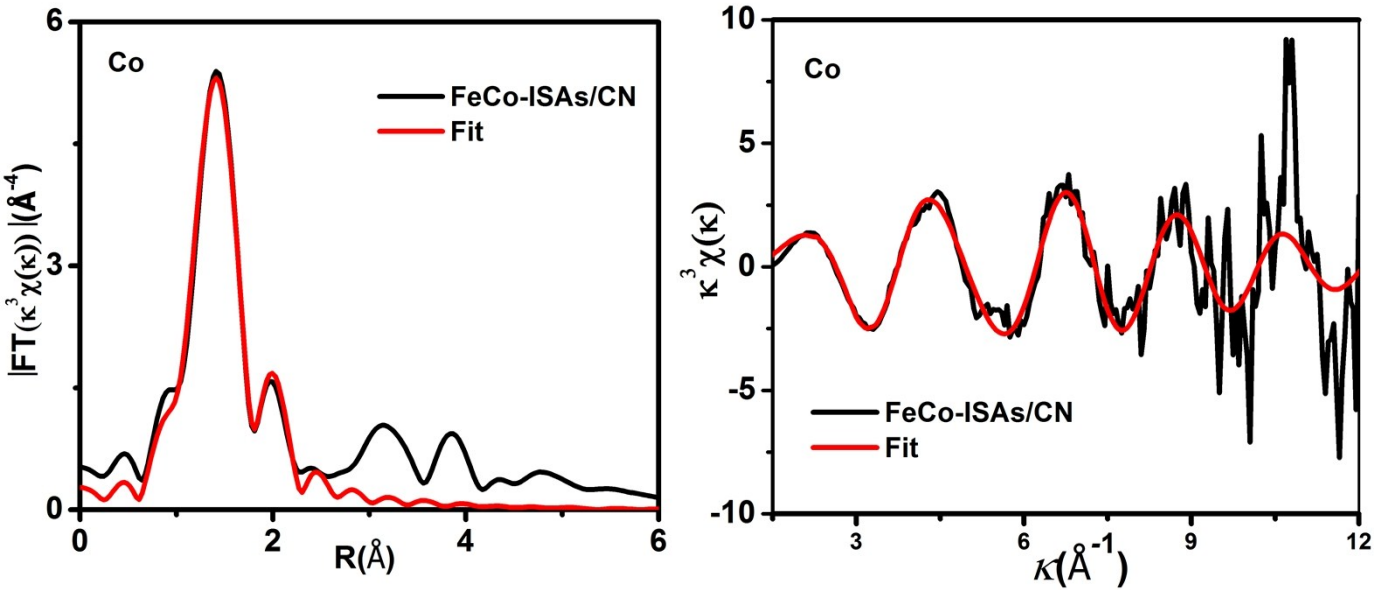
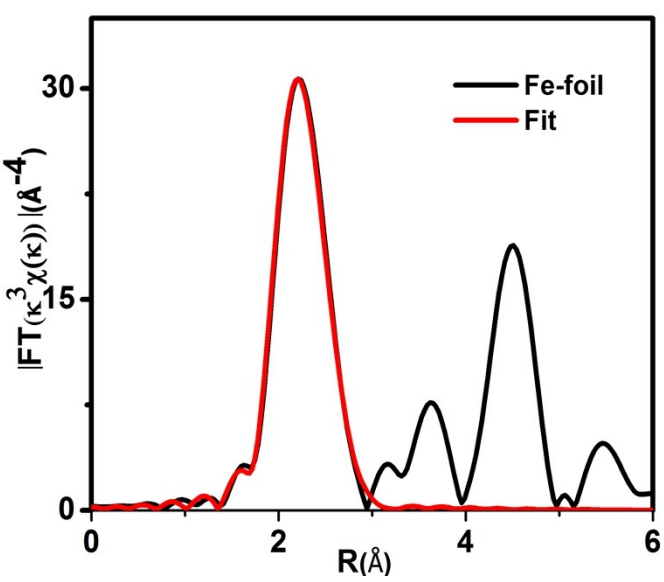


Figure S7. FT-EXAFS and k space fitting curves of the FeCo-ISAs/CN at Co K-edge.



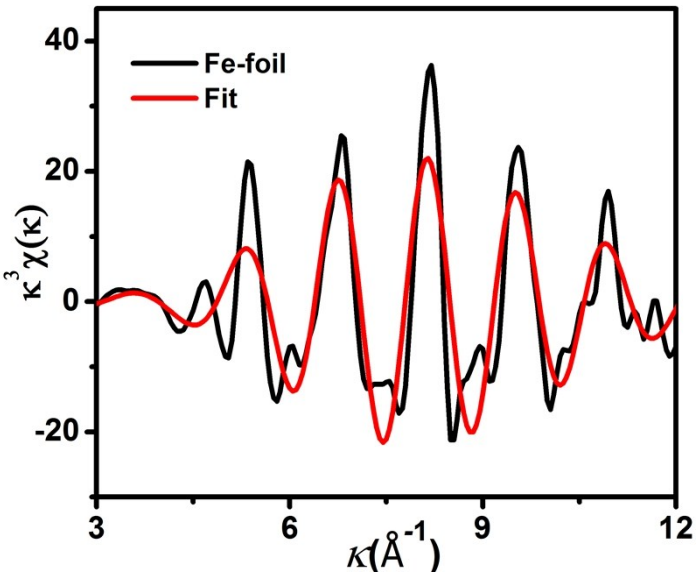


Figure S8. FT-EXAFS and k space fitting curves of the Fe-foil at Fe K-edge.

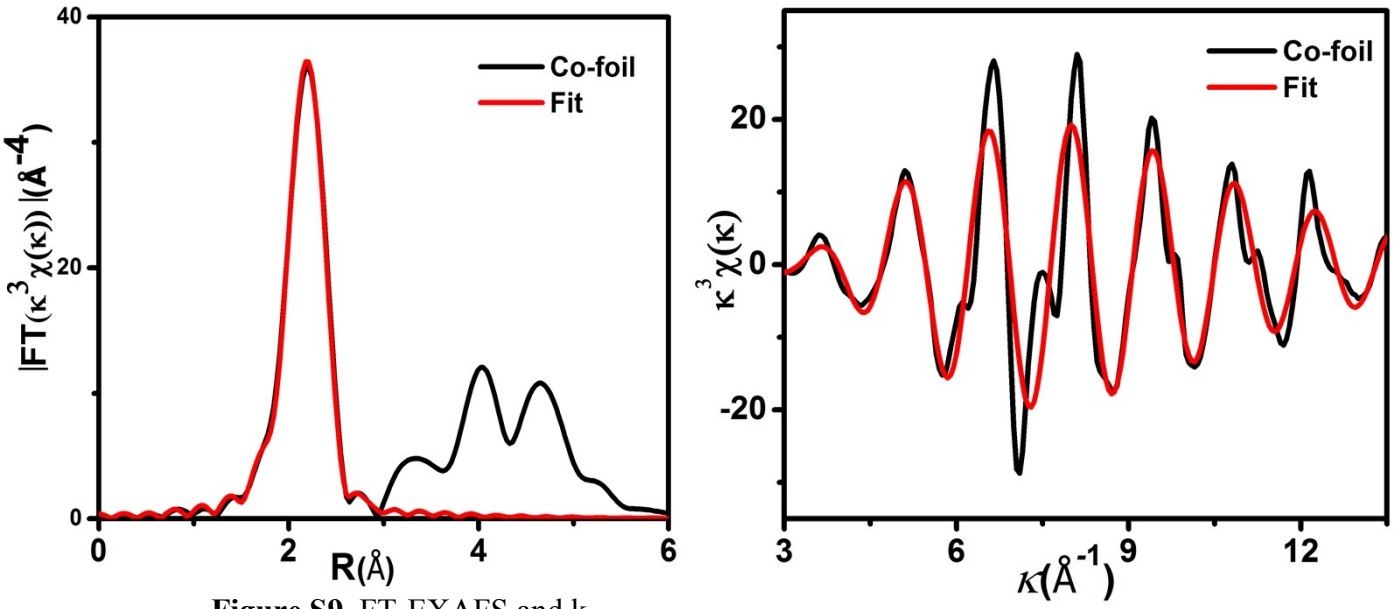


Figure S9. FT-EXAFS and k space fitting curves of the Co-foil at Co K-edge.

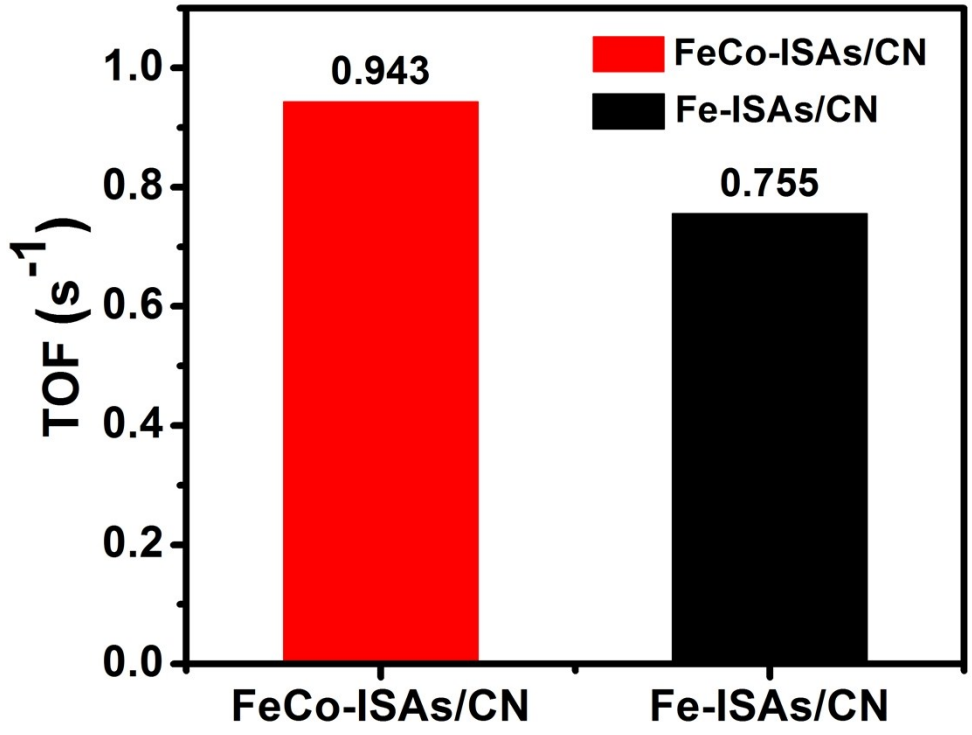


Figure S10. TOF of FeCo-ISAs/CN and Fe-ISAs/CN at 0.88 V.

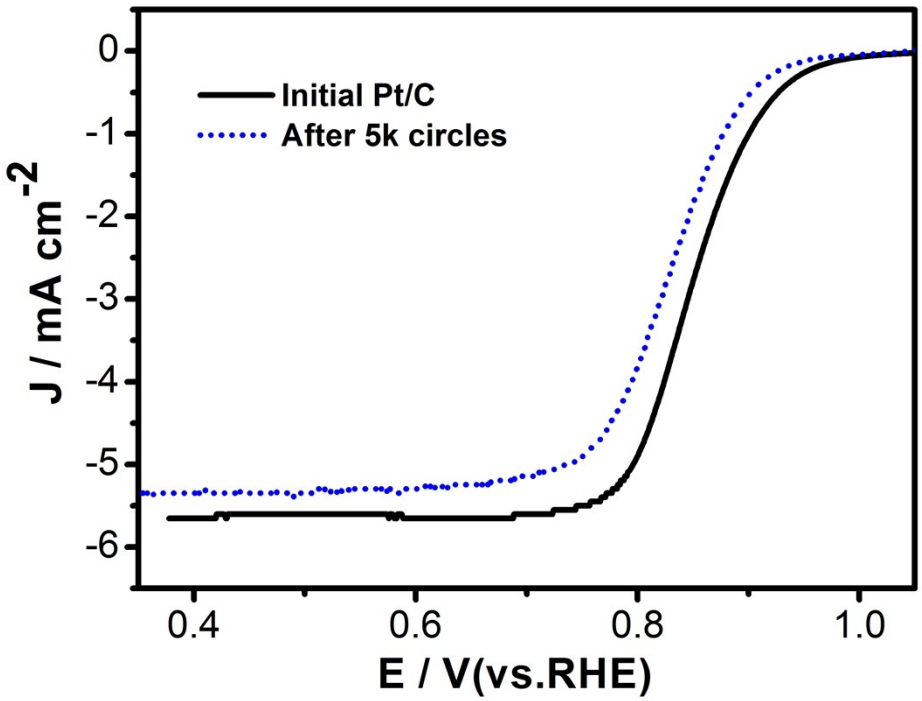


Figure S11. ORR polarization curve of Pt/C before and after 5000 cycles.

Table S1. Structural parameters extracted from the Co and Fe K-edge EXAFS fitting of FeCo-ISAs/CN. (S_0^2=0.86)

sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}Å^2)$	ΔE_0(eV)	R factor
Sample-Co	Co-N/C	3.8	1.96	7.9	-3.1	0.0034
Co foil	Co-Co	12*	2.49	5.4	6.8	0.0039
Sample-Fe	Fe-N/C	4.1	1.97	4.4	2.7	0.0052
Fe foil	Fe-Fe_1	8*	2.45	4.5	4.3	0.0036
	Fe-Fe_2	6*	2.84	4.1	3.9	

S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

* This value was fixed during EXAFS fitting, based on the known structure of Pd foil and PdO.

Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as N ± 20%; R ± 1%; σ^2 ± 20%; ΔE_0 ± 20%.

Table S2. The details of onset (E_{onset}) at 0.12mA cm^{-2} , and half-wave ($E_{1/2}$) potentials and J_k at 0.88V.

Electrocatalysts	E_{onset} (V vs RHE)	$E_{1/2}$ (V vs RHE)	J_k (mA/cm^2)
FeCo	0.995	0.920V	31.1
Fe	0.971	0.899	11.8
PtC	0.94	0.85	2.1

Table S3. Comparison of ORR performance between FeCo-ISAs/CN and other Fe Co based catalysts reported in the literatures under O_2-saturated 0.1 M KOH.

Class	Electrocatalysts	$E_{1/2}$ (V vs RHE)	J_k (mA/cm^2)	Loading (mg/cm)	Ref.
	FeCo-ISAs/CN	0.920	31.1 at 0.88V	0.408	This work
	Fe-ISAs/CN	0.900	37.83 at 0.85V	0.408	Angew. Chem. Int . Ed. 2017, 56, 1
	Fe@C-FeNCs-2	0.899	41.6 at 0.8 V	0.700	J. Am. Chem. Soc. 2016, 138, 3570
	FP-Fe-TA-N-850	0.820	7.8 at 8.0V	0.300	Angew. Chem. Int. Ed. 2016, 55, 1 355
	(Fe,Mn)-N-C	0.900	36.8 at 0.8 V	0.800	Nat. Commun.2015, 6, 8618.
Fe-Co based	{Co}[FeCo]O_4/NG	0.866	4.46 at 8.5V	0.600	Angew. Chem. 2016, 128, 1362
	FeCo/C-800	0.820	-	0.200	Adv. Mater. 2015, 27, 3431
Co based	Co SAs/N-C(900)	0.881	21.2 at 8.0V	0.408	Angew. Chem. Int. Ed. 2016, 55, 10800
	CoP-CMP800	0.790	-	0.600	Adv. Mater. 2014, 26, 1450.
	$MnCo_2O_4$/N-rmGO	0.880	-	0.100	J. Am. Chem. Soc. 2012, 134, 3517