Supporting Information

Fe_1N_4 - O_1 site with axial Fe-O coordination for high-selective CO_2

reduction over wide potential range

Chen et al.

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Experimental Procedures.

Materials and Chemicals

Iron Porphyrin (FePor, $C_{34}H_{32}ClFeN_4O_4$, 98%, Adamas), L-Alanine ($C_3H_7NO_2$, 99%, Adamas), Sodium carbonate (Na_2CO_3 , 99.8%, Innochem), N, N-Dimethylformamide (DMF, C_3H_7NO , 99.9%, Innochem), 18.2M Ω cm ultrapure water was obtained from milli-Q system. All the chemicals were used as received without any purification.

Material synthesis

Synthesis of CONP and CONP-30. The carbonaceous O, N-coordinated pre-support (CONP) sample were synthesized with a molten-salt assisted method, simply by fast pyrolysis of L-alanine in the molten-salt of sodium carbonate. Sodium carbonate melts at the temperature as high as 851°C, stable at high temperatures, soluble in water. Therefore, when sodium carbonate is used as template agent, the specific surface area of graphitized carbonaceous materials can be increased, but also after graphitization, sodium carbonate is easy to be washed away without residual impurities. Typically, 10 g mixtures of L-alanine and sodium carbonate (molar ratio, 1:4) were placed in a tube furnace, heated to 980 °C in 0.5 h and maintained for 1 minute under flowing N₂ gas. After rapidly cooling to room temperature in 40 mins, the collected product was further purified by washing with 18.2 M Ω cm ultrapure water to remove sodium carbonate following by a drying process at 80 °C for 5 h. The obtained sample was defined as CONP. The CONP-30 sample was synthesized by the similar method, except the maintaining time is 30 min after the mixture of L-alanine and sodium carbonate were

placed in a tube furnace, heated to 980 °C in 0.5 h under flowing N₂ gas.

Synthesis of CON_{400} , CON_{400} -30 and CN_{600} . The as-obtained CONP and CONP-30 powder was placed in a tube furnace. The CON_{400} and CON_{400} -30 samples was obtained when the CONP and CONP-30 powder heated to 400 °C for 3 h with the heating rate of 3 °C•min⁻¹ under flowing N₂ gas. The CN_{600} sample can be obtained when the CONP powder heated to 600 °C for 3 h with the heating rate of 3 °C•min⁻¹ under flowing 5% H₂/Ar gas. Then the CON₄₀₀ and CN₆₀₀ graphene nanosheet samples were directly used without any post-treatment after cooling to room temperature.

Synthesis of Fe-CON₄₀₀. In a typical synthesis of Fe-CON₄₀₀, 50 mg of CON₄₀₀ powder and 40 mg of Iron Porphyrin (FePor) were mixed in 40 mL of DMF, respectively. The above two mixtures were dispersed by sonication for at least 1 h. Then, FePor-DMF dispersion solution was added to the CON₄₀₀-DMF suspension drop by drop. The mixed suspension was further stirred for 24 h at room temperature. After vacuum filtration and washed with DMF for many times until colourless, the Fe-CON₄₀₀ sample can be obtained by a dry process in a vacuum oven at 60 °C for 12 h.

Synthesis of Fe-CON₄₀₀-x (x = 100, 200, 300, 400, 500, 600, 800, 1000). Typically, the powder of Fe-CON₄₀₀ was placed in a tube furnace, kept at desired temperature (100, 200, 300, 400, 800, 1000) for 2 h with a heating rate of 3 °C min⁻¹ under flowing N₂ gas, and then naturally cooled to room temperature. The Fe-CON₄₀₀-x (x = 100, 200, 300, 400, 500, 600, 800, 1000) samples were directly used without any post-treatment.

Synthesis of FePor-400 and Fe-CN₆₀₀-400. The synthesis methods of FePor-400 and Fe-CN₆₀₀-400 samples are similar to that of Fe-CON₄₀₀-400 sample, except without

support for FePor-400 and CN₆₀₀ support for Fe-CN₆₀₀-400.

Catalyst Characterizations.

X-ray diffraction pattern (XRD) was carried out with a Rigaku D/max 2500Pc X-ray powder diffractometer with monochromatized Cu K α radiation ($\lambda = 1.5418$ Å). Scanning electron microscope (SEM) was performed on a Hitachi S-4800 electron microscope. Transmission electron microscope (TEM) was operated by a Hitachi-7700 working at 100 kV. High resolution TEM (HRTEM) was carried out by a FEI Tecnai G2 F20S-TWIN HRTEM working at 200 kV. Atomic resolution HAADF-STEM images were obtained by using a Titan 80-300 scanning/transmission electron microscope operated at 300 kV, equipped with a probe spherical aberration corrector. Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on Thermo Fisher IRIS Intrepid II. X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI Quantera microscope. The binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.8 eV. Laser confocal Raman spectrometer was operated on a HR-800. N₂ adsorption-desorption experiments were carried out at 77 K on a Quantachrome SI-MP Instrument. Prior to the measurement, the samples were degassed at 300 °C. The surface area of the samples was estimated by method of Brunauer-Emmett-Teller (BET) and the estimation of the distribution of mesoporous and microporous was made by application of the Barrett-Joyner-Halenda (BJH) method to the adsorption data. X-ray absorption spectra were collected at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF, Beijing).

XAFS measurements.

The XAFS spectra were obtained at 1W1B station in BSRF (Beijing Synchrotron Radiation Facility, P. R. China) operated at 2.5 GeV with a maximum current of 250 mA. XAFS measurements at Fe K-edge were performed in fluorescence mode using a Lytle detector. All samples were pelletized as disks of 13 mm diameter with 1mm thickness using graphite powder as a binder.

EXAFS analysis.

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages¹. The EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge jump step. Then, $\chi(k)$ data in the k-space ranging from 2.5 to 12.25 Å⁻¹ were Fourier transformed to real (R) space using hanning windows (dk = 1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells. The quantitative information can be obtained by the leastsquares curve fitting in the R space with a Fourier transform k space range of 2.5 to 12.25 Å⁻¹, using the module ARTEMIS of programs of IFEFFIT. The backscattering amplitude F(k) and phase shift $\Phi(k)$ were calculated using FEFF8.0 code.

Catalytic performance test.

The H-type cell was used as the electrolyzer for CO₂ electrochemical reduction

reaction by linear sweep voltammetry (LSV) in CO₂-saturated 0.1 M NaHCO₃ solution. Nafion 117 membrane was inserted between the anodic and cathodic chambers. CO₂saturated 0.1 M NaHCO₃ solution was obtained by bubbling CO₂ to the sodium bicarbonate aqueous solution overnight. To prepare the working electrode, 100 µl ink prepared by dispersing 4 mg sample and 60 µl Nafion solution into 0.94 ml ethanol solution. Then 12.5 µl ink was loaded onto a carbon paper with 0.5 square centimeter area. Pt wire and Ag/AgCl was used as counter electrode and reference electrode respectively. The CO_2 flow rate was set at 27.4 sccm by a mass flow controller. The Princeton PMC-500 electrochemical workstation was used to conduct the LSV curses with scan rate of 10 mV/s. The electrochemical impedance spectroscopy (EIS) experiments were conducted at the potential of 5 mV vs open circuit potential. All the potential were reported with respect to the reversible hydrogen electrode (RHE). According to the previous literatures², the automatic iR compensation (85%) was used. The chronoamperometry tests were conducted at each potential for 15 min. The gas products of electrolysis were detected on the Shimazu 2010 plus gas chromatography equipped with BID detector and Shin Carbon ST 100/120 packed column. High purity helium (99.999%) was used as the carrier gas for the chromatography. The liquid products of electrolysis were analyzed by Bruker Avance III HD 400 NMR. The Faraday efficiency (FE) of gas products was calculated by the below equation:

$$FEg = \frac{2 \times 96485(\text{ c/mol}) \times V(\text{mL/min}) \times 10 \cdot 6(\text{m3/mL}) \times v(\text{vol \%}) \times 1.013 \times 105(\text{N/m2})}{8.314(\text{N} \cdot \text{m/mol} \cdot \text{K}) \times 298.15 \text{ K} \times \text{Itotal}(\text{C/s}) \times 60(\text{s/min})}$$

V (vol %) = volume concentration of CO in the exhaust gas from the cell (GC data).

V (mL/min) = Gas flow rate measured by a flow meter at the exit of the cell at room temperature and under ambient pressure.

Itotal (C/s) = steady-state cell current.

Computational methods.

All of the calculations were performed by means of spin polarized density functional theory (DFT) methods using the Vienna Ab initio Simulation Package (VASP)³. While the projector augmented wave (PAW) method was adopted to describe electron-ion interaction⁴. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within a generalized gradient approximation (GGA) was employed, and a 520 eV cut off energy for the plane-wave basis set was used for the valence electrons. The DFT +U method with U - J = 5.3 eV was used to describe the strong correlation of the localized Fe 3d states⁵. A DFT-D3 scheme⁶ of dispersion correction was used to describe the van der Waals (vdW) interactions in molecule adsorption. The selfconsistent filed (SCF) calculations were performed with an energy and force convergence criterion of 10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. And the intrinsic dipole correction was also considered in all DFT calculation. The Brillouin zone was sampled using the 4×4×1 Monkhorst-Pack sampling in structure optimization for Fe₁-Pyridinic N₄-Pyrrolic O₁, Fe₁-Pyridinic N₄-Pyrrolic N₁ and Fe₁-Pyridinic N₄-Pyridinic N₁ models. To avoid the interactions between two adjacent periodic images, the vacuum thickness was set to be 15 Å. The atomic structures were analyzed by using the VESTA code⁷. The free energy correction was obtained similarly by including the ZPE and entropic contributions from vibrational degrees of freedom calculated with the substrate fixed.

Computational details of the Gibbs free energy for CO₂RR.

The reaction steps considered for the electrochemical reduction of CO_2 to CO are as follows:

 $CO_2 + H^+ + e^- + * \rightarrow *COOH$ $*COOH + H^+ + e^- \rightarrow *CO + H_2O$

 $*CO \rightarrow CO + *$

where * represents either the catalytic active sites of vacant surface, or intermediate species adsorbed on the active sites.

By considering the zero-point energy (ZPE) and entropy corrections, the Gibbs free energy for OER can be calculated with the following equation⁸:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{1}$$

where ΔE indicates the adsorption energy difference for each species adsorbed on the catalyst, ΔZPE and ΔS are the zone point energy and entropy difference between the adsorbed state and corresponding free-standing state, respectively. The calculated values of ΔZPE and ΔS are listed as follow.

 	5,	•••••		
Species	Energy (eV)	ZPE (eV)	TS (eV)	G (eV)
H ₂ O (0.035 bar)	-14.220	0.570	0.580	-14.230

Thermodynamic correction used in the free energy calculations.

H_2	-6.760	0.282	0.402	-6.880
CO_2	-22.993	0.312	0.657	-23.338
СО	-14.799	0.136	0.614	-15.277
*СООН		0.622	0.222	
*CO		0.224	0.064	
*		0	0	

The zero point energy (ZPE) is calculated by9:

$$E(ZPE) \approx \frac{1}{2} \sum_{j} \hbar \omega_{j}$$
⁽²⁾

where \hbar is the reduced Planck constant and ω_j is the frequency associated with the harmonic mode in the gamma point. The same values for the adsorbed species are used throughout the entire text, as vibrational frequencies have been found to depend much less on the catalyst surface. The contributions (TS) values of the free molecules are taken from the NIST database¹⁰, For water, the entropy is calculated at 0.035 bar through $S=S_0+k_BTln(p/p^0)$ to derive the chemical potential of liquid water, because at this pressure gas-phase water is in equilibrium with liquid water at 298.15 K.

D-band theory.

Insights into the distinct property for catalysts can guide us to improve the catalytic performance and design better electrocatalysts. Thus according to the d-band theory¹¹, the binding of adsorbates on the metal is determined by the occupancy of state formed

between the adsorbates valence state and the d state of transition metal. The closer the d-band center to the Fermi energy level, the higher reactivity of the metal and higher interreaction with the adsorbed species¹². The d-band center can be also a measure of the states of Fe-3d in Fe₁-Pyridinic N₄-Pyrrolic O₁, Fe₁-Pyridinic N₄-Pyrrolic N₁ and Fe₁-Pyridinic N₄-Pyridinic N₁ structures. As the d-band center shifts up to the Fermi level, a distinctive antibonding state appears above the Fermi level. The antibonding states above the Fermi level are empty and easily accept the electron from the adsorbates, thus the bonding becomes stronger. And a weak bonding occurs if the antibonding states are shifted down through the Fermi level. The d-band center of Fe-3d can be obtained from their projected density of states (PDOS) using equation (1):

$$\varepsilon_{d} = \frac{\int_{-\infty}^{+\infty} x \rho(x) dx}{\int_{-\infty}^{+\infty} \rho(x) dx}$$
(1)

where, the $\rho(x)$ is the PDOS of at an energy level of x. The integral domain was set to [-7, 0] eV of Fe 3d-orbital states, which is the closest region near the Fermi energy. The chemical bonding energy $\Delta \varepsilon$ of intermediates on catalyst interface can be expressed by¹³⁻¹⁴:

$$\Delta \varepsilon \propto -\frac{V^2}{|\varepsilon_d - \varepsilon_s|} \tag{2}$$

where V is the coupling matrix element and can be assumed as a constant value; ε_s is the energy level of adsorbate states which can be set to be 0 eV. It can be seen that the chemical bonding energy will be increased when the value of $|\varepsilon_d - \varepsilon_s|$ decreases.

Electronic Structure Analysis.

Crystal orbital Hamilton population (COHP) analysis was performed with the LOBSTER 3.2.0 package, which reconstructs the orbital-resolved wave functions via projection of the delocalized PAW to localized atomic-like basis sets¹⁵⁻¹⁶. Basis sets given by Koga with additional functions fitted to atomic VASP-PBE wave functions were used¹⁷⁻¹⁸. The electron density differences were evaluated using the formula $\Delta \rho = \rho$ (Fe/substrate) - ρ (Fe) - ρ (substrate), then analyzed by using the VESTA code.



Figure S1. a) SEM of Na₂CO₃, b) SEM of CONP, c) TEM of Fe-CON₄₀₀-400 sample. The plate shaped of Na₂CO₃ can be seen in Figure S1a. The uniform mixure by fast pyrolysis of L-alanine in the molten-salt of sodium carbonate is shown in Figure S1b. No obvious Fe particles can be seen from the TEM of Fe-CON₄₀₀-400 sample in Figure S1c.



Figure S2. O 1s XPS spectrums of CON_{400} and CON_{400} -30 samples. Compared with CON_{400} sample, the content of O atoms decreased from 5.79 at% to 5.64 at% for CON_{400} -30 sample, especially, the atomic content of C-O decreased from 1.74 to 0.21 at%.



Figure S3. N₂ adsorption-desorption isotherms and pore size distribution curves of a, b) CONP, c, d) CON₄₀₀, e, f) CN₆₀₀. BET test results showed that, the specific surface area of CONP was only 6.4 m²/g, and after washed by water, the specific surface area would remarkable increase to 1358.5 m²/g for CON₄₀₀ and 1342.3 m²/g for CN₆₀₀.



Figure S4. Raman spectroscopy of different samples: washed CONP without calcination, CON_{400} and CN_{600} samples. It can be seen that, compared with the washed CONP without calcination sample, the degree of graphitization of CON_{400} and CN_{600} samples increased obviously.



Figure S5. O 1s XPS spectrums of CON₄₀₀, Fe-CON₄₀₀-400, CN₆₀₀ and Fe-CN₆₀₀-400 samples. Among them, N atoms include Fe-O peak (530.00 eV), C=O (531.08eV), C-O (532.17eV for Fe-CON₄₀₀-400, 532.03eV for other samples) can be found. The peak assigned to C-O for Fe-CON₄₀₀-400 clearly shift to the higher energy side, compared with CON₄₀₀, CN₆₀₀ and Fe-CN₆₀₀-400 samples.



Figure S6. N 1s XPS spectrums of CON₄₀₀, Fe-CON₄₀₀-400, CN₆₀₀ and Fe-CN₆₀₀-400 samples. Among them, N atoms include pyridinic N (398.10 eV for CON₄₀₀ and CN₆₀₀, 398.17 eV for Fe-CON₄₀₀-400 and Fe-CN₆₀₀-400), Fe-N (398.99 eV), pyrrolic N (400.30 eV for Fe-CN₆₀₀-400, 400.20 eV for other samples), graphitic N (401.2 eV), and N-O (402.7 eV) can be found.



Figure S7. O 1s XPS spectrums of Fe-CON₄₀₀-400, Fe-CON₄₀₀-500 and Fe-CON₄₀₀-600 samples. As shown in Figure S3, the content of O atoms decreased from 4.51 at% to 3.84 at% along with the calcination temperature increased from 400°C to 600°C, especially, the atomic content of Fe-O decreased from 0.21 at% to 0.



Figure S8. N 1s XPS spectrums of Fe-CON₄₀₀-x (x = 100, 200, 300, 400) samples. Among them, N atoms include pyridinic N (398.1 eV), N_x-Fe (398.99 eV), pyrrolic N (400.2 eV), graphitic N (401.2 eV), and N-O (402.7 eV) can be found. The similar characteristic peak positions of different types of N atoms among the three samples, indicating the similar coordination environments for them.



Figure S9. N 1s XPS spectrums of FePor-400, Fe-CON₄₀₀-400 and Fe-CN₆₀₀-400 samples. Among them, N atoms include pyridinic N (398.17 eV), Fe-N (398.99 eV), pyrrolic N (400.20 eV for FePor-400, Fe-CON₄₀₀-400; 400.30 eV for Fe-CN₆₀₀-400), graphitic N (401.20 eV), and N-O (402.70 eV). Compared with CON₄₀₀ and CN₆₀₀ samples with pyrrolic N (400.30 eV) and pyridinic N (398.10 eV), the pyridinic N of FePor-400, similarly, the pyrrolic N and pyridinic N for Fe-CN₆₀₀-400 samples shift to the higher energy side indicating the pyridinic N bond with the Fe atom in FePor-400, pyrrolic N and pyridinic N bond with the Fe atom in FePor-400, sample simultaneously. The similar characteristic peak positions of pyridinic N (398.17 eV) among the three samples, indicating the similar coordination environments for them.



Figure S10. R space and inverse FT-EXAFS fitting results for Fe-CON₄₀₀**-x** (**x=100, 200, 300, 400).** Fitting range: 1.0-2.1 Å, FT range: 2.5-12.25 Å⁻¹.



Figure S11. Fourier-transform EXAFS spectrums of Fe foil, FeO, Fe₂O₃, FePor, Fe-CON₄₀₀-800, and Fe-CON₄₀₀-1000. The FT spectra of the Fe-CON₄₀₀-800 and Fe-CON₄₀₀-1000 samples exhibit a sharp peak at 2 Å and 2.4 Å, which is in agreement with the characteristic peak Fe foil and Fe₂O₃.



Figure S12. R space and inverse FT-EXAFS fitting results for Fe-CON₄₀₀-400, Fe-CN₆₀₀-400 and FePor-400 samples. Fitting range: 1.0-2.1 Å, FT range: 2.5-12.25 Å⁻¹.



Figure S13. Wavelet transform of Fe foil, FeO, Fe₂O₃, FePor-400, Fe-CON₄₀₀-400 and Fe-CN₆₀₀-400 samples (from top to bottom). The WT contour maximum at 4.0 Å⁻¹ for FePor-400 and Fe-CN₆₀₀-400 were assigned to Fe-N coordination and 4.2 Å⁻¹ for Fe-CON₄₀₀-400. The difference of ~0.2 Å⁻¹ among them might arise from the shorter Fe-O path. Meanwhile, no intensity maximum corresponding to Fe-Fe was observed, compared with the WT contour plots of Fe foil, FeO, and Fe₂O₃.



Figure S14. Faradaic efficiency without IR compensation of Fe-CON₄₀₀-400, Fe-CN₆₀₀-400, FePor-400, CON₄₀₀.



Figure S15. Element mapping for the used Fe-CON_{400} -400 sample, C (blue), O (red), N (cyan) ,O (purple) and Fe (green).



Figure S16. Faradaic efficiency without IR compensation of Fe-CON₄₀₀-x (x=100, 200, 300, 400, 500, 600, 800, 1000).



Figure S17. FE_{H2} of Fe-CON₄₀₀-x (x=100, 200, 300, 400, 500, 600, 800 and 1000) catalysts. As shown in Figure S13, the FE_{H2} increased when the calcination temperature

of Fe-CON₄₀₀ rose from 100°C to 400 °C.



Figure S18. The top view for a) Fe_1 -Pyridinic N_4 ; b) Pyridinic N_4 ; c) Pyrrolic N_3 and d) Pyrrolic O₁-Pyrrolic N₂. Color code for elements is as follows: C, gray; N, blue; H, white; Fe, orange; O, red. Two stable doping modes of N in graphene were considered, including graphene layer with pyridine N and graphene layer with pyrrolic N. We fully optimized isolated substrate models and adsorbed FeN₄ clusters and found that the adsorption of Fe₁N₄ cluster on the N doping graphene layer results in Fe₁N₄-N₁ configuration. While the Fe1N4 cluster anchored on pyrrolic-O structure results in Fe_1N_4 - O_1 configuration.



Figure S19. Optimized configurations for a) Fe₁-Pyridinic N₄; b) Fe₁-Pyridinic N₄-

Pyridinic N₁; c) Fe₁-Pyridinic N₄-Pyrrolic N₁; d) Fe₁-Pyridinic N₄-Pyrrolic O₁.



Figure S20. The formation energy (Ef) comparation of pridinic N transferred to

pridinic O and Pyrrolic N transferred to Pyrrolic O.

To characterize the possibility and stability for O substitution pridinic N and Pyrrolic N nanosheets, the formation energy (${}^{\Delta E} f$) are calculated, the equation is given by:

$$\Delta E_f = E_{O-substitution} - E_{substrate} - \mu_O + \mu_N$$

where $E_{O-substitution}$ and $E_{substrate}$ are the total energies of O substitution and pristine N-doped graphene (pridinic N and pyrrolic N), μ_O and μ_N are the chemical potentials of the substituted O atom and the substitutional N atoms, which are calculated with respect to the naturally occurring bulk stable states. As shown in Figure S20, the formation energies are 2.80 eV for pridinic O and 1.29 eV for pyrrolic O, respectively. The lower formation energy indicates the energetically favorable for pyrrolic O than pridinic O according to thermodynamic views.



Figure S21. Adsorption enegies of *CO (eV) for a) Fe_1N_4 -Pyrrolic O₁; b) Fe_1N_4 -

Pyrrolic N₁; c) Fe₁N₄-Pyridinic N₁.



Figure S22. The charge density differences (a. top view, b. side view and c. 2D plot) of Fe₁-Pyridinic N₄. The isosurface level set to 0.003 e Å⁻³, where charge depletion and accumulation were depicted by cyan and yellow, respectively.



Figure S23. The charge density differences (a. top view, b. side view and c. 2D plot) of Fe₁-Pyridinic N₄-Pyrrolic N₁. The isosurface level set to 0.003 e Å⁻³, where charge depletion and accumulation were depicted by cyan and yellow, respectively.



Figure S24. The charge density differences (a. top view, b. side view and c. 2D plot) of Fe₁-Pyridinic N₄-Pyrrolic O₁. The isosurface level set to 0.003 e Å⁻³, where charge depletion and accumulation were depicted by cyan and yellow, respectively.

O species / atom %			N species / atom %					
	С=О	C-0	Fe-O	Pyridinic N	Fe-N	Pyrrolic N	Graphitic N	Oxidized N
CON ₄₀₀	4.05	1.74	0	0.83	0	1.07	0.36	0.13
CN ₆₀₀	5.45	0	0	0.86	0	1.10	0.49	0
Fe-CON ₄₀₀ -100	2.08	2.55	0	1.46	0.76	1.16	0.29	0.06
Fe-CON ₄₀₀ -200	2.07	2.54	0	1.49	0.78	1.15	0.32	0.05
Fe-CON ₄₀₀ -300	1.86	2.53	0.18	1.50	0.80	1.15	0.30	0.08
Fe-CON ₄₀₀ -400	1.82	2.48	0.21	1.52	0.83	1.12	0.31	0.07
FePor-400	4.91	4.91	0	6.57	2.82	0	0	0
Fe-CN ₆₀₀ -400	1.78	2.18	0	1.68	0.86	1.25	0.33	0

 Table S1. The relative concentrations of different N and O species based on XPS of different samples.

Notes: a. The relative concentration refer to the atom percentage of the every type of different species in catalyst; b. The relative concentration is based on the atom percentage of different species in catalyst and the area percentage of the every type of species in one species.

Catalyst	Shell	N	R _j (Å)	σ^2 (Å ²)	$\Delta E_0 (eV)$	R-factor	
FePor	Fe-N	4.0*	1.90(1)	0.0075(4)	-3.9(3)	0.01	
Fe-CON ₄₀₀ -100	Fe-N	4.0(4)	1.90(1)	0.0070(1)	-3.9(5)	0.01	
	Fe-N	4.0(5)	1.90(1)	0.0066(2)	-3.9(9)	0.01	
Fe-CON ₄₀₀ -200	Fe-O	0.1(3)	1.85(2)	0.0063(7)	-4.7(6)	0.01	
E. CON 200	Fe-N	4.0(6)	1.90(1)	0.0064(2)	-3.9(5)	0.01	
Fe-CON ₄₀₀ -300	Fe-O	0.7(5)	1.85(2)	0.0060(3)	-4.9(4)	0.01	
	Fe-N	4(3)	1.90(1)	0.0057(7)	-3.9(6)	0.01	
Fe-CON ₄₀₀ -400	Fe-O	1.1(6)	1.85(2)	0.0053(8)	-5.1(7)	0.01	
FePor-400	Fe-N	4.0(4)	1.90(1)	0.0075(4)	-3.9(3)	0.01	
Ea CNI 400	Fe-N1	4(5)	1.90(1)	0.0045(6)	-3.9(3)	0.01	
re-CN ₆₀₀ -400	Fe-N2	1.1(4)	1.86(5)	0.0045(7)	-3.9(4)	0.01	

Table S2. Structural parameters extracted from the EXAFS fitting.

Notes: S_0^2 is the amplitude reduction factor, S02 was fixed as 0.85; fitting range: 2.5 \leq k \leq 12.25 Å⁻¹, and 1.0 \leq R \leq 2.1 Å. 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); An E₀ value of 7112.0 eV was used to calibrate all data with respect to the first inflection point of the absorption K-edge of Fe foil. R factor is used to value the goodness of the fitting. **Table S3.** The calculated total energies (E) of CO_2RR intermediates, the Gibbs free energy changes (ΔG) of reaction steps, potential limiting step (PLS) and theoretical overpotentials (η) are provided.

		E _(*)	E _(*COOH)	E _(*CO)	E(*H)
Fe ₁ -Pyridinic N ₄ -Pyridinic N ₁		-1582.01	-1610.34	-1599.29	1585.11
Fe ₁ -Pyridinic N ₄ -Pyrrolic N ₁		-1592.17	-1618.99	-1609.06	1594.54
Fe ₁ -Pyridinic N ₄ -Pyrrolic O ₁		-1593.37	-1619.51	-1608.34	1594.96
	ΔG_1	ΔG_2	ΔG_3	PLS	η
Fe ₁ -Pyridinic N ₄ -Pyridinic N ₁	-1.16	0.02	1.85	*CO→*	1.85
Fe ₁ -Pyridinic N ₄ -Pyrrolic N ₁	0.36	-1.11	1.46	*CO→*	1.46
Fe ₁ -Pyridinic N ₄ -Pyrrolic O ₁	1.04	0.14	-0.47	*→*COOH	1.04

Catalyst	Peak FE _{CO}	Peak Potential ^a	ΔE (FE _{CO} > 99%)	Electrolyte	Reference
FeN ₄ -O ₁	> 99 %	-0.56 V to -0.87 V	310 mV	0.1 M NaHCO ₃	This work
FeN ₄ /C	> 90 %	-0.3 V to -0.8 V	-	0.1 M NaHCO ₃	Chem.2021 ¹⁹ .
CoCoPCP/CNTs	94 %	-0.55 V	-	0.5 M KHCO3	Appl. Catal. B- Environ.2021 ²⁰ .
Ag ₁ /MnO ₂	95.7%	-0.85 V	-	0.5 M KHCO3	Angew. Chem. Int. Ed.2020 ²¹ .
Fe ³⁺ -N-C	80 % ~ 93 %	-0.2 V to -0.5 V	-	0.5 M KHCO3	Science. 2019 ² .
FeN ₄ /C	90 % ~ 93 %	-0.5 V to -0.6 V	-	0.1 M KHCO ₃	Adv. Sci. 2020 ²² .
NiPc-OMe-MDE	> 99 %	-0.54 V to -0.68 V	140 mV	0.5 M KHCO3	Nat. Energy. 2020 ²³ .
Ni-N ₃ -V	90 % ~ 94 %	-0.7 V to -0.9 V	-	0.5 M KHCO3	Angew. Chem. Int. Ed.2020 ²⁴ .
Co particle @ pyridinic N/C	84 %	-0.9 V	-	0.5 M KHCO ₃	Angew. Chem. Int. Ed.2020 ²⁵ .
STPyP-Co	90 % ~ 97.8 %	-0.6 V to -0.72 V	-	0.5 M KHCO ₃	Angew. Chem. Int. Ed.2019 ²⁶ .
Co-N ₅ /HNPCSs	> 90 %	-0.57V to -0.88V	60 mV	0.1 M NaHCO ₃	J. Am. Chem. Soc. 2018 ¹ .
Ni-NCB	> 95 %	-0.6 V to -0.84 V	~100 mV	0.5 M KHCO ₃	Joule. 2019 ²⁷ .
Ni-NG	90 % ~ 95 %	-0.6 V to -0.75 V	-	0.5 M KHCO ₃	Energy Environ. Sci. 2018 ²⁸ .
Vo-rich ZnO	83 %	-1.1 V	-	0.1 M KHCO ₃	Angew. Chem. Int. Ed. 2018 ²⁹ .
A-Ni-NSG	94 % ~ 98 %	-0.65 V to -0.9 V	-	0.5 M KHCO ₃	Nat. Energy. 2018 ³⁰ .
C-Zn ₁ Ni ₄ ZIF-8	92 % ~ 98 %	-0.53 V to -1.03 V	-	0.5 M KHCO ₃	Energy Environ. Sci. 2018 ³¹ .

Table S4. Performance comparison of typical transition metal CO₂RR catalysts.

a: (V) vs. RHE with IR compensation.

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