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Tuning the coordination number of Fe single atoms for the efficient reduction of CO₂[†]

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CO₂ electroreduction into valuable products holds great promise for energy supply and environmental remediation but remains a challenge due to the lack of high-performance electrocatalysts. Herein, we developed an efficient strategy to prepare highly active Fe single-atom catalysts (Fe–N₅/Fe–N₆) by tuning the coordination number of Fe with N towards CO₂ electroreduction. The faradaic efficiency of CO for Fe–N₅ exceeded 90% ranging from –0.35 to –0.65 V versus the reversible hydrogen electrode (vs. RHE) towards CO₂ electroreduction. The turnover frequency of CO for Fe–N₅ reached 5006 h^{–1} at –1.05 V vs. RHE, which was 3.8 times that (1324 h^{–1}) of Fe–N₆. Besides, CO was generated at an overpotential as low as 50 mV over Fe–N₅, smaller than that (90 mV) over Fe–N₆. Density functional theory calculations demonstrated that Fe–N₅ facilitated the adsorption and activation of CO₂ to form the *COOH intermediate, thus leading to superior selectivity and activity for CO₂ electroreduction.

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1. Introduction

The ever-increasing combustion of depletable fossil fuels has resulted in a serious energy crisis and environmental pollution worldwide due to the massive release of atmospheric carbon dioxide (CO₂).^{1,2} CO₂ electroreduction into value-added carbon products is considered as an ideal approach to mitigate the energy and environmental issues.^{3,4} To achieve high energy efficiency and feasible scalability, the reaction must occur rapidly and selectively at low overpotentials. However, this technology is still hindered by the high overpotential, low activity, and limited product selectivity of electrocatalysts nowadays, arising from the chemical inertness of linear CO₂ and the thermodynamically favorable competing hydrogen evolution reaction.^{5–12} To overcome these drawbacks, it is crucial to develop efficient and robust catalysts towards CO₂ electroreduction.

Carbon monoxide (CO) has emerged as one of the most practical products of CO₂ electroreduction owing to its indis-

pensable role in the preparation of synthetic liquid fuels *via* the industrial Fischer–Tropsch process.¹³ The benchmark electrocatalysts for the CO₂-to-CO conversion are Ag- and Au-based materials, which demonstrated over 90% faradaic efficiency for CO formation with an overpotential of 240 mV,^{14–16} but their high price, scarcity and inadequate activity warrant further research endeavors to explore low-cost and Earth-abundant nonprecious-metal catalysts to replace those noble-metal catalysts. Recently, single-atom catalysts (SACs) have been identified as promising candidates in the field of electrochemical conversion processes.^{17–21} This is because the unique features of SACs such as tailorable electronic structure, maximized atomic utilization, and unsaturated coordination environment render them intriguing properties for catalysis dramatically different from their bulk counterparts.²² To this end, various strategies (*e.g.* defect engineering, structural manipulation, and interfacial regulation) have been proposed to develop nonprecious-metal (Fe, Co, Ni, and Sb) SACs for the CO₂-to-CO conversion.^{23–31} Nevertheless, their electrocatalytic performance still suffers from either the large overpotential or the tradeoff between high faradaic efficiency and appreciable current density.^{32–34} Typically, the faradaic efficiency of CO₂ electroreduction drops rapidly with increasing potential in order to deliver reasonable current density. In such a context, it remains a challenge to develop robust nonprecious-metal SACs to address the aforementioned two limitations for the practical implementation of CO₂ electroreduction.

Herein, we developed an efficient strategy to prepare highly active Fe SACs (Fe–N₅/Fe–N₆) by tuning the coordination number of Fe with N towards CO₂ electroreduction. The mass

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loading of Fe in Fe-N₅ and Fe-N₆ was determined to be 0.57% and 0.58%, respectively, by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The faradaic efficiency (FE) of CO (FE_{CO}) for Fe-N₅ exceeded 90% within a wide potential window from -0.35 to -0.65 V *versus* the reversible hydrogen electrode (*vs.* RHE). Meanwhile, the turnover frequency (TOF) of CO (TOF_{CO}) for Fe-N₅ reached 5006 h⁻¹ at -1.05 V *vs.* RHE, which was 3.8 times as high as that (1324 h⁻¹) for Fe-N₆. Besides, CO was generated at an overpotential as low as 50 mV over Fe-N₅, smaller than that (90 mV) over Fe-N₆. Experimental results and density functional theory (DFT) calculations demonstrated that Fe-N₅ facilitated the adsorption and activation of CO₂ to form the key *COOH intermediate, thus leading to the superior selectivity and activity for CO₂ electroreduction. Our findings highlight the significance of regulating the coordination number of active centers in SACs to simultaneously enhance the catalytic activity and selectivity towards CO₂ electroreduction.

2. Experimental methods

2.1. Materials and chemicals

Anhydrous ferric chloride (FeCl₃, 99%, Sigma), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%, Aladdin), 2-methylimidazole (2-mIm, 99%, Sigma), potassium hydroxide (KOH, 99%, Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China)), potassium bicarbonate (KHCO₃, 99%, Sigma), iron nanoparticles (Fe NPs, 99%, Sigma), ferric oxide (Fe₂O₃, 99%, Sigma), ferrihydrite (Fe₃O₄, 99%, Sigma), methanol (99.8%, Fisher), and ethanol (99.8%, Fisher) were used as received without further purification. Carbon paper, Nafion 115 membrane, and Nafion solution (5% wt%) were supplied by Sigma-Aldrich. Ultrapure Millipore water (18.2 MΩ cm, Milli-Q, Millipore Co.) was used in all experiments.

2.2. Preparation of catalysts

In a typical synthetic process of Fe-doped ZIF-8, 0.09 g of FeCl₃ and 5.03 g of Zn(NO₃)₂·6H₂O were dissolved in 480 mL of methanol containing 11.1 g of 2-mIm. Then the mixture was kept at 25 °C for 12 h. The resultant solid products were separated by centrifugation and thoroughly washed with methanol five times, followed by drying at 60 °C under vacuum overnight. The synthetic procedure of ZIF-8 was the same as the above except no FeCl₃ was introduced. The as-obtained Fe-doped ZIF-8 was placed in a tube furnace and pyrolyzed (900 °C for Fe-N₅, 800 °C for Fe-N₆) for 6 hours with a heating rate of 5 °C min⁻¹ under an Ar flow (100 mL min⁻¹). After naturally cooling to room temperature, Fe-N₅ and Fe-N₆ were obtained as black powder and directly used without any further treatment. The synthetic process of pyrolyzed ZIF-8 was the same with Fe-N₅/Fe-N₆ except that the precursor was pure ZIF-8 instead of Fe-doped ZIF-8. Pyrolyzed ZIF-8 at 800 and 900 °C is denoted as ZIF-8-800 and ZIF-8-900, respectively.

2.3. Electrochemical measurements

All electrochemical experiments were carried out on a CHI760E electrochemical workstation (CHI660E, Shanghai CHI Instruments Company) at atmospheric pressure and ambient temperature. In a typical preparation procedure of the working electrode, 3 mg of the catalyst and 37 μL of Nafion solution was dispersed in 2.0 mL of water-ethanol solution with a volume ratio of 1:3, followed by sonication for 1 hour to obtain the homogeneous catalyst ink. The ink was then uniformly loaded onto one side of carbon paper with an area of 2 × 2 cm², which was directly used for the electrochemical measurements after drying. A flow-cell was used as the electrolyzer for CO₂ electrochemical reduction in 1.0 M KOH. The cathodic chamber and anodic chamber were separated by a proton exchange membrane (Nafion 115). A mass flow controller was used to set the CO₂ flow gas at 10 sccm. The deposited carbon paper, Pt wire, and Ag/AgCl served as the working electrode, counter electrode, and reference electrode, respectively. All potentials reported in this study were *vs.* RHE *via* the equation $E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 \text{ V} + 0.0592 \times \text{pH}$. The pH value of the electrolyte was determined with a Mettler Toledo FE 28 Desktop pH meter (Mettler Toledo International Inc., Shanghai, China). Controlled potential electrolysis was performed at each potential for 40 min. The current density was normalized with the geometric surface area of the carbon paper. Cyclic voltammetry measurements of Fe-N₅ and Fe-N₆ were carried out from 1.08 to 1.18 V *vs.* RHE and 1.06 to 1.16 V *vs.* RHE at various scan rates under a CO₂ atmosphere to obtain the double layer capacitance (*C*_{dl}). The *C*_{dl} was determined by plotting the current density difference Δj (*j*_a - *j*_c) at 1.13 and 1.11 V *vs.* RHE against the scan rates, where *j*_a and *j*_c represent the anodic and cathodic current density, respectively. The *C*_{dl} is half of the linear slope and positively correlated with the electrochemical active surface area.

2.4. Determination of reduction products

The products of CO₂ electrochemical reduction were determined by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy. Particularly, the gas products were monitored by an online gas chromatograph (Shimadzu 2010 plus GC) equipped with a thermal conductivity detector (TCD) and Molsieve 5 A column every five minutes. The liquid products were analyzed using BRUKER AVANCE III HD 400 NMR by mixing 0.5 mL of electrolyte after electrolysis, 0.1 mL of deuterium oxide (D₂O) and 0.1 mL of 6 mM 1-propanesulfonic acid 3-(trimethylsilyl) sodium salt (DSS) solution. CO and H₂ are the only two gas products and no liquid products are detected after electrolysis for both Fe-N₅ and Fe-N₆.

3. Results and discussion

3.1. Structural characterization

Fe-N₅ and Fe-N₆ were obtained *via* pyrolyzing an Fe-containing derivative of zeolitic imidazolate framework-8 (ZIF-8) at

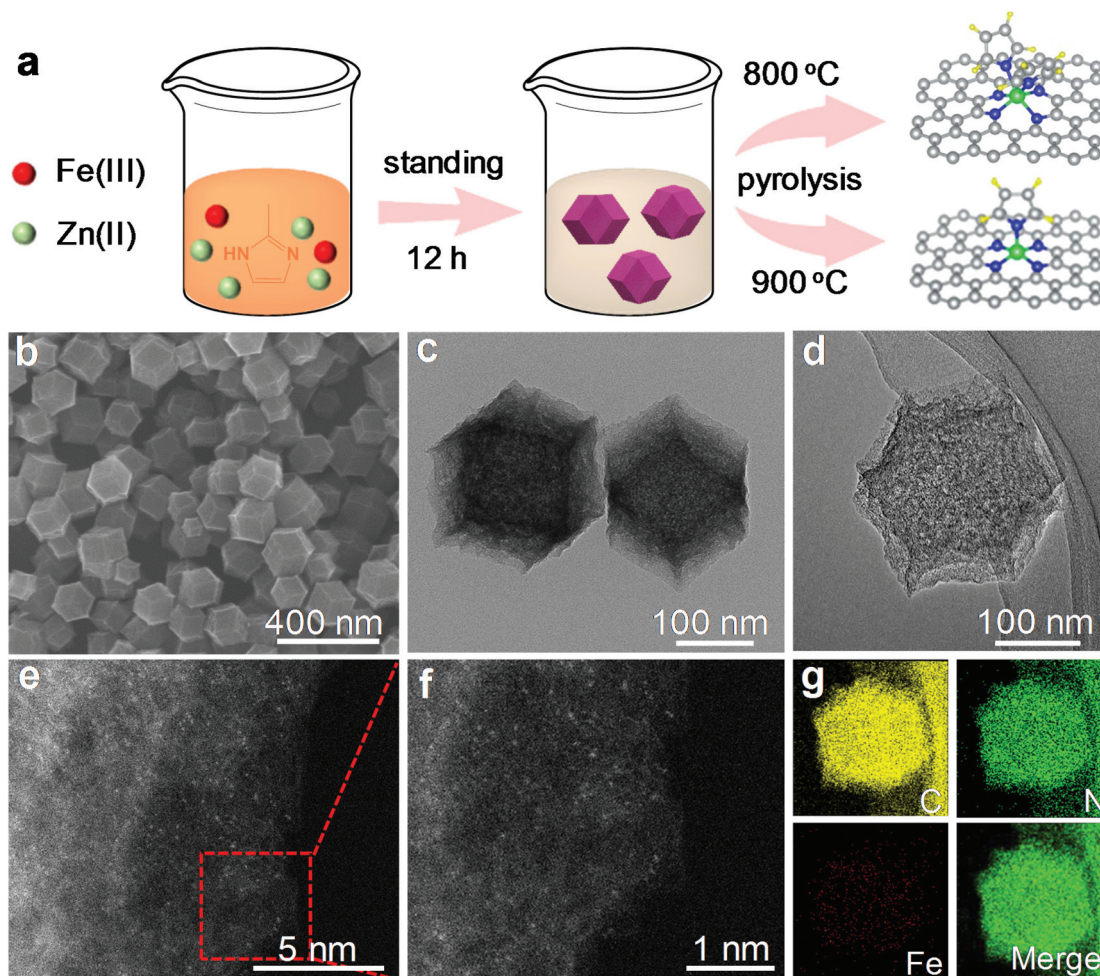


Fig. 1 (a) Schematic of the formation process of Fe-N₆ and Fe-N₅. (b) SEM, (c) TEM, and (d) HAADF-STEM images of Fe-N₅. (e) and (f) Magnified HAADF-STEM images of Fe-N₅ demonstrate the atomic dispersion of Fe atoms. (g) EDS elemental mapping reveals the homogeneous distribution of Fe, N, and C in Fe-N₅.

900 and 800 °C, respectively. The synthetic scheme of Fe-N₅ and Fe-N₆ is illustrated in Fig. 1a. The Fe-containing derivative of ZIF-8 was synthesized through the standard synthetic route of ZIF-8 except for partially substituting Zn(NO₃)₂ with FeCl₃. As shown by transmission electron microscopy (TEM) images, the Fe-containing derivative of ZIF-8 exhibited a homogeneous rhombododecahedral morphology with an average size of 220 nm (Fig. S1†). Scanning electron microscopy (SEM), TEM, and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Fe-N₅ suggested that the original structure of the Fe-containing derivative of ZIF-8 shrank into regular microporous rhombododecahedra with an average size of 200 nm after the pyrolysis process (Fig. 1b–d). Magnified HAADF-STEM images of Fe-N₅ clearly demonstrated that individual Fe atoms were uniformly dispersed in the microporous frame (Fig. 1e and f). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping of Fe-N₅ displayed the homogeneous distribution of C, N, and Fe over the entire architecture (Fig. 1g). Compared with Fe-N₅,

Fe-N₆ displayed a similar morphology and elemental composition (Fig. S2†).

To gain insights into the structure and composition information of Fe-N₅ and Fe-N₆, we conducted a series of characterization techniques. The X-ray diffraction (XRD) patterns of Fe-N₅ and Fe-N₆ exhibited two broad peaks at 24.1° and 43.3°, which can be assigned to the (002) and (101) facets of graphite carbon, respectively (Fig. 2a).⁸ No characteristic peaks of Fe or FeO_x crystals appeared in the XRD patterns of Fe-N₅ and Fe-N₆, which further demonstrated that Fe species were atomic Fe in Fe-N₅ and Fe-N₆. As displayed in Fig. 2b, the N 1s spectra of Fe-N₅ and Fe-N₆ were deconvoluted into four distinct peaks at 398.6, 399.7, 400.9, and 402.3 eV, which could be assigned to pyridinic N, Fe-N, pyrrolic N, and graphitic N, respectively.^{35,36} Notably, the fraction of Fe-N decreased from 15.16% for Fe-N₆ to 8.44% for Fe-N₅, indicating that the elevated temperature reduced the coordination number of Fe with N (Table S1†). We further carried out Raman measurements to study the structure difference between Fe-N₅ and Fe-N₆. As shown in

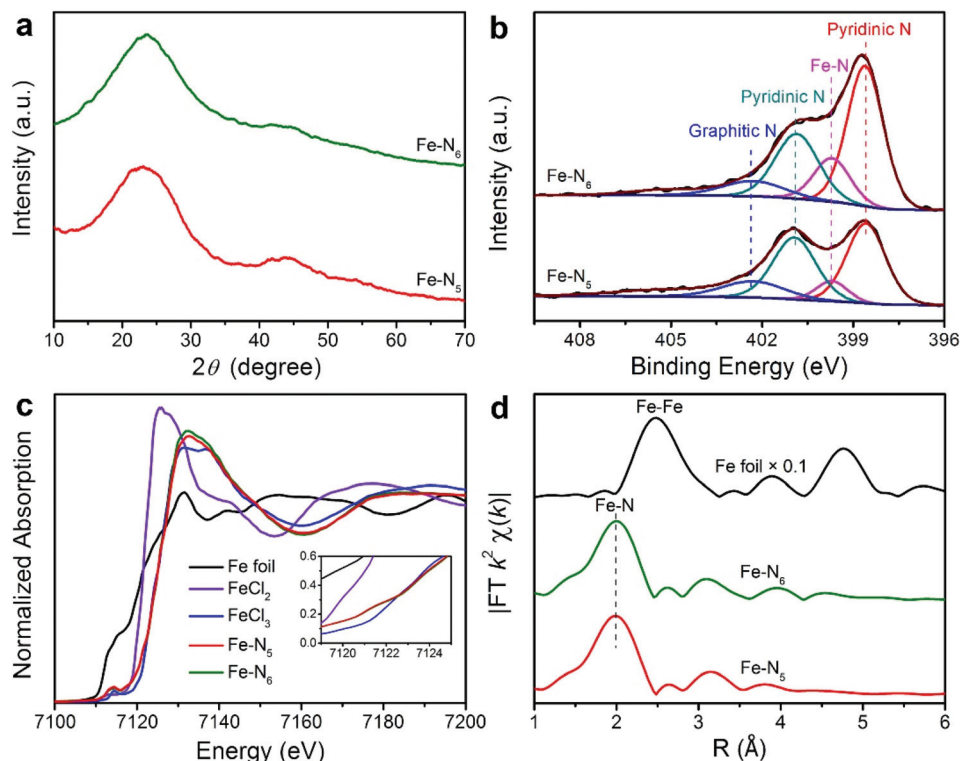


Fig. 2 (a) XRD patterns of Fe-N₅ and Fe-N₆. (b) High-resolution N 1s XPS spectra of Fe-N₅ and Fe-N₆. (c) Fe K-edge XANES spectra of Fe-N₅, Fe-N₆ and Fe foil/FeCl₂/FeCl₃ reference materials. (d) Fe K-edge k²-weighted FT-EXAFS spectra of Fe-N₅, Fe-N₆, and Fe foil.

Fig. S3,† two peaks at 1350 and 1585 cm⁻¹ are assigned to the D band and G band of graphite carbon, respectively.^{37,38} The intensity ratio of D band to G band (I_D/I_G) for Fe-N₅ is 0.99, which is lower than that (1.02) for Fe-N₆. This implies that a higher temperature enhanced the graphitization of carbon in Fe-N₅. To further investigate the electronic and coordination structure of Fe-N₅ and Fe-N₆, we conducted X-ray absorption fine structure (XAFS) spectroscopy measurements. Fig. 2c shows the Fe K-edge X-ray absorption near-edge structure (XANES) profiles for Fe-N₅, Fe-N₆, FeCl₂, FeCl₃, and Fe foil. Fe-N₅ and Fe-N₆ exhibited similar energy absorption edge profiles with FeCl₃ in the energy range between 7120 and 7124 eV, indicating that the valence state of Fe species in both Fe-N₅ and Fe-N₆ was *ca.* +3. As shown in Fig. 2d, the extended X-ray absorption fine structure (EXAFS) spectra of both Fe-N₅ and Fe-N₆ exhibited only one prominent peak at approximately 2.0 Å, which could be attributed to Fe-N bonds. No significant contribution of the Fe-Fe bond was observed at 2.49 Å, further revealing the atomic dispersion of Fe atoms throughout the whole Fe-N₅ and Fe-N₆ structure. We also conducted a least-squares EXAFS fitting. When the EXAFS fitting parameter of bond length was set to 2.00 Å with the coordination number of *ca.* 5.4 and 6.0 for Fe-N₅ and Fe-N₆, respectively, the fitting curves of Fe-N₅ and Fe-N₆ perfectly matched with the EXAFS result (Table S2 and Fig. S4†). The coordination number of Fe with N decreased when increasing the pyrolysis temperature from 800 to 900 °C, which is due to the fact that more Fe^{III}-imi-

dazolate-Fe^{III} linkages would decompose to release CN fragments at elevated temperatures, thus resulting in the decay of Fe-N bonds.

3.2. Electrocatalytic performance towards CO₂ electroreduction

We used a flow-cell system with 1.0 M KOH as the electrolyte to evaluate the electrocatalytic performance of Fe-N₅ and Fe-N₆ towards CO₂ electroreduction (Fig. S5†). During the process of chronoamperometry electrolysis, the gaseous products of H₂ and CO were quantified *via* online gas chromatograph (GC) (Fig. S6a†). Meanwhile, no liquid products were detected in the cathodic electrolyte *via* ¹H nuclear magnetic resonance (¹H NMR) (Fig. S6b†). Fe-N₅ demonstrated a significantly higher reduction current density than Fe-N₆ throughout the potential range based on the cyclic voltammograms (CVs), indicating the superior electrocatalytic performance of Fe-N₅ compared to Fe-N₆ (Fig. S7†). Fig. 3a shows the FE_{CO} of Fe-N₅ and Fe-N₆ at various applied potentials. Fe-N₅ exhibited a higher FE_{CO} than Fe-N₆ at each applied potential. In particular, the FE_{CO} of Fe-N₅ was higher than 90% within a wide electrochemical window from -0.35 to -0.65 V *vs.* RHE. Note that the FE_{CO} of Fe-N₅ reached nearly 100% (99%) at -0.35 V *vs.* RHE. More importantly, CO was already detected at a low potential of -0.16 and -0.20 V *vs.* RHE for Fe-N₅ and Fe-N₆, respectively (Fig. S8†). Considering the CO₂/CO equilibrium potential is -0.11 V *vs.* RHE, the overpotential to produce CO was merely

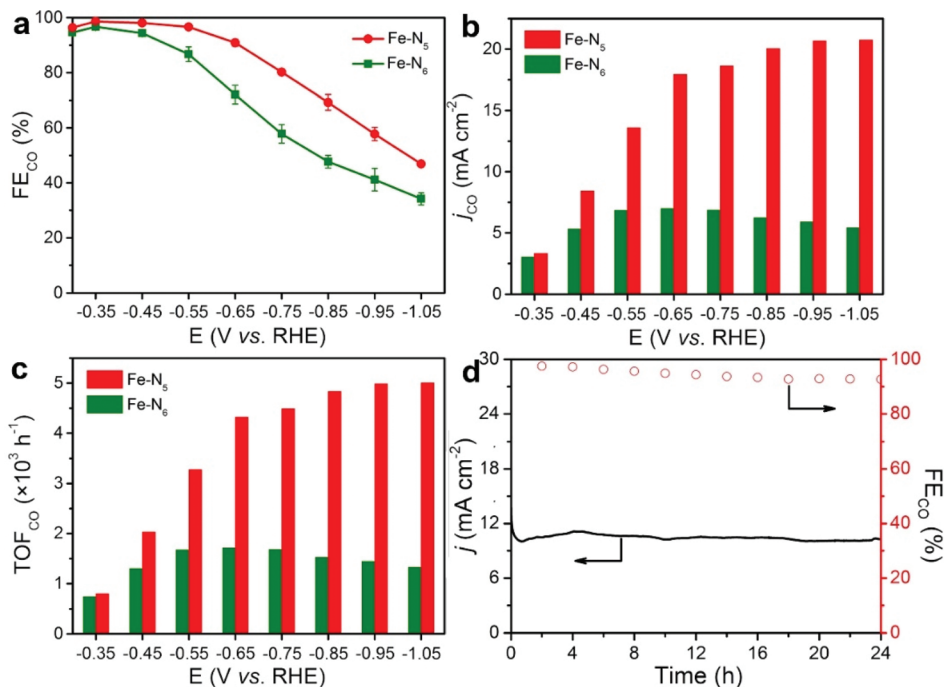


Fig. 3 CO₂ electroreduction catalytic performance of Fe-N₅ and Fe-N₆. (a) Faradaic efficiency of CO at different potentials. (b) j_{CO} in 1.0 M KOH electrolyte. (c) TOF_{CO} at various applied potentials. (d) 24 h stability test of Fe-N₅ at -0.4 V vs. RHE and the corresponding FE_{CO}.

50 and 90 mV for Fe-N₅ and Fe-N₆, respectively, even outperforming that for noble-metal catalysts such as Ag and Au.^{39–43} Fig. 3b shows the partial current density of CO (j_{CO}) of Fe-N₅ and Fe-N₆. Fe-N₅ exhibited higher j_{CO} at all applied potentials. At -1.05 V vs. RHE, the j_{CO} of Fe-N₅ was up to -20.8 mA cm⁻², which was 3.8 times as high as that for Fe-N₆. The C_{dl} (2.58 mF cm⁻²) of Fe-N₅ was close to that (2.25 mF cm⁻²) of Fe-N₆ (Fig. S9†), implying that Fe-N₅ and Fe-N₆ possessed comparable electrochemical active surface area. Given the significantly higher FE_{CO} and j_{CO} of Fe-N₅ relative to Fe-N₆, it is safe to conclude that Fe-N₅ had a higher intrinsic activity towards CO₂ electroreduction. To probe the active center and eliminate the interference of the substrate (N-doped porous carbon), we further pyrolyzed pure ZIF-8 at 800 and 900 °C, which was denoted as ZIF-8-800 and ZIF-8-900, respectively (Fig. S10†). It is worth noting that the FE_{CO} of ZIF-8-800 and ZIF-8-900 was lower than 25% (Fig. S11†), demonstrating that Fe atoms in Fe-N₅ and Fe-N₆ are largely responsible for the electroreduction of CO₂ to CO. Moreover, the FE_{CO} of commercial Fe nanoparticles, Fe₃O₄, and Fe₂O₃ were negligible at -0.55 V vs. RHE, demonstrating that atomically distributed Fe sites are the active center rather than bulk Fe species (Fig. S12†). As shown in Fig. 3c, the TOF of CO (TOF_{CO}) was normalized by the mass loading of Fe at different applied potentials. It can be seen that the TOF_{CO} of Fe-N₅ significantly exceeded that of Fe-N₆ throughout the applied potential range. Particularly, for Fe-N₅, the TOF_{CO} reached 5006 h⁻¹ at -1.05 V vs. RHE, which was 3.8 times that for Fe-N₆. All these results strongly corroborate the intrinsically higher CO₂ electroreduction performance of Fe-N₅ relative to that of Fe-N₆,

which is comparable to the best reported SACs for CO₂ electroreduction (Table S3†). In view of the excellent selectivity and activity of Fe-N₅ for CO₂ electroreduction, we performed potentiostatic measurements to assess its durability in 1.0 M KOH aqueous solution at -0.4 V vs. RHE. As shown in Fig. 3d, the current density and the FE_{CO} of Fe-N₅ remained basically unchanged during the 24 h continuous electrolysis. TEM and HAADF-STEM images of Fe-N₅ after the stability test show that the Fe single atoms were still atomically dispersed on the N-doped carbon support (Fig. S13†). The N1s XPS spectra of spent Fe-N₅ resembled that of pristine Fe-N₅, indicating the superior stability after the reaction (Fig. S14 and Table S4†).

3.3. Mechanistic studies on CO₂ electroreduction

To further investigate the origin of the intrinsically high electrocatalytic performance of Fe-N₅, we conducted CO₂ temperature-programmed desorption (CO₂-TPD). As shown in Fig. 4a, the CO₂ desorption peak of Fe-N₅ was located at 141 °C, which was higher than that (118 °C) of Fe-N₆. As such, the binding strength of CO₂ on Fe-N₅ was stronger than that on Fe-N₆. The strong binding of CO₂ on Fe-N₅ indicated the facilitated adsorption of CO₂, thus resulting in the high activity of Fe-N₅.^{44,45} This is in line with the enhanced CO₂ adsorption on Fe-N₅ compared to that on Fe-N₆ (Fig. S15†). To provide a theoretical insight into the relationship between the coordination number and the reaction pathway, we calculated the Gibbs free energy for each step involved in CO₂ electroreduction (Table S5†). The structural models of Fe-N₅ and Fe-N₆ were established *via* the obtained XPS and EXAFS fitting results (Table S2 and Fig. S16†). The structural model of Fe-N₆

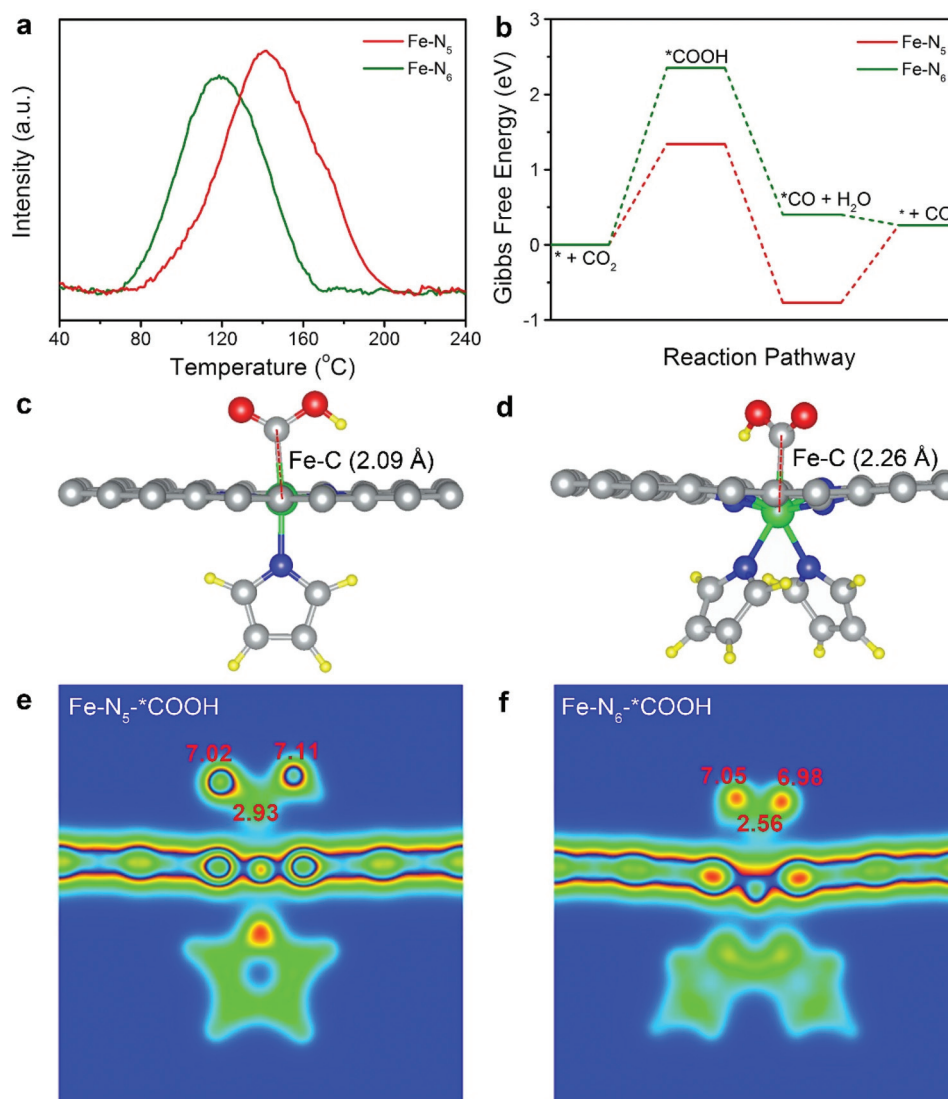


Fig. 4 (a) CO₂-TPD profiles for Fe-N₅ and Fe-N₆. (b) Calculated Gibbs free energy diagrams for CO₂ electroreduction to CO over Fe-N₅ and Fe-N₆. (c) and (d) Optimized structures of Fe-N₅ and Fe-N₆ with adsorbed *COOH, * denotes the adsorption site. The gray, green, blue, red and yellow spheres represent C, Fe, N, O, and H atoms, respectively. (e) and (f) Slice of calculated charge densities of Fe-N₅ and Fe-N₆ with adsorbed *COOH. Bader partial atomic charges are labeled by the red numbers.

with one pyrrole ring on each side of carbon matrix was excluded after structure optimization (Fig. S17†). As shown in Fig. 4b, the formation of *COOH required the highest energy barrier among all the steps of CO₂ electroreduction on both Fe-N₅ and Fe-N₆. Therefore, the formation of *COOH serves as the potential-limiting step over Fe-N₅ and Fe-N₆ towards CO₂ electroreduction. Particularly, the Gibbs free energy for the formation of *COOH on Fe-N₅ was 1.34 eV, which was significantly lower than that on Fe-N₆ (2.35 eV). As shown in Fig. 4c and d, the C-Fe bond length of adsorbed *COOH for Fe-N₅ and Fe-N₆ increased from 2.09 to 2.26 Å, respectively, further revealing that Fe-N₅ was more beneficial for *COOH adsorption relative to Fe-N₆. Apart from that, the C atom of adsorbed *COOH on Fe-N₅ displays higher electron density compared to that on Fe-N₆, confirming the stronger stabilization of *COOH

on Fe-N₅ (Fig. 4e and f).⁴⁶ As such, Fe-N₅ promoted the activation of CO₂, leading to the enhanced electrocatalytic activity for CO₂ electroreduction relative to Fe-N₆.

4. Conclusions

In summary, we have synthesized two Fe SACs for CO₂ electroreduction. Compared with Fe-N₆, Fe-N₅ demonstrated a lower onset potential (−0.16 V vs. RHE), higher turnover frequency (5006 h^{−1}), and remarkable faradaic efficiency (99%) for CO production. This was attributed to the facile adsorption and activation of CO₂ arising from the favourable coordination structure. This work should pave a promising avenue to rationally design novel single-atom electrocatalysts with a tunable

coordination environment in energy and environment related fields.

Conflicts of interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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