Title: Atomically dispersed Fe³⁺ sites catalyze efficient CO₂ electroreduction to CO

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Abstract: Currently the most active electrocatalysts for the conversion of CO₂ to CO are gold-based nanomaterials, whereas non-precious metal catalysts have shown low to modest activity. Here we report a catalyst of dispersed single-atom iron sites that produces CO at an overpotential as low as 80 mV. Partial current density reaches 94 mA·cm⁻² at an overpotential of 340 mV. Operando x-ray absorption spectroscopy revealed the active sites to be discrete Fe³⁺ ions, coordinated to pyrrolic N atoms of the N-doped carbon support, that maintain their +3 oxidation state during electrocatalysis, probably through electronic coupling to the conductive carbon support. Electrochemical data suggest the Fe³⁺ sites derive their superior activity from faster CO₂ adsorption and weaker CO absorption than conventional Fe²⁺ sites.

Main text.

Electrochemical reduction of CO₂ is a promising approach to store intermittent renewable solar and wind energy in carbon-based fuels and chemicals, leading to reduced anthropogenic CO₂ emission (1). To achieve high energy efficiency and scalability, the reaction must occur rapidly and selectively at low overpotentials. Numerous electrocatalysts have been developed for CO₂ reduction (2), among which Au, and to a less degree, Ag, are the most efficient at low overpotentials. For example, the Faradaic efficiency of CO formation can exceed 90% with Au (3-5) and Ag (6, 7) based catalysts. On certain Au nanostructures the partial current density of CO (denoted as j_{CO}) reached 10 mA·cm⁻² at overpotentials even lower than 300 mV (4, 5). Catalysts composed solely of Earth-abundant elements typically have low selectivity for CO₂ reduction (8-12). Recently, many single-atom catalysts (13, 14) have been developed, in which numerous catalytic metal sites separated from each other were chemically and electronically constrained on solid supports. These catalysts exhibit properties and activity distinct from both nanoparticles and molecular complexes of the same metal elements. Among them, Fe (15, 16), Co (17) and Ni (18-20) catalysts were reported to exhibit Faradaic efficiency of CO formation comparable to those of Au and Ag catalysts. However, with these non-precious metal catalysts much larger overpotentials were required to obtain the same j_{CO} . Herein, we report a catalyst with dispersed single-atom Fe sites with ultrahigh activity for CO₂ electroreduction to CO.

The Fe catalyst (Fe³⁺-N-C) was prepared by the pyrolysis of Fe doped Zn 2-methylimidazolate framework (ZIF-8) (21) under N₂ at 900 °C. The precursor adopts the same crystal structure as undoped ZIF-8 (fig. S2A) with a mole ratio of Fe:Zn of 4:96 (fig. S2E). Fe ions occupy Zn sites and are coordinated by 4 pyrrolic-type nitrogens, as revealed by the fitting

of the Fe K-edge extended x-ray absorption fine structure (EXAFS) spectrum (fig. S2G-I, table S1). Fe³⁺-N-C is porous, with a Brunauer-Emmett-Teller (BET) surface area of 772 m²·g⁻¹ (fig. S3A) and an electrochemical (double-layer) surface area of 554 m²·g⁻¹ (fig. S3D). The porosity was confirmed by high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) (Fig. 1A). Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis showed the weight fractions of Fe and Zn to be 2.8% and 3.4%, respectively, corresponding to a nearly equal mole ratio of Fe:Zn. A similar Fe:Zn mole ratio was found by x-ray photoelectron spectrometry (XPS, fig. S3E) and energy dispersive X-ray spectroscopy (EDS, fig. S4F) measurements. The majority of Zn ions in the ZIF-8 precursor were presumably reduced to Zn particles, which then evaporated during pyrolysis. The X-ray diffraction (XRD) pattern of Fe³⁺-N-C (Fig. S3G) showed a broad feature at about 25° corresponding to the interlayer distance of the carbon matrix (with a *d* value of about 0.35 nm). No diffraction peaks of any crystalline species of Fe and Zn were observed. Likewise no nanoparticles were found in the transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images; only curved fringes of the layered carbon matrix were observed (fig. S4D-E). The EDS mappings (Fig. 1B-C) revealed the homogeneous distributions of Fe and N in the carbon matrix. In the aberration-corrected HAADF-STEM image with atomic resolution (Fig. 1D), the bright spots with size of ~0.2 nm correspond to atomically dispersed Fe and Zn sites. The Fe 2p_{3/2} XPS spectrum (fig. S3F) and the Fe K-edge x-ray absorption near edge structure (XANES) spectrum (Fig. 1F) showed binding and edge energies close to those of Fe₂O₃ and Fe³⁺-tetraphenylporphyrin-Cl (Fe³⁺TPPCl), indicating that the Fe ions in the as-synthesized Fe³⁺-N-C were in the +3 oxidation state. Thus, the Fe ions were oxidized from +2 to +3 during the

pyrolysis, in agreement with previous reports of pyrolysis of Fe-containing organic precursors (15, 22). The oxidants might be the same species such as protons or residual oxygens that oxidized the carbon skeleton of the ZIF precursor. Fe K-edge EXAFS (Fig. 1H) supported the atomic dispersion of Fe sites in Fe^{3+} -N-C. The fitting of the spectrum (table S1) indicated that the Fe center adopts a planar Fe-X_4 ($\text{X} = \text{N}$ or C) structure. The average coordination numbers of Fe-N and Fe-C paths were 3.4 and 0.5, respectively. No Fe-Fe bond was detected.

Figure 1. Characterizations of Fe^{3+} -N-C. (A) HAADF-STEM image and the corresponding EDS mappings of (B) Fe and (C) N of the region enclosed by the red square. (D) Aberration-

corrected HAADF-STEM image and (E) EDS spectrum of the red-square region. (F) Fe K-edge XANES spectra of Fe³⁺-N-C (black), Fe₂O₃ (blue dashed), Fe³⁺TPPCl (green dashed), FeO (pink dashed) and Fe foil (orange dashed). The inset shows the enlargement of the main edges. (G) k-space and (H) R-space Fe K-edge EXAFS spectra. Data (black) and fitting curves (red).

As shown by the linear sweep voltammetry (LSV) curve of Fe³⁺-N-C in CO₂ saturated 0.5 M KHCO₃ electrolyte (fig. S5), the onset potential was more positive than -0.20 V vs reversible hydrogen electrode (RHE). Compared to Fe³⁺-N-C, the current density of the Fe-free control sample, Zn-N-C (prepared by pyrolysis of undoped ZIF-8), was negligible, indicating that the electrocatalytic activity of Fe³⁺-N-C originates from Fe sites. We first tested the electrocatalytic activity in CO₂ reduction using carbon paper electrodes in an H-cell shown in fig. S6A. CO and H₂ were the only gas-phase products and no solution-phase product was detected (fig. S6B-D). CO was detected after electrolysis at -0.19 V vs RHE, equivalent to an overpotential of 80 mV (fig. S6E-F). The Faradaic efficiency of CO was higher than 80% between -0.2 V and -0.5 V vs RHE (Fig. 2A). The j_{CO} reached 20 mA·cm⁻² at -0.47 V vs RHE (overpotential of 360 mV, Fig. 2B). The rate of CO₂ reduction might be limited by mass transport in an H-cell (23). Thus, we deposited Fe³⁺-N-C on a gas diffusion electrode (GDE) (24). The electrolysis was then conducted in a flow cell with N₂ saturated 0.5 M KHCO₃ as the catholyte and CO₂ gas was fed behind the GDE (fig. S7A). Ni-Fe layered double hydroxide (LDH) nanosheets (25) were used as the electrocatalyst for the anodic reaction (oxygen evolution). At -0.45 V vs RHE (overpotential of 340 mV), j_{CO} reached 94 mA·cm⁻² (corresponding to 1.75 mmol_{CO}·h⁻¹·cm⁻², Fig. 2B), with Faradaic efficiency of CO on the cathode higher than 90% (Fig. 2A). Good

reproducibility was observed in measurements of three independently prepared samples, giving a small standard deviation (Fig 2A-B).

We compare the j_{CO} of Fe^{3+} -N-C to other state-of-the-art catalysts in Fig. 2C and fig. S8. The j_{CO} of Fe^{3+} -N-C measured in an H-cell between -0.2 and -0.5 V vs RHE is higher than that attained by other non-precious metal catalysts and even Ag catalysts (7), reaching comparable levels to oxide-derived Au catalysts (3). The mole-normalized current of Fe^{3+} -N-C is significantly higher than that of Au catalysts in this potential range (fig. S8B). Assuming all Fe atoms to be catalytically active, the apparent turnover frequencies (TOFs) of Fe^{3+} -N-C (fig. 2D) are comparable to those of Au catalysts (3, 4, 26) and greatly exceed those of other non-precious metal catalysts (15, 16, 19). Unlike for catalysts based on Cu, Ag, and Au (27), ultrapure electrolyte solutions were not necessary for Fe^{3+} -N-C. When KHCO_3 with a purity of 99.5% was used to prepare electrolyte, or even tap water was used in place of deionized water (18.2 $\text{M}\Omega\cdot\text{cm}$), the Faradaic efficiency and j_{CO} show no significant change, and the performance was stable for at least 12 hours (Fig. 2E). After 12 hours of electrolysis, the weight fraction of Fe in Fe^{3+} -N-C (measured by ICP-OES) was 2.6%, indicating no significant leaching of Fe ions from the catalyst. No aggregation of Fe or Zn species was detected in TEM images, and a high density of discrete Fe and Zn atoms was still observed (fig. S9).

Figure 2. CO₂ electroreduction performance. (A) Faradaic efficiency of CO (solid lines) and H₂ (dashed lines) production and (B) j_{CO} of Fe³⁺-N-C in an H-cell (red) and on a GDE (blue), and of Fe²⁺-N-C in an H-cell (black). Data from the H-cell were obtained by chronoamperometry whereas data from the GDE were obtained by chronopotentiometry. Each error bar was the standard deviation determined based on tests of three individual electrodes. Loading: 0.6 mg·cm⁻² for Fe³⁺-N-C and Fe²⁺-N-C; 2.5 mg·cm⁻² for Fe³⁺-N-C/DGE. Comparison of (C) j_{CO} and (D) apparent TOFs of CO production of Fe³⁺-N-C in an H-cell (red circles) and

on a GDE (red stars) and of Fe^{2+} -N-C in an H-cell (red squares), to that of other reported catalysts: other Fe-N-C catalysts (Fe-0.5d (15) and Fe-N-C (16)), a Co-N-C catalyst with 2 coordinating nitrogen atoms (Co-N2) (17), atomically dispersed Ni on nitrogen-sulfur co-doped graphene (A-Ni-NSG) (19), oxide-derived Au electrode (OD-Au) (3), carbon black supported Au nanowires with a length of 500 nm (C-Au-500) (4), needle-shape Au nanostructures (Au needles) (5), nanoporous Ag electrode (np-Ag) (7) and Au-polymer-multiwall carbon nanotubes composite loaded on GDE (Au/GDE) (28) in bicarbonate electrolytes. (E) Chronoamperometry curve and Faradaic efficiency of CO production (dots) by Fe^{3+} -N-C in H-cell at -0.37 V vs RHE. The electrolytes were prepared from K_2CO_3 (99.999%) and deionized water (18.2 $\text{M}\Omega\cdot\text{cm}$) (black), KHCO_3 (99.5%) and deionized water (red), and KHCO_3 (99.5%) and tap water (blue), respectively.

The performance of Fe^{3+} -N-C was stable between -0.2 V and -0.5 V vs RHE, though at potentials more negative than -0.5 V vs RHE, the activity became unstable (fig. S7B). As shown in fig. S7C, the current density at -0.41 V was stable during a 28-h chronoamperometry test. Whereas at -0.51 V vs RHE, the initial j_{CO} was much higher, it decreased rapidly to a value similar to that obtained at -0.41 V vs RHE. This result indicates some changes of Fe^{3+} -N-C around -0.5 V vs RHE. To explore the nature of this change, operando XAS measurements were conducted in the CO_2 -saturated 0.5 M KHCO_3 catholyte. Fe K-edge spectra were obtained on dry samples and on samples that were loaded on glassy carbon electrodes and immersed in the electrolyte at open circuit potential (OCP) as well as at -0.1 V to -0.6 V vs RHE (Fig. 3A). For Fe^{3+} -N-C, the Fe K-edge showed no obvious shift between the dry powder and the in-situ

sample at -0.4 V vs RHE. The edge energy was close to that of $\text{Fe}^{3+}\text{TPPCl}$, indicating that the Fe ions in $\text{Fe}^{3+}\text{-N-C}$ remained in the +3 oxidation state during CO_2 electroreduction at potentials as negative as -0.4 V vs RHE. When the applied potential was shifted further negative, to -0.5 V vs RHE and beyond, the Fe K-edge shifted to lower energies, which were comparable to that of FeO, suggesting the reduction of Fe^{3+} to Fe^{2+} . This reduction process occurred at the same potential as the above-mentioned deactivation of $\text{Fe}^{3+}\text{-N-C}$, implying Fe^{3+} sites are more active for generating CO. Moreover, the fitting of EXAFS spectra (fig. S10C) indicates that the reduction of Fe^{3+} sites is accompanied by a change of local structure around the Fe ions. Before the reduction of Fe^{3+} sites, the first shell coordination number of Fe (Fe-N and Fe-C) was about 4, whereas as the Fe^{3+} sites were reduced to Fe^{2+} sites, the first shell coordination number of Fe decreased to about 3.

Figure 3. Operando XAS characterization. Fe K-edge XANES spectra (left) and the 1st derivative of the spectra (right) of (A) Fe³⁺-N-C and (B) Fe²⁺-N-C as dry powder (black), and loaded on glassy carbon electrodes at open circuit potential (OCP, blue), -0.1 V (light blue), -0.2 V (green), -0.3 V (dark green), -0.4 V (dark blue), -0.5 V (red) and -0.6 V (pink) vs RHE, with the spectra of Fe₂O₃ (blue dashed), Fe³⁺TPPCl (green dashed), FeO (pink dashed) and Fe foil (orange dashed) as references.

To investigate the origins of the improved activity of Fe³⁺-N-C compared to previously reported single-atom Fe catalysts, we measured in-situ Fe K-edge XANES spectra of Fe0.5d (fig. S11E-F) (15). Under potentials between -0.2 V and -0.5 V vs RHE, the energy of the Fe K-edge was close to that of FeO, indicating a +2 rather than +3 oxidation state for the Fe sites during CO₂ reduction. This difference in oxidation state might be due to different ligand environments, particularly with regard to the N atoms. For Fe0.5d (15) and Fe-N-C (16), Fe ions coordinated with four pyridinic N were proposed as the active sites. For Fe³⁺-N-C, XANES and XPS spectra of N indicate that the Fe ions were coordinated to pyrrolic N. In the N K-edge XANES spectrum (fig. S12A), π^* and σ^* features of Fe³⁺-N-C were similar to those of a metal-porphyrin derivative (29). In the N 1s XPS spectrum (fig. S12B), the major peak at 398.6 eV was attributed to pyrrolic N coordinated to Fe, in agreement with the spectrum of Fe³⁺TPPCl. This assignment is consistent with the atomic fractions of N and metals and the coordination number of metal-N (table S4).

To further test the above hypothesis, we directly compared the Fe³⁺-N-C catalyst with an analogous Fe-N-C catalyst in which the Fe ions were coordinated by pyridinic N atoms.

Considering that pyrolysis of Fe precursors containing either pyridinic ligands or pyrrolic ligands seemed to conserve the pyridinic or pyrrolic nature of the N atoms, we prepared the reference sample ($\text{Fe}^{2+}\text{-N-C}$) by pyrolysis of a composite containing a Fe-phenanthroline complex at 700 °C (22). Aberration-corrected HAADF-STEM (fig. S13D) and Fe K-edge EXAFS (fig. S14E and table S1) confirmed the single-atom nature of the Fe sites in $\text{Fe}^{2+}\text{-N-C}$. In the N 1s XPS spectrum (fig. S12C), the major feature at 399.7 eV was assigned to pyridinic N coordinated to Fe, in agreement with the assignments of the spectra of Fe-phenanthroline complexes and previously reported metal-N-C catalysts with pyridinic N ligands (16). This assignment is also consistent with the percentage of coordinated N measured by other methods (table S4). Thus, $\text{Fe}^{2+}\text{-N-C}$ contained Fe ions coordinated by pyridinic N atoms. A XANES spectrum (fig. S14D) showed that initially the energy of Fe K-edge of $\text{Fe}^{2+}\text{-N-C}$ was considerably higher than that of FeO. The Fe 2p XPS (fig. S14C) spectrum showed that the binding energy of Fe ion was similar to that of Fe_2O_3 . These data suggested a significant number of Fe^{3+} sites in the as-prepared sample of $\text{Fe}^{2+}\text{-N-C}$. The in-situ XANES (Fig. 3B) showed that Fe^{3+} in the as-prepared $\text{Fe}^{2+}\text{-N-C}$ started to be reduced to Fe^{2+} at -0.1 V to -0.2 V vs RHE. During CO_2 electroreduction (at potentials more negative than -0.2 V vs RHE), the energy of the Fe K-edge was slightly lower than that of FeO. Thus, the Fe sites in $\text{Fe}^{2+}\text{-N-C}$ under reaction conditions had an oxidation state of +2 or lower. The TOF of CO production of $\text{Fe}^{2+}\text{-N-C}$ is more than an order of magnitude lower than that of $\text{Fe}^{3+}\text{-N-C}$ under the same potential (Fig. 2D). The current density of $\text{Fe}^{2+}\text{-N-C}$ decreased significantly during 2-hour chronoamperometry tests (fig. S6G), indicating its lower stability compared to the $\text{Fe}^{3+}\text{-N-C}$ catalyst. These data suggest that pyrrolic type ligands are important to keep Fe sites in the +3

oxidation state during CO₂ electroreduction, and consequently maintain the high activity and stability of Fe³⁺ sites. This hypothesis is further supported by the different reactivity of Fe³⁺-N-C and Fe²⁺-N-C towards NaBH₄. The Fe³⁺ ions coordinated by pyridinic N ligands in Fe²⁺-N-C could be reduced by NaBH₄, whereas those coordinated by pyrrolic N ligands in Fe³⁺-N-C could not (fig. S15).

For Fe²⁺-N-C, the j_{CO} at a fixed potential versus the standard hydrogen electrode (SHE) is largely independent of the concentration of the proton donor (fig. S16A-B), indicating that the 1 e reduction (adsorption) of CO₂ is decoupled from a proton transfer (30, 31). At modest overpotentials the j_{CO} of Fe²⁺-N-C has a Tafel slope of 117 mV/dec (fig. S16E), suggesting that CO₂ adsorption is slow and rate-limiting (Supplementary text: kinetic and mechanistic analysis). On the other hand, the j_{CO} of Fe³⁺-N-C is approximately first-order in the concentration of HCO₃⁻ (fig. S16D) and has a Tafel slope of 64-71 mV/dec at low overpotentials (fig. S16E). These kinetic data suggest that for Fe³⁺-N-C the 1 electron reduction of CO₂ is also decoupled from a proton transfer. Moreover, CO₂ adsorption is fast and the rate-limiting step is the protonation of the adsorbed CO₂⁻ to form an adsorbed COOH intermediate (Supplementary materials, kinetic and mechanistic analysis). These results indicate CO₂ adsorption as a descriptor of catalytic activity at low to modest overpotentials. They also reveal a faster CO₂ adsorption in Fe³⁺-N-C than in Fe²⁺-N-C, which explains why Fe³⁺-N-C has a lower onset overpotential. The CO₂ electroreduction was conducted in the presence of CO (0.2 atm) (fig. S17). External CO did not influence the activity of Fe³⁺-N-C, but it significantly decreased the activity of Fe²⁺-N-C. This result suggests that at high overpotentials CO desorption becomes rate-limiting for Fe²⁺-N-C. Because CO desorption is a non-Faradaic step, once it becomes rate

limiting, the rate will hardly increase with increasing overpotentials. Indeed, at higher overpotentials the Tafel slope of Fe²⁺-N-C becomes enormous (546 mV/dec, fig. S16E) and j_{CO} cannot exceed 2 mA·cm⁻². On the other hand, the reaction at Fe³⁺ sites was not limited by CO desorption and could reach a very high current density. Thus, the higher activity of Fe³⁺-N-C compared to Fe²⁺-N-C at high overpotentials can be rationalized by a weaker CO binding at an Fe³⁺ center than at an Fe²⁺ center.

The spectroscopic data indicate that Fe³⁺-N-C comprises pyrrolic N ligands whereas Fe²⁺-N-C comprises pyridinic N ligands. The pyrrolic N ligands may stabilize Fe³⁺ relative to Fe²⁺, while the pyridinic N ligands have the opposite effect. Thermodynamically, the respective reduction potentials support this hypothesis: the standard reduction potential of [Fe(phen)₃]^{3+/2+} is 1.06 V vs SHE, whereas that of Fe^{3+/2+} couple in Fe-porphyrin complexes can reach as low as -0.4 V vs SHE (32). Preservation of the +3 oxidation state during CO₂ electroreduction is counterintuitive as the formation of highly reduced, low-valent Fe species is necessary for molecular Fe catalysts (33). Once conjugated to a conductive carbon matrix, however, the Fe³⁺ site is electronically coupled to the conductive support so that the Fe^{3+/2+} reduction potential moves to the same degree as the Fermi level of the carbon support when applying an external bias (fig. S18A and S18B). The Fe^{3+/2+} reduction potential remains more negative than the Fermi level of the carbon support, leading to the stabilization of the Fe³⁺ ions. An analogous "strong-coupling" effect was formulated to explain the lack of redox chemistry on conjugated molecular sites during potential cycling (34). The reduction of Fe³⁺ sites in Fe³⁺-N-C at -0.5 V vs RHE is probably enabled by a change of their coordination environment. In-situ EXAFS (fig. S10C) revealed that the Fe ion lost one pyrrolic N ligand at this potential, possibly due to protonation

or hydrogenation of the ligand driven by the electric field. The new coordination environment increases the $\text{Fe}^{3+/2+}$ reduction potential to be more positive than the Fermi level of the carbon support, resulting in conjugated Fe^{2+} ions (fig. S18C).

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Competing interests: European priority patent applications (no. 18156529.2 and 18193304.5) titled “Fe-N-C Catalyst, method of preparation and uses thereof” were filed by GAZNAT SA with J. Gu and X.L. Hu as inventors.

Data and materials availability: All results are reported in the main text and supplementary materials. EXAFS, XANES, and microscopy data files are deposited in Zenodo (35). Unless

restricted by patent, the materials are available for purpose of reproducing or extending the analysis.

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SUPPLEMENTARY MATERIALS

Materials and Methods

Supplementary Text

Figs. S1 to S18

Tables S1 to S4

References (36-43)

Material synthesis

Chemicals: Anhydrous iron(II) chloride (FeCl_2 , 99%, Acros), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Roth), 2-methylimidazole (2-mIm, 99%, Acros), potassium iodide (KI, 99%, Acros), anhydrous iron(II) acetate ($\text{Fe}(\text{OAc})_2$, 97%, Strem), 1,10-phenanthroline ($\text{C}_{12}\text{N}_2\text{H}_8$, 98%, Fluorochem), magnesium hydroxide ($\text{Mg}(\text{OH})_2$, 99%, Sigma), methanol (MeOH, 99.8%, Fisher), ethanol (EtOH, 99.8%, Fisher) and nitric acid (HNO_3 , 65%, Merck) were used as received without any purification.

Synthesis of Fe doped ZIF-8: The preparation followed reported synthetic procedures of pure (21) and metal doped (36) ZIF-8. The synthesis was conducted in a glove box under an N_2 atmosphere. First, 1.314 g of 2-mIm and 0.076 g of KI were dissolved in 20 mL of MeOH to form solution A, and 0.063 g of FeCl_2 and 1.190 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL of MeOH to form solution B. Then, solution B was added into solution A dropwise under stirring during 1 hour, and the solution mixture became turbid gradually. The mixture was kept under stirring for 1 day under an N_2 atmosphere, and the precipitate was separated by ambient-pressure filtration and washed with MeOH for three times under an N_2 atmosphere. After drying under vacuum at room temperature for 1 hour, Fe doped ZIF-8 was obtained as a white powder.

Synthesis of undoped ZIF-8: Undoped ZIF-8 was synthesized with the same method as Fe-doped ZIF-8 except that no FeCl_2 was added and the reaction was conducted in air.

Synthesis of Fe^{3+} -N-C: Fe doped ZIF-8 was loaded into a corundum crucible and immersed by hexane, then transferred into a tube furnace with an N_2 flow ($100 \text{ mL} \cdot \text{min}^{-1}$). The program of pyrolysis is: from 25°C to 120°C with a ramping rate of $1^\circ\text{C} \cdot \text{min}^{-1}$ for the evaporation of hexane; from 120°C to 900°C with a ramping rate of $5^\circ\text{C} \cdot \text{min}^{-1}$; kept at 900°C for 3 hours. After natural cooling, Fe^{3+} -N-C was obtained as a black powder. Zn-N-C was synthesized with the same method by using undoped ZIF-8 as the precursor.

Synthesis of Fe0.5d: This catalyst was prepared according to a reported method (15). 31 mg of $\text{Fe}(\text{OAc})_2$, 400 mg of 1,10-phenanthroline and 1.60 g of undoped ZIF-8 were mixed and ball-milled to form a pink powder. The resulting powder was pyrolyzed in N_2 at 1050°C for 1 hour. Then, Fe0.5d was obtained as a black powder.

Synthesis of Fe^{2+} -N-C: The synthetic method in a previous report (22) was modified. 0.087 g of $\text{Fe}(\text{OAc})_2$ and 0.270 g of 1,10-phenanthroline were first dissolved in 150 mL of EtOH to form a red solution. After an ultrasound treatment for 30 min, 4 g of $\text{Mg}(\text{OH})_2$ was added. The dispersion was treated with ultrasound for another 30 min, then heated at 60°C for 4 hours. Ethanol was removed by rotary evaporation and a reddish powder was obtained. This precursor was loaded into a corundum crucible and placed in a tube furnace with N_2 flow ($100 \text{ mL} \cdot \text{min}^{-1}$). The program of pyrolysis is: from 25°C to 700°C with a ramping rate of $5^\circ\text{C} \cdot \text{min}^{-1}$; kept at 700°C for 2 hours. The black powder obtained after pyrolysis was added to 150 mL of 1 M nitric acid and stirred for 2 hours. A black powder was then separated by filtration and washed with deionized water for 3 times. The product was finally dried in vacuum.

Characterization

XRD patterns were collected on a X'Pert Philips diffractometer with monochromatic Cu K α radiation and a fast Si-PIN multi-strip detector. The as-synthesized samples in powder form were directly used for XRD analysis. The contribution of Cu K α 2 radiation was subtracted.

XPS characterizations were performed on a PHI5000 VersaProbe II XPS system by Physical Electronics (PHI) with a detection limit of 1 at%. Monochromatic x-rays were generated by an Al K α source (1486.7 eV). Data were fitted by using PHI MultiPak software.

Raman spectrum was recorded on a LabRAM high resolution Raman spectrometer. The power of laser was set as 0.1% in order to alleviate the damage of carbon matrix caused by stronger laser beams.

Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume (desorption branch) were calculated from N₂-physisorption measurements on a Micromeritics 3Flex apparatus at liquid nitrogen temperature between 10⁻⁵ and 0.99 relative N₂ pressure. Samples (ca. 150 mg) were dried at 120 °C (temperature reached with a ramp of 2 °C/min) under vacuum (< 10⁻³ mbar) for 4 h and a leak test was performed prior to analysis.

SEM images were taken using a Zeiss Merlin microscope operated at 2 kV and equipped with an Inlens secondary electron detector. TEM were performed on an FEI Talos operated at 200 kV and with high brightness XFEG gun. EDX mapping images were taken under HAADF-STEM mode. For atomic resolution imaging, the measurements were performed on an FEI Titan Themis at 200 kV with spherical aberration corrected under HAADF-STEM mode. Samples for TEM were prepared by drop-drying the samples from their diluted ethanol suspensions onto carbon coated copper grids.

ICP-OES results were obtained by a NexIon 350 (Perkin Elmer) machine. For the sample preparation, 3 mg of the sample was dispersed in 1 mL of ethanol followed by an ultrasonic treatment. 200 μ L of the dispersion was loaded into a glass vial and dried at 70 °C. Then the sample was heated to 600 °C in muffle for complete removal of carbon. The resulting sample after cooling was dissolved in 0.5 mL of ultrapure nitric acid at 80 °C for 12 hours, followed by dilution to a volume of 10 mL by deionized water. To measure the Fe contents in the catalysts after electrolysis, the post-catalytic samples on carbon papers were burnt at 600 °C in muffle. After cooling the ashes were dissolved in 0.5 mL of ultrapure nitric acid at 80 °C for 12 hours, followed by dilution to a volume of 10 mL by deionized water.

X-ray absorption spectroscopy including x-ray absorption near edge spectra (XANES) and extended x-ray absorption fine structure (EXAFS) at Fe K-edge and Zn-K-edge were collected in total-fluorescence-yield mode at ambient condition in Taiwan BL-12B2 of National Synchrotron Radiation Research Center (NSRRC) at SPring-8, JARSI. The electron storage ring was operated at 8.0 GeV with a constant current of $\sim$ 100 mA. The scan range was kept in an energy range of 7000-7700 eV for Fe K-edge and 9480-10450 eV for Zn K-edge. Subtracting the baseline of pre-edge and normalizing that of post-edge obtained the spectra. EXAFS analysis was conducted using Fourier transform on k³-weighted EXAFS oscillations to evaluate the contribution of each bond pair to Fourier transform peak. On the other hand, the XANES of N K-edge was measured in total X-ray electron yield mode at room temperature using BL-20A at TLS in National Synchrotron Radiation Research Center (NSRRC), Taiwan. The electron storage ring was operated at 1.5 GeV with a constant current of $\sim$ 300 mA. The samples were subjected to an ultrahigh vacuum chamber (1 $\times$ 10⁻⁹ torr).

Electrochemical measurements

General

All electrochemical measurements were carried out on a Gamry Reference 3000 electrochemical instrument. The automatic iR compensation (85%) was used. Ag/AgCl electrode with a saturated KCl filling solution was used as the reference electrode. Potential versus SHE was calculated as $E_{vs.RHE} = E_{vs.Ag/AgCl} + 0.197$ V, and potential versus RHE was calculated as $E_{vs.RHE} = E_{vs.Ag/AgCl} + 0.197$ V + 0.0592 V $\times$ pH. The pH values of the electrolytes were measured by a pH meter (HI 991002, Hanna instruments). The pH values of CO₂ and N₂ saturated 0.5 M KHCO₃ electrolyte used in this work are 7.25 and 8.36, respectively.

0.5 M KHCO₃ electrolyte with the highest purity was prepared by first dissolving 0.25 M K₂CO₃ (99.999%, Roth) in deionized water (18.2 M Ω ·cm) obtained from a Milli-Q integral water purification system (Merck Millipore Corporation), then bubbling CO₂ for 6 hours followed by bubbling N₂ for another 6 hours. It was used for collections of cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) curves as well as CO₂ reduction electrolysis in a H-type cell unless otherwise specified. 0.5 M KHCO₃ electrolyte from KHCO₃ (99.5%, Sigma) and deionized water was used for the 12-h chronoamperometry test in a H-type cell and all tests in a flow cell. 0.5 M KHCO₃ electrolyte from KHCO₃ (99.5%, Sigma) and tap water was also used for the 12-h chronoamperometry test in an H-type cell.

A mass flow controller (Red-y smart serie, Vögtlin) was used to control the flow rate of CO₂. The CO₂ flow was pre-humidified by a 0.5 M KHCO₃ solution. Gas-phase products of CO₂ reduction were quantified by a homemade gas chromatography (GC) equipped with a Carboxen®-1010 PLOT capillary column and a thermal conductivity detector (VICI). Helium (He) was used as the carrier gas for the analysis of CO and argon (Ar) for the analysis of H₂. The temperature program was: keeping at 35 °C for 3 min; heating to 80 °C with a ramping rate of 20 °C·min⁻¹; keeping at 80 °C for 5 min. ¹H-NMR (Bruker, 400 MHz) was used to detect the solution phase product. 240 μ L of the electrolyte after electrolysis was mixed with 200 μ L of a dimethyl sulfoxide (DMSO) solution containing 25 ppm (volume fraction) DMSO and 50 μ L of D₂O for ¹H-NMR analysis.

CV and LSV curves

A glassy carbon rotating disk electrode with the diameter of 5 mm (area: 0.196 cm²) was used as the working electrode for CV and LSV tests. 3 mg of catalyst and 40 μ L of a Nafion® perfluorinated resin solution (5 wt.%, Sigma) were dispersed in 1 mL of a mixture of H₂O and ethanol (volume ratio of H₂O to ethanol was 3:1). The mixture was treated with ultrasound for 30 min and 19.6 μ L of the mixture was dropped onto the rotating disk electrode. The electrode was dried under mild N₂ flow. The loading on the electrode was 0.3 mg·cm⁻².

The test was done in a five-neck flask. A Pt wire was used as the counter electrode. A piece of frit was used to separate the counter electrode from the working and reference electrodes. The electrolyte was bubbled with CO₂ or N₂ for at least 30 min to get the electrolyte saturated. 20 cycles of CV sweeps were conducted before the collection of LSV curves. LSV curves in fig. S5 were collected with the rotating speed of 2500 rpm and the scanning rate was 1 mV·s⁻¹.

Electrolysis in an H-type cell

A homemade two-chamber H-type cell made of glass (fig. S6A) was used. Working and reference electrodes were fixed in one chamber and the counter electrode was fixed in the other chamber. The two chambers were separated by an anion exchange membrane (Fumapem FAA-3-50). A piece of frit was fixed at the gas inlet to generate small bubbles. A Pt wire was used as the counter electrode.

Belt-shape carbon paper (AvCarb MGL280) was used as the working electrode for electrolysis at a constant potential. The area exposed to the electrolyte was fixed at 1 cm² by shading the carbon paper by a sealing film. 3 mg of catalyst and 40 μL of a Nafion® perfluorinated resin solution were dispersed in 1 mL of ethanol. The mixture was treated with ultrasound for 30 min and 200 μL of the mixture was dropped onto the carbon paper. The electrode was dried naturally for 1 hour. The loading on the electrode was 0.6 mg·cm⁻².

0.5 M KHCO₃ electrolyte was used for both chambers. The volume of the working-electrode chamber is 20.0 mL (excluding the volume of the reference electrode). 12.0 mL of electrolyte was added into this chamber. The volume of the head-space in the working-electrode chamber is 8.0 mL. The electrolyte in working-electrode chamber was saturated by bubbling CO₂ with a flow rate of 50 standard cubic centimeters per minute (sccm). At first, 20 cycles of CV sweep between -0.07 V and -0.47 V vs RHE were conducted to generate stable CV curves. Chronoamperometry was used for CO₂ reduction tests in the H-type cell. Vigorous stirring (1500 rpm) was applied during electrolysis.

If the current density was smaller than 5 mA·cm⁻², the inlet and the outlet of gas were closed before electrolysis. As the integral charge reached about -2 C, 0.5 mL of the head-space of the working-electrode chamber was extracted by a syringe to inject into GC. The time t was recorded at the same time. The electrolyte was then purged with CO₂ with a flow rate of 50 sccm during the rest time of the electrolysis. Then the Faradaic efficiencies of CO and H₂ (FE_g , $g = \text{CO or H}_2$) were calculated from the equation below:

$$FE_g = \frac{2n_g \cdot F}{Q} = \frac{2pVx_g F / RT}{\int_0^t Idt} \quad (S1)$$

In this equation: n_g is the amount of gas generated before time t (unit: mol); F is the Faraday constant (96485 C·mol⁻¹); Q is the integrated charge (unit: C); V is the volume of the head-space (8.0 mL); x_g is the fraction of gas g detected by GC; p and T are ambient pressure (101 kPa) and temperature (298 K), respectively; R is the gas constant (8.314 J·mol⁻¹·K⁻¹); I is the current of the chronoamperometry curve.

If the current density was larger than 5 mA·cm⁻², the gas phase products were measured online. The inlet and the outlet of gas were open, and the outlet was directly connected to the GC. If the current density was between 5 mA·cm⁻² and 15 mA·cm⁻², the flow rate of inlet CO₂ was 5 sccm; if the current density was larger than 15 mA·cm⁻², the flow rate of inlet CO₂ was 10 sccm. An initial equilibration time of 500 s between the electrochemical cell and the online GC was used. Then the Faradaic efficiencies of CO and H₂ (FE_g , $g = \text{CO or H}_2$) were calculated from the equation below:

$$FE_g = \frac{2r_g \cdot F}{I} = \frac{2pfx_g F / RT}{I} \quad (S2)$$

In this equation: r_g is the formation rate of gas g (unit: mol·s⁻¹); f is the gas flow rate (unit: cm³·min⁻¹); I is the stable current of the chronoamperometry test; p is 101 kPa and T is 273 K. The sum of FE_{CO} and FE_{H_2} is between 85% and 100% for all the single tests.

Each geometric current density (j) at a given potential (e.g., in Fig. 2A) was the 2-hour averaged current density of the chronoamperometry curve. The partial current density of CO (j_{CO}) was calculated according to:

$$j_{\text{CO}} = j \cdot FE_{\text{CO}} \quad (S3)$$

All the error bars for j , FE and j_{CO} are based on tests of 3 individual electrodes. The current of CO formation normalized to the moles of metal ($j_{\text{m,CO}}$) was calculated according to:

$$j_{m,CO} = \frac{j_{CO}}{m \cdot w\% / M} \quad (S4)$$

In this equation, m is the loading of the catalysts (unit: $\text{mg} \cdot \text{cm}^{-2}$). $w\%$ is the weight fraction of metal in the catalyst. M is the molecular weight of the metal (unit: $\text{g} \cdot \text{mol}^{-1}$).

For ‘single atom’ type catalysts, each metal site was regarded as a catalytic site. Then, the apparent turnover frequency (TOF) of CO formation was calculated according to:

$$\text{TOF}_{CO} = j_{m,CO} / 2F \quad (S5)$$

For the reported metal catalysts shown in fig. 2D, all atoms on surface were regarded as sites to calculate the apparent TOF. The equation is:

$$\text{TOF}_{CO} = \frac{j_{CO}}{2e \cdot r \cdot d} = \frac{j_{CO}}{2e \cdot m \cdot S \cdot d} \quad (S6)$$

In this equation, e is the charge of an electron ($1.6 \times 10^{-19} \text{ C}$); r is the roughness factor of the metal electrode; d is the estimated atomic density on the metal surface (unit: cm^{-2}); m is the loading of the metal (unit: $\text{mg} \cdot \text{cm}^{-2}$) and S is the specific surface area of the catalyst (unit: $\text{m}^2 \cdot \text{g}^{-1}$).

Electrolysis in a flow cell

A four-part home-made cell (fig. S7A) was used. The two parts made of stain steel were used as current collectors for cathode (for CO_2 reduction) and anode (for O_2 evolution). The windows for electrolysis were set to $1 \text{ cm} \times 1 \text{ cm}$. The cathode current collector also served as the chamber for gas flow behind the gas diffusion electrode (GDE). A window was also opened on the anode current collector for the escape of O_2 generated on the anode GDE. The two chambers for catholyte and anolyte were made of polyether ether ketone (PEEK), and the thickness for each chamber was 1 cm. Each chamber had an inlet and an outlet for electrolyte, and a Ag/AgCl/saturated KCl reference electrode was fixed in the catholyte chamber. CeTech carbon cloths with a micropore layer on (MPL) one side (W1S1009) were used as GDEs for cathode and anode. The GDEs were placed between the current collector and the electrolyte chamber with the MPL facing the electrolyte. The electrodes were cut into $1.5 \text{ cm} \times 1.5 \text{ cm}$ pieces when assembling the cell. A silicone gasket with a $1 \text{ cm} \times 1 \text{ cm}$ window was placed between each GDE and the electrolyte chamber for sealing. A bipolar membrane (Fumasep FBM) was used to separate the catholyte and anolyte chambers. All the pieces were pressed together by four pairs of screws and nuts at the four corners.

Fe^{3+} -N-C and NiFe-LDH nanosheets (25) were used as the catalysts for the cathode and anode, respectively. The catalysts were coated on the MPL face of the GDE by air-brush. The catalyst ink was prepared by mixing 50 mg of catalyst, 10 mL of deionized water, 2.5 mL of isopropanol and 100 μL of a Nafion® perfluorinated resin solution. The mixture was sonicated for 30 min. The GDE was mounted on a virtually placed heating plate at 120°C , and the ink was sprayed uniformly onto the GDE. The loading of the catalyst was determined by weighting the GDE before and after air-brush.

N_2 saturated 0.5 M KHCO_3 solution was used as the catholyte and N_2 saturated 1 M KOH solution was used as the anolyte. The catholyte and anolyte were cycled with a flow rate of $10 \text{ mL} \cdot \text{min}^{-1}$ by using a peristaltic pump (REGLO Digital MS-4/8, Ismatec). The gas inlet and outlet on the cathode current collector were linked to a CO_2 gas-flow meter and a GC, respectively. The data points in Fig 2A-B and fig. S7D-E were from chronopotentiometry tests. The current density was set to 1, 2, 5, 10, 20, 50, 100 and $200 \text{ mA} \cdot \text{cm}^{-2}$, and the flow rate of CO_2 was set to 1, 2, 5, 5, 10, 20, 40 and 50 sccm , respectively. An initial equilibration time of 500 s between the electrochemical cell and the online GC was used. The Faradaic efficiencies of CO and H_2 were calculated according to eq. S2. The potential at a given current density was averaged over 2-hour chronopotentiometry curve. All the error bars were standard deviations based on tests of 3 individual

electrodes. Once the potential was more negative than -0.5 V vs RHE, a continuous cathodic shift of the potential was observed during chronopotentiometry tests. Therefore, only the data at potentials more positive than -0.5 V vs RHE were plotted. For the chronoamperometry tests in fig. S7C, the flow rate of CO₂ was 40 sccm.

Kinetic and mechanistic analysis:

Here we elaborate the correlation of kinetic data (rate order in proton source and Tafel slopes) with the reaction pathways of CO₂ electroreduction to CO (31). Fig. S1 describes two general catalytic cycles. The adsorbed COOH intermediate can be formed by either decoupled (A1 + A2) or coupled (B) electron-proton transfers. A further proton-coupled electron transfer to the adsorbed COOH intermediate leads to adsorbed CO (C), which releases the free CO to regenerate the catalytic site (D).

Figure S1. Proposed reaction pathways of CO₂ electroreduction to CO.

If the reaction goes through a proton-decoupled electron transfer step (A1), which is the rate determining step, according to the Butler-Volmer equation under the condition of irreversible electron transfer, the partial current density of CO formation is:

$$j_{\text{CO}} = 2ed\theta_{\text{Fe}}a_{\text{CO}_2}k_{\text{A1}}^0 \exp\left(-\frac{\beta FE}{RT}\right) \quad (\text{S7})$$

In this equation, d is the density of Fe sites (unit: cm⁻²); θ_{Fe} is the coverage of free Fe sites; a_{CO_2} is the activity of CO₂ in electrolyte; k_{A1}^0 is the rate constant of this step at 0 V vs SHE; β is the transfer coefficient; E is the potential vs SHE. In low-overpotential region, $\theta_{\text{Fe}} \rightarrow 1$. Under this circumstance, j_{CO} is independent of the concentration of proton source. The Tafel slope is:

$$\frac{\partial(-E)}{\partial \lg j_{\text{CO}}} = \frac{2.3RT}{\beta F} \quad (\text{S8})$$

Assuming $\beta = 0.5$, the Tafel slope at 298 K is 118 mV/dec.

If the reaction goes through a fast decoupled electron-proton transfer (A1) followed by a rate-determining protonation step (A2), the partial current density of CO formation is:

$$j_{\text{CO}} = 2ed\theta_{\text{CO}_2^-}a_{\text{HA}}k_{\text{A2}} \quad (\text{S9})$$

In this equation, $\theta_{\text{CO}_2^-}$ is the coverage of adsorbed CO₂⁻ intermediate; a_{HA} is the activity of the proton source of this step; k_{A2} is the rate constant of this step. Assuming A1 as a fast equilibrium,

$$\frac{\theta_{\text{CO}_2^-}}{\theta_{\text{Fe}} a_{\text{CO}_2}} = K_{\text{A1}}^0 \exp\left(-\frac{FE}{RT}\right) \quad (\text{S10})$$

In this equation, K_{A1}^0 is the equilibrium constant of A1 at 0 V vs SHE. Then:

$$j_{\text{CO}} = 2ed a_{\text{HA}} k_{\text{A2}} \theta_{\text{Fe}} a_{\text{CO}_2} K_{\text{A1}}^0 \exp\left(-\frac{FE}{RT}\right) \quad (\text{S11})$$

In the low-overpotential region, $\theta_{\text{Fe}} \rightarrow 1$. Under this circumstance, the order of j_{CO} on the concentration of proton source is 1. The Tafel slope is:

$$\frac{\partial(-E)}{\partial \lg j_{\text{CO}}} = \frac{2.3RT}{F} \quad (\text{S12})$$

At 298 K, the Tafel slope is 59 mV/dec.

If the reaction goes through coupled electron-proton transfer (B) as the rate determining step, the partial current density of CO formation is:

$$j_{\text{CO}} = 2ed \theta_{\text{Fe}} a_{\text{CO}_2} a_{\text{HA}} k_{\text{B}}^0 \exp\left(-\frac{\beta FE}{RT}\right) \quad (\text{S13})$$

In this equation, k_{B}^0 is the rate constant of this step at 0 V vs SHE. Supposing $\theta_{\text{Fe}} \rightarrow 1$, the order of j_{CO} on the concentration of proton source is 1. The Tafel slope is:

$$\frac{\partial(-E)}{\partial \lg j_{\text{CO}}} = \frac{2.3RT}{\beta F} \quad (\text{S14})$$

Assuming β is 0.5, the Tafel slope at 298 K is 118 mV/dec.

If step C is the rate determining step, the Tafel slope will be about 40 mV/dec (31). This Tafel slope is not observed in this paper, nor in previous reports. Therefore, this scenario is not analyzed here.

If step D is the rate determining step, the partial current density of CO formation is:

$$j_{\text{CO}} = 2ed k_{\text{D}} \theta_{\text{CO}} \quad (\text{S15})$$

In this equation, k_{D} is the rate constant of CO desorption; θ_{CO} is the coverage of adsorbed CO intermediate. If the overpotential is high enough to form high coverage of CO on Fe sites ($\theta_{\text{CO}} \rightarrow 1$), j_{CO} will be independent of the concentration of proton source and potential. The Tafel slope will be ∞ .

The measurements of pH dependence of j_{CO} are complicated by the change of proton donors in different pH buffers (fig. S16A and S16C). Thus, we measured the rate orders of proton donor in the bicarbonate electrolyte (fig. S16B and S16D), assuming HCO_3^- as the proton source, as reported HCO_3^- earlier for CO_2 electroreduction to CO on OD-Au at low overpotential (3).

Our data showed that j_{CO} of Fe^{2+} -N-C had an order of close to 0 (0.15) in the concentration of HCO_3^- and a Tafel slope of close to 118 (117) mV/dec at low to modest overpotentials. These data indicate a rate-determining decoupled electron transfer step for Fe^{2+} -N-C at low current densities. At high overpotentials the Tafel slope increased to 546 mV/dec, consistent with CO desorption becoming rate-limiting. On the contrary,

the j_{CO} of Fe^{3+} -N-C had an order of close to 1 (0.8-0.9) in the concentration of HCO_3^- and a Tafel slope of close to 59 (64-71) mV/dec at low to modest overpotentials. These data indicate a fast 1e reduction of CO_2 (A1) followed by a rate-determining protonation step (A2) for Fe^{3+} -N-C. Assuming protonation of adsorbed CO_2 has a similar rate for Fe^{2+} -N-C and Fe^{3+} -N-C, the data also indicate that 1e reduction of CO_2 is faster on Fe^{3+} -N-C than on Fe^{2+} -N-C.

Figure S2. Characterizations of Fe doped ZIF-8. (A) XRD patterns of Fe doped ZIF-8 (red) and undoped ZIF-8 (black). (B) An SEM image of Fe doped ZIF-8. (C) Size distribution diagram based on SEM images. (D) An HAADF-STEM image and the corresponding EDS mapping images of Zn (green), Fe (red) and N (blue). (E) The corresponding EDS spectrum of the region in the red square in (D). The Cu signal came from the Cu grid support on which the sample was casted. (F) Fe K-edge XANES spectra of Fe doped ZIF-8 (black), Fe_2O_3 (blue dashed), FeO (pink dashed) and Fe foil (orange dashed). (G) The k-space and (H) the R-space Fe K-edge EXAFS spectra (black) and the fitting curves (red). The fitting result is listed in table S1. (I) Local structure of Fe doped ZIF-8 around Fe: one Fe atom coordinates with four 2-methylimidazolate ligands. The EXAFS fitting result agrees with this structure.

Figure S3. Characterizations of Fe^{3+} -N-C. (A) N_2 physisorption isotherm. (B) BJH pore size distribution. (C) CV curves in 0.5 M KHCO_3 electrolyte at different scanning rate. (D) Linear fittings of the differences of current densities between anodic and cathodic scans with the scan rates to determine the double layer capacitance (C) and electrochemical surface area (ECSA). * (E) Survey XPS spectrum. The atomic ratio of Fe:Zn from XPS of 2p electrons is shown. (F) Fe 2p XPS spectrum. The red and blue vertical lines indicate the binding energy of Fe 2p_{3/2} of Fe_2O_3 and FeO, respectively (37, 38). (G) XRD pattern. (H) Zn K-edge XANES spectra of Fe^{3+} -N-C (black) and ZnO (red dashed). (I) R-space and k-space (inset) of Zn K-edge EXAFS of Fe^{3+} -N-C. Spectrum (black) and the fitting curves (red) are shown. The fitting result is listed in table S2.

* The ECSA was calculated from the double layer capacitance obtained here. Assuming the double layer capacitance per cm^2 of the electrochemical surface area of the catalyst is identical to that of graphene, namely $21 \mu\text{F}\cdot\text{cm}^{-2}$ (39), the electrochemical surface area on the electrode was $0.166 \text{ m}^2\cdot\text{cm}^{-2}$. The loading of the catalysts was $0.3 \text{ mg}\cdot\text{cm}^{-2}$. Thus, the mass normalized electrochemical surface area was $554 \text{ m}^2\cdot\text{g}^{-1}$.

Figure S4. Electron microscopy characterization of $\text{Fe}^{3+}\text{-N-C}$. (A-B) SEM images. (C) Size distribution diagram based on SEM images. (D) A TEM image. (E) A HRTEM image of the region in red square of (D). The inset shows the Fast-Fourier-Transform pattern of the region in red square of (E). (F) The EDS spectrum. The atomic ratio of Fe:Zn from EDS is shown. The Cu signal came from the Cu grid support on which the sample was casted.

Figure S5. (A) LSV curves of Fe³⁺-N-C (red), Fe²⁺-N-C (blue) and Zn-N-C (grey) in CO₂ (solid) and N₂ (dashed) saturated 0.5 M KHCO₃ electrolyte. The working electrode was a glassy carbon rotating disk electrode; the rotating speed was 2500 rpm. The scanning rate was 1 mV·s⁻¹. (B) A zoom-in view of the LSV curves in CO₂ saturated 0.5 M KHCO₃ electrolyte. The equilibrium reduction potential of CO₂ to CO (-0.11 V vs RHE) is indicated by the dashed black line.

Figure S6. Electrocatalytic tests in an H-type cell. (A) Scheme of the H-type cell. GC curve with (B) He and (C) Ar as the carrier gas obtained on Fe³⁺-N-C in an H-type cell at -0.37 V vs RHE. The temperature program is shown. (D) ¹H-NMR spectrum of the electrolyte after the test of Fe³⁺-N-C in an H-type cell at -0.37 V vs RHE. DMSO was added as inner standard. (E) Chronoamperometry curve of Fe³⁺-N-C at -0.19 V vs RHE in CO₂ saturated 0.5 M KHCO₃ electrolyte. (F) GC curve of the gas in the head space after the electrolysis in panel (E). (G) Comparison of chronoamperometry curves of Fe³⁺-N-C and Fe²⁺-N-C at -0.37 V and -0.47 V vs RHE. (H) Total geometric current density of Fe³⁺-N-C (red) and Fe²⁺-N-C (black) in CO₂ saturated 0.5 M KHCO₃ electrolyte.

Figure S7. Electrocatalytic tests of $\text{Fe}^{3+}\text{-N-C}$ in a flow cell. (A) Scheme of the flow cell with catalyst deposited on GDE with micropore layer. (B) Chronopotentiometry curves with the loading of catalyst at 2.5 mg cm^{-2} . At potentials more positive than -0.5 V vs RHE , the activity was stable. At potentials more negative than -0.5 V vs RHE , the activity was unstable as the potentials shifted to more negative values over time. (C) Chronoamperometry curves (solid curves) and Faradaic efficiency of CO (squares and triangles) at -0.51 V (red) and -0.41 V (black) vs RHE. The loading of catalyst was 2.5 mg cm^{-2} . (D) Faradaic efficiency of CO and (E) j_{CO} in an H-type cell (black) and in a flow cell with different loadings of catalysts on the GDEs. Data of the H-type cell were from chronoamperometry tests and data of the flow cell were from chronopotentiometry tests. At a loading of 2.5 mg cm^{-2} , the flow cell showed the highest j_{CO} .

Figure S8. Comparison of the activity of Fe³⁺-N-C, Fe²⁺-N-C and other catalysts in CO₂ electroreduction in an H-type cell. (A) Faradaic efficiency of CO production. (B) Mole-normalized partial current of CO production. The brief descriptions of catalysts, test conditions (working electrode, electrolyte, loading of the catalysts) and sources of the data are listed as below.

Fe0.5d: From ref. (15). Prepared by the pyrolysis of a mixture of Fe²⁺(phen)₃ and ZIF-8. The catalyst was tested on carbon paper in 0.5 M NaHCO₃ electrolyte. The loading was 1.0 mg·cm⁻² and the weight fraction of Fe was 1.5%. The Faradaic efficiency of CO was extracted from Fig. 4A of ref. (15). The partial current density of CO was calculated from the production rate of CO in fig. S4 of ref. (15). The mole normalized partial current of CO and the apparent TOF of CO were calculated according to Eq. S4 and S5, respectively.

Fe-N-C: From ref. (16). Prepared by the pyrolysis of an Fe²⁺-bipyridyl composite followed by acid leaching. This catalyst was tested in 0.1 M KHCO₃ electrolyte. The loading was 0.76 mg·cm⁻² and the weight fraction of Fe was 1.73%. The Faradaic efficiency of CO were extracted from Fig. 4B of ref. (16). The partial current density of CO was calculated from the mass normalized current in Fig. 4D of ref. (16). The mole normalized partial current of CO and the apparent TOF of CO were calculated according to Eq. S4 and S5, respectively.

Co-N2: From ref. (17). Prepared by the pyrolysis of a Co-Zn bimetallic ZIF. The coordination number of Co-N was 2. This catalyst was tested on carbon fiber paper in 0.5 M KHCO₃. The loading was 0.8 mg·cm⁻². The Faradaic efficiency of CO was extracted from Fig. 3B of ref. (17). The partial current density of CO at -0.63 V vs RHE was extracted from Fig. 3D of ref. (17) and those at other potentials were calculated according to the proportion in Fig. 3C of ref. (17).

A-Ni-NSG: From ref. (19). The catalyst comprised of atomically dispersed Ni⁺ ions on nitrogen-sulfur co-doped graphene. This catalyst was tested on carbon fiber paper in 0.5 M KHCO₃. The loading was 0.4 mg·cm⁻² and the weight fraction of Fe was 2.8%. The Faradaic efficiency of CO was extracted from Fig. 3B of ref. (19). The total current density was extracted from fig. S6K of ref. (19) and the partial current density of CO was calculated from total current density and Faradaic efficiency. The mole normalized partial current of CO and the apparent TOF of CO were calculated according to Eq. S4 and S5, respectively.

OD-Au: From ref. (3). An oxide-derived Au electrode was prepared from electrochemical reduction of Au foil annealed in air. The electrode was directly tested in 0.5 M NaHCO₃ electrolyte. The Faradaic efficiency and partial current density of CO were extracted from Fig. 3 and Fig. 4A of ref. (3), respectively. The roughness factor of the electrode was 72. Assuming the atomic density on the electrochemical surface is that on Au (111) facet (1.39×10¹⁵ cm⁻²), the number of Au atom sites on electrode per cm² of geometric area was 1.00×10¹⁷ cm⁻², which was used to calculate TOF according to Eq. S6.

C-Au-500: From ref. (4). The catalyst comprised of Au nanowires with a length of 500 nm supported on carbon black. The catalyst was tested on carbon paper in 0.5 M KHCO₃ electrolyte. The loading of Au was 4.4 mg·cm⁻². The Faradaic efficiency was extracted from Fig. 2C of ref. (4) and the partial current density of

CO was calculated from mass normalized current (Fig. 2D of ref. (4)). The mole normalized partial current of CO was calculated according to Eq. S4. Assuming that the Au nanowires are cylinders with the diameter of 2.1 nm and the surface atomic density is $1.39 \times 10^{15} \text{ cm}^{-2}$, the TOF was calculated from the mass normalized current according to Eq. S6.

Au needles: From ref. (5). The catalyst comprises of electrochemically grown Au nanoneedles on carbon fiber paper. The Faradaic efficiency and partial current density of CO were extracted from Fig. 4C and Extended Data Fig. 3J of ref. (5), respectively.

np-Ag: From ref. (7). The catalyst was a nanoporous Ag electrode. The catalyst was tested in 0.5 M KHCO_3 electrolyte. The loading of Ag was $40 \text{ mg} \cdot \text{cm}^{-2}$. The Faradaic efficiency and the partial current density of CO were extracted from fig. S5 and Fig. 3 of ref. (7), respectively. The mole normalized partial current of CO was calculated according to Eq. S4. The electrochemical surface area per 1 cm^2 of electrode was 2650 cm^2 . TOF was calculated by assuming Ag (111) facet as the active sites, which had an atomic density of $1.39 \times 10^{15} \text{ cm}^{-2}$ according to Eq. S6.

Figure S9. TEM characterization of Fe^{3+} -N-C after 12 hours of electrocatalysis at -0.37 V vs RHE. (A) A TEM image. (B) An HRTEM image. (C) An HAADF-STEM image and the corresponding EDS mappings of Fe (red) and N (blue). (D) Comparison of EDS spectra before and after electrolysis. The mole ratios of Fe:Zn are listed on the right side. The Cu signals came from the Cu grid support on which the sample was casted (E) An aberration corrected HAADF-STEM image. (F) The EDS spectrum of the region in red square in

panel (E). The Cu signals came from the Cu grid support on which the sample was casted

Figure S10. R-space Fe K-edge EXAFS spectra of (A) Fe^{3+} -N-C and (B) Fe^{2+} -N-C. The detailed fitting results are listed in table S1. (C) The fitted first-shell coordination number of Fe (Fe-N and Fe-C) of Fe^{3+} -N-C (black) and Fe^{2+} -N-C (red) at different conditions. *

* The first-shell coordination number of Fe of the dry powder of Fe^{2+} -N-C was close to 5. But this number decreased to about to 4 when the sample was merged in the electrolyte.

Figure S11. Characterization of Fe0.5d synthesized with a literature method (15). (A) Fe K-edge XANES spectra of Fe0.5d (black), Fe₂O₃ (blue dashed), Fe³⁺TPPCL (green dashed), FeO (pink dashed) and Fe foil (orange dashed). The inset shows the enlargement of the main edges. (B) R-space Fe K-edge EXAFS curve. The inset shows the K-space curve. (C) Faradaic efficiency and (D) partial current density of CO of Fe0.5d from the literature (orange), Fe0.5d reproduced by us (red) and Fe^{III}-N-C (blue). For Fe0.5d, the test conditions were identical to the literature: loading of Fe0.5d was 1.0 mg·cm⁻² and the electrolyte was 0.5 M NaHCO₃. The performance of Fe0.5d reproduced by us was comparable to that in the literature. (E) Operando Fe K-edge XANES spectra of Fe0.5d. The spectra of dry powder (black), catalysts loaded on glassy carbon electrodes at the open circuit potential (OCP, blue), -0.1 V (light blue), -0.2 V (green), -0.3 V (dark green), -0.4 V (dark blue), -0.5 V (red) and -0.6 V (pink) vs RHE are shown, with the spectra of Fe₂O₃ (blue dashed),

Fe³⁺TPPCL (green dashed), FeO (pink dashed) and Fe foil (orange dashed) as references. (F) The 1st derivative of the Fe K-edge XANES spectra at different conditions.

Figure S12. (A) N K-edge XANES spectra of Fe³⁺-N-C (red) and Fe²⁺-N-C (blue). The dashed vertical lines indicate the energy of π^* and σ^* features of a reported metal porphyrin derivative (2,8,12,18-tetraethyl-5,15-diethynyl-3,7,13,17-tetramethylporphyrinatozinc(II)) (29). (B) N 1s XPS spectra of Fe³⁺-N-C and Fe³⁺TPPCl. Red, green and pink peaks are assigned to pyrrolic N coordinated to metals, uncoordinated pyrrolic N and graphitic N, respectively. (C) N 1s XPS spectra of Fe²⁺-N-C, ferroin sulfate (Fe²⁺(phen)₃SO₄) and ferric-phenanthroline bis(trifluoromethylsulfonyl)imide (Fe³⁺(phen)₃(Tf₂N)₃). Red, blue, green, pink and cyan peaks are assigned to uncoordinated pyridinic N, pyridinic N coordinated to metals, protonated pyridinic N, graphitic N and oxidized N, respectively.* (D) Raman spectra of Fe³⁺-N-C (red) and Fe²⁺-N-C (blue). D band (1350 cm⁻¹) and G band (1600 cm⁻¹) were observed for these two samples.†

* Since Fe²⁺-N-C was treated with nitric acid, protonated N and oxidized N exist. Detailed fitting results of N-1s XPS spectra of Fe³⁺-N-C and Fe²⁺-N-C are listed in table S3. The fraction of the peaks assigned to

nitrogen coordinated with metals among all N 1s signal (denoted as N-M/N) is close to the theoretical value calculated from the content of metal and N obtained by ICP-OES and element analysis as well as the coordination number of M-N path from EXAFS, as shown in table S4.

† The intensity ratio of D:G is higher for Fe³⁺-N-C, indicating a higher defect density. The high defect density should result from the existence of 5-member rings with pyrrolic N in the carbon matrix of Fe³⁺-N-C.

Figure S13. Electron spectroscopy characterization of Fe^{2+} -N-C. (A) An SEM image. (B) An HADDF-STEM image and the corresponding EDS mappings of Fe (red) and N (green). (C) An HRTEM image. (D) An aberration-corrected HAADF-STEM image.

Figure S14. Characterization of $\text{Fe}^{2+}\text{-N-C}$. (A) XRD pattern. (B) Survey XPS spectrum. (C) Fe 2p XPS spectrum. The red and blue vertical lines indicate the binding energy of Fe 2p_{3/2} of Fe_2O_3 and FeO, respectively (37, 38). (D) Fe K-edge XANES spectra of $\text{Fe}^{2+}\text{-N-C}$ (black), Fe_2O_3 (blue dashed), $\text{Fe}^{3+}\text{TPPCI}$ (green dashed), FeO (pink dashed) and Fe foil (orange dashed). The inset shows the enlargement of the main edges. (E) R-space and k-space (inset) Fe K-edge EXAFS spectra. Data (black) and fitting curves (red). The fitting result is listed in table S1. (F) N_2 physisorption isotherm. The inset shows BJH pore size distribution. (G) Linear fittings of the differences of current densities between anodic and cathodic scans with the scan rates to determine the double layer capacitance (C) and electrochemical surface area (ECSA).

Figure S15. GC curves of the gas products of the reactions of NaBH_4 with Zn-N-C (black), Fe^{3+} -N-C (red) and Fe^{2+} -N-C (blue). Ar was used as the carrier gas and the peaks at 1.32 min corresponded to H_2 . In the reactions, 5 mg of a catalyst sample and 1 mL of a 0.1 M aqueous solution of NaBH_4 was mixed into a 2 mL air-tight vial. The vial was sealed immediately and put into an ice-water bath for 10 min. The gas in the head space was extracted by a syringe and injected into a GC for analysis. H_2 generated from the reaction with Zn-N-C was treated as the background control. The H_2 formed there might come from the reaction NaBH_4 with water and some oxidizing species other than Fe^{3+} in the N-doped carbon support. The reaction with Fe^{2+} -N-C released a significantly higher amount of H_2 than the reaction with Zn-N-C, due to reduction of Fe^{3+} ions. The reaction with Fe^{3+} -N-C released a same amount of H_2 to the reaction with Zn-N-C, indicating no reduction of Fe^{3+} ions.

Figure S16. Dependence of j_{CO} at fixed potentials vs SHE of (A, B) Fe²⁺-N-C and (C, D) Fe³⁺-N-C on (A, C) pH value of electrolyte and (B, D) concentration of HCO₃⁻. * For pH dependence experiment, 0.5 M KHCO₃ solution (pH = 7.25), 0.17 M K₃PO₄ solution (pH = 7.00), 0.25 M K₂HPO₄ solution (pH = 6.69) and 0.5 M KH₂PO₄ solution (pH = 4.37) were used as the electrolytes. For HCO₃⁻ dependence experiment, KHCO₃ and KClO₄ were used to make the electrolyte and the concentration of K⁺ was kept at 0.5 M. The orders of the dependence are labeled on the right side. (E) Tafel plots of Fe²⁺-N-C (black spots) and Fe³⁺-N-C in an H-cell (red spots) and Fe³⁺-N-C on a gas diffusion electrode (GDE) in a flow cell (blue spots). The data at low current densities for each sample were fitted to give the respective Tafel slopes. † For Fe²⁺-N-C, a second Tafel slope at j_{CO} around 1 mA·cm⁻² (green line) was also fitted.

* The kinetic analysis using rate orders in pH is complicated because the proton donors in different pH buffers change. Thus, kinetic analysis was done using rate orders in the bicarbonate electrolyte. See Supplementary materials, Kinetic and mechanistic analysis for details.

† The data of Fe³⁺-N-C in an H-cell deviated from the linear Tafel fitting line when the partial current density of CO production reached 2 mA·cm⁻² due to the limitation of mass transport. For Fe³⁺-N-C on a GDE in a

flow cell, the deviation occurred from about $20 \text{ mA} \cdot \text{cm}^{-2}$, indicating improved mass transport on a GDE. The data of Fe^{2+} -N-C in an H-cell from $1 \text{ mA} \cdot \text{cm}^{-2}$ and onward could be fit with a very large Tafel slope of 546 mV/dec, which suggested rate-limiting CO release at high current densities for Fe^{2+} -N-C. This behavior was not observed for Fe^{3+} -N-C in both H- and flow cells.

Figure S17. (A) Chronoamperometry curves of Fe²⁺-N-C (black) and Fe³⁺-N-C (red) in 0.5 M KHCO₃ electrolyte at -0.37 V vs RHE. From 0 s to 1200 s the electrolyte was purged with a mixed gas of 0.8 atm of CO₂ and 0.2 atm of N₂, and from 1200 s to 3000 s the electrolyte was purged with a mixed gas of 0.8 atm of CO₂ and 0.2 atm of CO. LSV curves of (B) Fe²⁺-N-C and (C) Fe³⁺-N-C in 0.5 M KHCO₃ electrolyte purged with a mixed gas of 0.8 atm of CO₂ and 0.2 atm N₂ (black) or 0.8 atm of CO₂ and 0.2 atm of CO (red). Carbon papers were used as the working electrodes and the scanning rate was 20 mV·s⁻¹.

Figure 1 consists of three energy level diagrams (a, b, c) showing the potential energy (eV) versus distance from the surface (nm) for a photocatalytic system. The diagrams illustrate the mechanism of photocatalytic reduction of Fe(III) to Fe(II) on TiO2.

(a) Initial state: The diagram shows the conduction band (CB) and valence band (VB) of TiO2. The Fermi level (E_F) is indicated. The potential energy of the Fe(III) complex ($E(\text{Fe}^{3+/2+} \text{X}_4)$) is shown. A proton (H^+) is present in the VB. The OHP (Outer Helmholtz Plane) is marked at a distance of 0 nm from the surface.

(b) Removal of one ligand: A blue arrow indicates the transition from (a) to (b). The diagram shows the removal of one ligand from the Fe(III) complex, resulting in the formation of a Fe(III) complex with three ligands ($\text{Fe}^{3+/2+} \text{X}_3$). The potential energy of this complex is shown. The Fermi level (E_F) is also indicated.

(c) Reduction of Fe(III): A blue arrow indicates the transition from (b) to (c). The diagram shows the reduction of Fe(III) to Fe(II) in the CB, resulting in a Fe(II) complex with three ligands ($\text{Fe}^{2+/+} \text{X}_3$). The potential energy of this complex is shown. The Fermi level (E_F) is also indicated.

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Fe^{3+} -N-C at -0.5 V vs. RHE. For a molecular complex dissolved in solution (scenario A), the $\text{Fe}^{3+/2+}$ reduction potential remains constant while the Fermi level of the electrode changes with the bias. Reduction of Fe^{3+} to Fe^{2+} can be observed in voltammetry. OHP is the outer Helmholtz plane. For the Fe-X_4 conjugated to the carbon support (scenario B), the $\text{Fe}^{3+/2+}$ reduction potential moves to the same degree as the Fermi level of the electrode when applying a bias. The Fe^{3+} remains stable. When one N ligand is removed from Fe-X_4 to form an Fe-X_3 , the $\text{Fe}^{3+/2+}$ reduction potential changes to a more positive value due to the change of coordination environment. We hypothesize that this $\text{Fe}^{3+/2+}$ reduction potential is now more positive than the Fermi level of the electrode, so reduction of Fe^{3+} to Fe^{2+} occurs. Once formed, the Fe^{2+} ions are also conjugated to the carbon support and should remain electronically stable.

Table S1. Fitting parameters of Fe K-edge EXAFS spectra.

Condition	Path	R (Å)	Coordination Number	ΔE_0 (eV)	σ^2 (Å ²)	R factor
Fe doped ZIF-8						
Dry powder	Fe-N	2.03(4)	4.5(6)	2.3(4)	0.0060(5)	2.206
	Fe-C1	3.06(8)	5.9(9)	-0.2(8)	0.0026(8)	
	Fe-C2	3.43(9)	3.3(7)	0.4(9)	0.0085(9)	
Fe ³⁺ -N-C						
Dry powder	Fe-N	1.97(4)	3.4(9)	-9.8(5)	0.0066(6)	8.753
	Fe-C1	1.92(9)	0.5(9)	-1.9(9)	0.0090(9)	
	Fe-C2	3.16(4)	3.6(8)	-9.6(6)	0.0091(8)	
OCP †	Fe-N	1.97(7)	3.4(7)	-6.4(7)	0.0071(6)	9.433
	Fe-C1	1.92(9)	0.5(8)	-1.5(6)	0.0090(9)	
	Fe-C2	3.16(4)	3.6(6)	-1.3(5)	0.0068(6)	
-0.1 V ‡	Fe-N	1.99(4)	3.7(7)	-9.8(6)	0.0066(4)	8.563
	Fe-C1	1.94(9)	0.5(5)	-1.9(9)	0.0025(9)	
	Fe-C2	3.18(8)	3.5(9)	-9.6(5)	0.0091(6)	
	Fe-C(ad) §	1.49(8)	0.1(4)	0.2(8)	0.0059(4)	
-0.2 V	Fe-N	1.99(5)	3.7(8)	-8.9(5)	0.0068(3)	9.921
	Fe-C1	1.89(4)	0.5(5)	-2.6(9)	0.0063(9)	
	Fe-C2	3.12(4)	3.6(9)	-4.5(5)	0.0070(6)	
	Fe-C(ad)	1.50(6)	0.2(4)	-2.9(9)	0.0034(8)	
-0.3 V	Fe-N	1.99(5)	3.6(8)	-8.4(6)	0.0065(4)	8.868
	Fe-C1	1.82(4)	0.6(7)	-3.6(7)	0.0104(9)	
	Fe-C2	3.00(5)	3.5(9)	-4.7(8)	0.0104(6)	
	Fe-C(ad)	1.47(6)	0.3(4)	1.8(7)	0.0011(9)	
-0.4 V	Fe-N	1.99(6)	3.6(5)	-7.6(4)	0.0068(5)	7.673
	Fe-C1	1.90(8)	0.5(6)	-3.8(6)	0.0099(9)	
	Fe-C2	3.19(9)	3.6(4)	-2.8(5)	0.0069(8)	
	Fe-C(ad)	1.48(4)	0.2(6)	-0.8(7)	0.0021(8)	
-0.5 V	Fe-N	2.01(5)	2.4(4)	-7.5(6)	0.0079(6)	2.468
	Fe-C1	1.96(8)	0.4(4)	-8.2(9)	0.0052(9)	
	Fe-C2	3.14(4)	2.1(6)	-2.8(5)	0.0076(5)	
	Fe-C(ad)	1.49(8)	0.1(4)	3.2(9)	0.0025(9)	
	Fe-O	2.21(6)	0.4(7)	8.9(8)	0.0010(9)	
-0.6 V	Fe-N	2.07(4)	2.2(5)	-7.2(6)	0.0075(8)	1.142
	Fe-C1	2.01(6)	0.3(7)	-11.6(5)	0.0036(9)	
	Fe-C2	3.17(5)	2.4(6)	-2.5(4)	0.0092(6)	
	Fe-C(ad)	1.57(5)	0.3(6)	1.3(9)	0.0024(9)	
	Fe-O	2.20(4)	0.5(5)	9.4(4)	0.0000(9)	

Continue of table S1.

Condition	Path	R (Å)	Coordination Number	ΔE_0 (eV)	σ^2 (Å ²)	R factor
Fe ²⁺ -N-C						
Dry powder	Fe-N	1.99(5)	4.3(4)	-15.7(6)	0.0084(8)	7.099
	Fe-C1	1.91(6)	0.5(7)	-6.9(6)	0.0062(9)	
	Fe-C2	2.82(7)	3.4(6)	0.8(8)	0.0155(6)	
	Fe-C3	3.23(9)	3.5(9)	-1.4(9)	0.0110(9)	
OCP	Fe-N	2.09(6)	3.7(4)	-5.5(5)	0.0116(4)	9.244
	Fe-C1	1.90(7)	0.6(5)	-12.6(9)	0.0067(9)	
	Fe-C2	2.84(6)	3.5(7)	4.6(7)	0.0100(7)	
	Fe-C3	3.24(8)	3.6(9)	-2.9(5)	0.0095(9)	
-0.1 V	Fe-N	2.09(4)	3.7(7)	-7.3(7)	0.0090(8)	2.813
	Fe-C1	1.98(9)	0.4(9)	2.0(4)	0.0045(9)	
	Fe-C2	2.88(6)	3.4(4)	-7.4(5)	0.0138(7)	
	Fe-C3	3.23(8)	3.6(9)	-12.8(7)	0.0091(8)	
	Fe-C(ad)	1.52(5)	0.4(5)	2.0(9)	0.0078(5)	
-0.2 V	Fe-N	2.09(4)	3.2(4)	-6.7(6)	0.0102(4)	5.045
	Fe-C1	1.89(9)	0.1(6)	-0.8(9)	0.0054(9)	
	Fe-C2	2.88(5)	3.5(6)	-3.7(7)	0.0144(6)	
	Fe-C3	3.23(7)	3.7(9)	-5.5(6)	0.0103(9)	
	Fe-C(ad)	1.55(5)	0.3(4)	2.4(5)	0.0040(9)	
-0.3 V	Fe-N	2.17(6)	3.0(8)	1.5(6)	0.0111(5)	3.993
	Fe-C2	2.92(9)	3.3(7)	8.5(8)	0.0119(5)	
	Fe-C3	3.27(4)	3.6(9)	2.9(6)	0.0096(9)	
	Fe-C(ad)	1.58(5)	0.5(7)	13.4(9)	0.0045(4)	
-0.4 V	Fe-N	2.19(5)	3.5(6)	-3.0(4)	0.0096(8)	4.156
	Fe-C2	2.84(5)	3.4(6)	1.5(6)	0.0156(9)	
	Fe-C3	3.25(5)	3.6(9)	4.0(3)	0.0130(9)	
	Fe-C(ad)	1.61(6)	0.5(4)	-4.9(8)	0.0045(9)	
-0.5 V	Fe-N	2.14(6)	3.3(8)	-12.2(5)	0.0101(4)	9.065
	Fe-C2	2.86(7)	3.3(5)	-13.7(8)	0.0150(8)	
	Fe-C3	3.28(6)	3.6(5)	-2.5(7)	0.0146(9)	
	Fe-C(ad)	1.64(6)	0.5(4)	-5.5(7)	0.0060(9)	
-0.6 V	Fe-N	2.15(4)	3.2(6)	-0.7(5)	0.0096(5)	5.624
	Fe-C2	2.86(7)	3.3(5)	-6.2(7)	0.0125(6)	
	Fe-C3	3.24(7)	3.7(8)	-5.1(6)	0.0096(9)	
	Fe-C(ad)	1.54(8)	0.4(4)	-2.5(9)	0.0040(9)	

* The data were normalized to the incoming incident energy and processed with the REX2000 software from the IFEFFIT package. An E_0 value of 7112.0 eV was used to calibrate all data with respect to the first inflection point of the absorption K-edge of an Fe foil. EXAFS curve fitting was performed with REX2000 and IFEFFIT software using ab initio-calculated phases and amplitudes from the program FEFF 8.2. S_0^2 is an amplitude reduction factor due to shake-up/shake-off processes at the central atom(s). The EXAFS

equation was used to fit the experimental data using coordination number, R , and the EXAFS Debye-Waller factor (DW; σ^2) as variable parameters. R : distance between absorber and backscatter atoms; ΔE_0 : inner potential correction; σ^2 : Debye–Waller factor to account for both thermal and structural disorders; R factor indicates the goodness of the fit. The S_0^2 values was determined as 0.89.

† OCP: Open circuit potential.

‡ All the potential is vs RHE.

§ Fe-C(ad) is originated from the CO adsorption on Fe site.

Table S2. Fitting parameters of Zn K-edge EXAFS spectrum of Fe³⁺-N-C. *

Path	R (Å)	Coordination Number	ΔE_0 (eV)	σ^2 (Å ²)	R factor
Zn-N	1.96(4)	3.6(2)	-9.9(8)	0.0075(8)	3.156
Zn-C	1.75(1)	0.9(2)	-8.8(2)	0.0074(2)	

* The data collected were normalized to the incoming incident energy and processed with the REX2000 software from the IFEFFIT package. An E_0 value of 8659.0 eV was used to calibrate all data with respect to the first inflection point of the absorption K-edge of an Zn foil. EXAFS curve fitting was performed with REX2000 and IFEFFIT software using ab initio-calculated phases and amplitudes from the program FEFF 8.2. The EXAFS equation was used to fit the experimental data using coordination number, R , and the EXAFS Debye-Waller factor (DW; σ^2) as variable parameters. The S_0^2 values was determined as 0.86.

Table S3. Fitting of N 1s XPS spectra of Fe³⁺-N-C and Fe²⁺-N-C.

Sample	B.E. (eV)	Fraction (%)	Assignment
Fe ³⁺ -N-C	398.6	68	Pyrrolic N coordinates to metals (40)
	399.6	2	Pyridinic N coordinates to metals (16, 41)
	400.8	26	Un-coordinating pyrrolic N (42)
	402.2	4	Graphitic N (16)
Fe ²⁺ -N-C *	398.4	27	Un-coordinating pyridinic N (16, 43)
	399.7	40	Pyridinic N coordinates to metal (16, 41)
	400.8	17	Un-coordinating pyrrolic N (16, 42) or protonated pyridinic N (41)
	402.2	7	Graphitic N (16)
	405.2	9	N oxide (16)

Table S4. Fraction of N coordinated with metal among all N element ((N-M)/N).

	Fe ³⁺ -N-C	Fe ²⁺ -N-C
Atomic ratio of M in XPS	Fe: 0.74%; Zn: 0.77% Sum: 1.51%	Fe: 0.69%
Atomic ratio of N in XPS	7.29%	7.74%
Atomic ratio of N/M from XPS	4.83	11.2
Weight content of M in ICP-OES	Fe: 2.8%; Zn: 3.4%	Fe: 2.6%
Weight content of N in element analysis (EA)	6.8%	7.6%
Atomic ratio of N/M from EA/ICP *	4.8	11.6
Coordination number of M-N from EXAFS	Fe-N: 3.4; Zn-N: 3.6 Average: 3.5 †	Fe-N: 4.3
Theoretical (N-M)/N ‡	72%	38%
(N-M)/N in N 1s XPS assignment §	70%	40%

* Calculated according to: $w_N/M_N/(w_{Fe}/M_{Fe}+w_{Zn}/M_{Zn})$. w_N , w_{Fe} and w_{Zn} stand for the weight content of N, Fe and Zn, respectively. M_N , M_{Fe} and M_{Zn} stand for the atomic weight of N, Fe and Zn, respectively.

† Coordination numbers of Fe-N and Zn-N are from table S1 and table S2, respectively. For Fe³⁺-N-C, the atomic ratio of Fe:Zn is about 1:1, according to ICP-OES, XPS or EDS. Therefore, the averaged coordination number of M-N (M = Fe and Zn) is 3.5.

‡ Calculated according to: $CN_{M-N}/(N/M)_{XPS}$. CN_{M-N} is the coordination number of M-N from EXAFS fitting. $(N/M)_{XPS}$ is the atomic ratio of N/M from XPS.

§ Sum the fractions of ‘pyrrolic N coordinates with metals’ and ‘pyridinic N coordinates with metal’ in table S3.

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