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Isolated FeN$_4$ Sites for Efficient Electrocatalytic CO$_2$ Reduction

Xiaogang Li, Shibo Xi, Libo Sun, Shuo Dou, Zhenfeng Huang, Tan Su, and Xin Wang*

The construction of isolated metal sites represents a promising approach for electrocatalyst design toward the efficient electrochemical conversion of carbon dioxide (CO$_2$). Herein, Fe-doped graphitic carbon nitride is rationally prepared by a simple adsorption method and is used as template to construct isolated FeN$_4$ sites through a confined pyrolysis strategy, which avoids the agglomeration of metal atoms to particles during the synthesis process and thus provides abundant active sites for the CO$_2$ reduction reaction. The isolated FeN$_4$ sites lower the energy barrier for the key intermediate in the CO$_2$ reduction process, leading to the enhanced selectivity for CO production with a faradaic efficiency of up to 93%.

The accumulation of CO$_2$ in atmosphere due to the excessive consumption of fossil fuels has posed potential environmental concerns.$^{[1]}$ Electrocatalytic CO$_2$ reduction offers a promising approach to mitigate CO$_2$ levels and convert it to value-added fuels.$^{[2]}$ Many efforts have been dedicated to developing efficient electrocatalysts for CO$_2$ reduction. Nevertheless, the low selectivity of the reduction products is still a key obstacle which restricts the further development of CO$_2$ conversion technologies.$^{[3]}$ Homogeneous catalytic systems could possess excellent selectivity due to its homogeneously distributed and well-defined active sites, while its inferior stability and difficulty of separation hinder the further development toward industrial applications.$^{[4]}$

In contrast, heterogeneous catalysts could provide stable catalytic performance, while the diverse nature of active sites restricts the selectivity.$^{[5]}$ Thus the development of catalysts that combine the advantages of both heterogeneous and homogeneous catalysts is urgently imperative for the efficient conversion of CO$_2$.

Single-atom-based catalysts provide a great potential to bridge the gap between heterogeneous and homogeneous catalysts.$^{[6]}$ Apart from the maximum atom efficiency, single-atom catalysts afford the isolated and well-defined active sites confined in the support of inorganic solid material, offering high selectivity and stability toward catalytic reaction.$^{[7]}$ Benefitting from the unique structure, the single-atom catalysts present comparable catalytic activity to that of homogeneous catalysts, meanwhile possessing high recyclability and stability arising from heterogenization. Among the single-atom catalysts, the isolated metal atoms coordinated with nitrogen (MN$_x$) in carbon substrates have shown excellent performance in electrocatalysis,$^{[8]}$ providing a promising way for electrocatalytic CO$_2$ reduction. However, construction of MN$_x$ sites is still a challenge since isolated active sites are easily agglomerated to particles during the synthesis process, leading to loss of catalytic performance. Recently, isolated NiN$_4$ sites have been successfully constructed via a confined pyrolysis strategy, in which Ni-doped graphitic carbon nitride (g-C$_3$N$_4$) acts as the template and nitrogen source during the confined pyrolysis process.$^{[9]}$

Considering the synthesis of metal-doped g-C$_3$N$_4$ by pyrolyzing the precursor of g-C$_3$N$_4$ and metal salts is uncontrollable, a more simple and universal design of metal-doped g-C$_3$N$_4$, which is the pivotal step in the confined pyrolysis strategy, is still much desirable but remains challenging for the construction of MN$_x$ sites. Herein, we report the construction of isolated FeN$_4$ sites in carbon substrates (denoted as FeN$_4$/C) by the rational design of Fe-doped g-C$_3$N$_4$. A simple adsorption method was adopted for g-C$_3$N$_4$ to trap Fe atoms, making it an excellent template for the formation of FeN$_4$ sites. Then the formation of a carbon layer on the surface of Fe-doped g-C$_3$N$_4$ would provide a confined environment to suppress the agglomeration of Fe atoms to particles during the pyrolysis process, thus effectively constructing the isolated active sites. Benefitting from the unique structure and coordination environment, the isolated FeN$_4$ sites show high selectivity for the electrocatalytic conversion of CO$_2$ to CO, with the highest faradaic efficiency of 93% at −0.6 V versus RHE. The isolated configuration was revealed by spherical aberration correction electron microscopy and extended X-ray absorption fine structure analysis. The theoretical calculation demonstrates that

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isolated FeN₄ sites lower the energy barrier for the formation of COOH* (COOH*) which leads to the enhanced activity for CO production. We believe this study would pave a new avenue for rational design of highly efficient single-atom catalysts with abundant active sites.

The morphology of the catalysts was confirmed by transmission electron microscopy (TEM). Figure 1a shows the TEM image of FeN₄/C, which presents a sheet-like structure, similar to that of bare N-doped carbon (denoted as N/C) and g-C₃N₄, as seen in Figure S1 (Supporting Information). No particles are observed from the high-magnification TEM image for FeN₄/C, as shown in Figure 1b. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of FeN₄/C in Figure 1c reveals that isolated bright spots corresponding to Fe atoms are homogeneously dispersed, demonstrating the single-atom form of Fe in the FeN₄/C. Energy-dispersive X-ray spectroscopy (EDX) mapping analysis in Figure 1d indicates that Fe and N atoms distribute homogeneously in carbon substrate.

The Raman spectrum for FeN₄/C and N/C in Figure S2 (Supporting Information) shows two distinct peaks at about 1570 and 1330 cm⁻¹, which could be assigned to graphitic sp² carbon (G-band) and disordered sp³ carbon (D-band).[10] The ratio of the relative intensity of the D band to the G band presents no much difference for FeN₄/C and N/C, with an I₉/I₆ value of 1.38 and 1.31, respectively, indicating the similar extent of graphitization and disorder in the catalysts. The X-ray diffraction (XRD) patterns of FeN₄/C and N/C in Figure S3 (Supporting Information) both show two typical broad peaks at about 24° and 44°, which could be ascribed to (0 0 2) and (1 0 1) lattice plane of graphite.[11] Apparently there is no new crystal phase present in the FeN₄/C. While without the confinement of the carbon layer during pyrolysis, Fe₃C and Fe particles would appear in the synthesized catalyst (denoted as Fe/C). As shown in the TEM images in Figure S4 (Supporting Information), the catalyst shows a morphology of particles wrapped with outer carbon layer. XRD pattern of Fe/C in Figure S5 (Supporting Information) presents the distinct peaks corresponding to Fe₃C (JCPDS Card No. 350772) and Fe (JCPDS Card No. 060696), demonstrating the dominant species in Fe/C are Fe₃C and metallic Fe. Note that the further additional loading of Fe will also result in the formation of Fe nanoparticles in FeN₄/C (denoted as Fe NPs/C). As seen in Figure S6a (Supporting Information), the XRD pattern of Fe NPs/C shows a distinct peak at 44.6°, corresponding to the (1 1 0) lattice planes of metallic Fe (JCPDS Card No. 060696). The TEM image in Figure S6b (Supporting Information) shows the presence of small particles on the Fe NPs/C. The EDX mapping clearly shows the aggregation of Fe atoms to particles, as shown in Figure S6c (Supporting Information). The high resolution TEM (HRTEM) image of Fe NPs/C in Figure S6d (Supporting Information) presents a lattice distance of 0.20 nm, which could be ascribed to the (1 1 0)
Figure 2. a) Fe K-edge XANES spectra of Fe foil, FeN₄/C, and Fe NPs/C. b) FT of the Fe K-edge EXAFS oscillations of Fe foil, FeN₄/C, and Fe NPs/C. c) EXAFS fitting curve for FeN₄/C. Inset is the schematic model of FeN₄ structure, with Fe in orange, N in blue, and C in gray. d) N 1s XPS spectra of FeN₄/C and N/C.

plane of Fe particles (JCPDS Card No. 060696), agreed well with the XRD result.

Synchrotron-based X-ray absorption spectroscopy was further adopted to determine the precise local chemical configuration around isolated Fe sites. Figure 2a presents the Fe K-edge X-ray absorption near-edge structure (XANES) curves of FeN₄/C, in comparison to Fe NPs/C and Fe foil. It is clearly seen that the absorption-edge of FeN₄/C shifts toward higher energy compared with Fe NPs/C and Fe foil, suggesting Fe in FeN₄/C is in an oxidation state. As a comparison, the absorption-edge of Fe NPs/C is located between the FeN₄/C and Fe foil, which could be ascribed to the coexistence of oxidized Fe single atoms and metallic Fe particles. The Fe 2p X-ray photoelectron spectroscopy (XPS) of FeN₄/C is shown in Figure S7 (Supporting Information), in which the characteristic Fe 2p₃/2 peak is located at about 710 eV, indicating the existence of Fe²⁺ species in FeN₄/C. The Fourier-transformed (FT) k³-weighted extended X-ray absorption fine structure (EXAFS) spectra are shown in Figure 2b. For FeN₄/C, its FT curve only displays a prominent peak at 1.5 Å, which is generally attributed to the Fe–N first coordination shell. Beyond this distance, no obvious FT peaks are observed, especially at the distance of Fe–Fe interaction, indicating that the Fe atoms in FeN₄/C are atomically dispersed. For Fe NPs/C, a distinct peak corresponding to Fe–Fe bond appears, demonstrating the existence of metallic Fe particles. The quantitative simulation for the EXAFS of FeN₄/C was performed to obtain the precise chemical configuration around Fe atoms. Figure 2c shows that the experimental FT-EXAFS curve of the FeN₄/C has been perfectly reproduced. The fitting results reveal isolated Fe atoms are coordinated with four N atoms at a distance of 1.97 Å. The FeN₄ structure has been also demonstrated as a more reasonable configuration after the high-temperature pyrolysis process. The relevant fitting parameters are given in Table S1 (Supporting Information). To further determine the chemical bond for FeN₄ sites, N 1s XPS was performed, as shown in Figure 2d. The N 1s spectra of N/C could be deconvoluted into four peaks with binding energy at 398.4, 399.1, 401, and 404.14 eV, corresponding to pyridinic N, pyrrolic N, graphitic N, and N-oxide, respectively. For FeN₄/C, the peak assigned to pyridinic N clearly shifts to the higher energy side compared with that of N/C, indicating the pyridinic N bonds with the Fe atoms. Thus, the local structure of FeN₄ sites is revealed that the isolated Fe atoms coordinated with four pyridinic N atoms.

The electrocatalytic CO₂ reduction measurement demonstrates the introduction of isolated FeN₄ sites in carbon substrate greatly enhances the catalytic performance. The linear sweep voltammetry (LSV) curves (Figure 3a) show that FeN₄/C gives a much higher catalytic current density than that of N/C and Fe/C, demonstrating the excellent activity of the isolated FeN₄ sites for CO₂ reduction. To evaluate the selectivity for CO₂ reduction, faradaic efficiency (FE) toward CO was measured and presented in Figure 3b. The results show that FeN₄/C exhibited high
conversion efficiency to CO and greatly suppressed the competitive H₂ evolution reaction (no liquid product was detected, as shown in the ¹H NMR spectroscopy in Figure S8, Supporting Information), achieving a maximum FE of 93% for CO at −0.6 V. This performance could be comparable with the state-of-the-art catalysts for CO₂ reduction (Table S2, Supporting Information). In contrast, the N/C and Fe/C only give a maximum FE of 46% and 23%, respectively. The partial current density for CO production of the catalysts is presented in Figure 3c. It is clearly seen that FeN₄/C shows a much higher catalytic current density of 2.5 mA cm⁻² at −0.8 V, which is 35 times and 17 times of that for N/C and Fe/C, respectively. This agrees with the electrochemical impedance spectroscopy (EIS) measurement. As presented by the Nyquist plots in Figure 3d, FeN₄/C has the much smaller charge transfer resistance than that of N/C and Fe/C, correlating to a faster charge-transfer process for the CO₂ reduction reaction. The influence of the Fe loading on the catalytic activity of FeN₄/C is shown in Figure S10 (Supporting Information). As seen in the LSV curves, the initial increase of Fe loading leads to a better catalytic activity of CO₂ reduction, while a further increase of loading to 2.5 wt% (Fe NPs/C) will decrease the catalytic performance. Apparently, the appearance of Fe particles is detrimental to CO₂ reduction. The FE results in Figure S11 (Supporting Information) also show that the existence of Fe particles suppresses the selectivity for CO₂ reduction to CO. To compare the intrinsic activity of FeN₄/C and Fe NPs/C, their electrochemical active surface area (ECSA) was determined by performing cyclic voltammetry test (Figure S12a,b, Supporting Information) to get the double-layer capacitance (Figure S12c, Supporting Information). Fe NPs/C shows a lower ECSA compared with that of FeN₄/C, indicating a decreased ability for affording the active sites. The intrinsic activity after normalization by the ECSA for the FeN₄/C and Fe NPs/C is shown in Figure S12d (Supporting Information), in which FeN₄/C presents an enhanced current density for CO production than that of Fe NPs/C. Based on the catalytic performance, we could see the unique structure and coordination environment endow the isolated FeN₄ sites with excellent catalytic performance for CO₂ conversion.

To ravel the high activity of FeN₄/C for CO₂ conversion to CO, density functional theory (DFT) calculations were performed. Considering the formation of COOH* is the initial step for the reduction of CO₂ to CO, we first explored the electronic structure of FeN₄ and N/C sites with adsorbed COOH*. Figure 4a,b present the charge density difference of FeN₄/C and N/C with COOH* adsorption from the section (two-dimensional contour map along z-axis) and three-dimensional view. For FeN₄ sites, it could be seen that the depletion of electron density appears at Fe site and the electron density accumulation occurs on the C atom of adsorbed COOH*, indicating a charge transfer happens from the Fe site to C atom. While there is no obvious electron interaction between N/C and COOH*. This charge transfer for FeN₄ sites results in the effective binding strength for the
adsorbed intermediate, thereby effectively modulating the energy barrier in CO₂ reduction process. As shown in Figure 4c, for both N/C and FeN₄/C, the formation of COOH⁺ is the rate-limiting step for CO₂ reduction reaction (detailed energies of adsorbates can be found in Tables S3 and S4, Supporting Information). Benefiting from the charge transfer, the introduction of FeN₄ sites greatly decreases the barrier for the formation of COOH⁺ compared with that of N/C, thus facilitating the subsequent reduction process, eventually resulting in the enhanced activity for CO production. Different from FeN₄ structure, Fe nanoparticle shows much stronger adsorption for CO*, as shown in Figure S13 (Supporting Information), which restricts the further desorption of CO, and thus leads to relative low selectivity.

Considering that H₂ evolution is the competitive reaction, the difference between thermodynamic limiting potentials for CO₂ reduction and H₂ evolution (U_l(CO₂) – U_l(H₂)) was also calculated as a reference for the selectivity in CO₂ reduction reaction. A more positive value would indicate a better selectivity for CO₂ conversion.[20] As shown in Figure 4d, the FeN₄/C presents a more positive value than that of N/C, demonstrating a higher selectivity for CO₂ reduction. Based on the DFT analysis, FeN₄ sites endow the catalyst with a lowered energy barrier for CO₂ reduction, thus leading to the enhanced activity for CO production.

In conclusion, we have constructed isolated FeN₄ sites on carbon substrate through a confined pyrolysis strategy using Fe doped g-C₃N₄ as a template. The isolated and well-defined FeN₄ sites endow the catalyst with the advantages of both heterogeneous and homogeneous catalysts, showing high activity toward electrocatalytic CO₂ reduction. Benefiting from the unique structure and coordination environment, the intermediate could be easily formed on the FeN₄ sites during CO₂ reduction process, resulting in the greatly improved selectivity for CO production. We anticipate our work will provide valuable guidance for the design of isolated active sites and would inject new vitality to the related electrocatalytic field.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

CO₂ reduction, confined pyrolysis, electrocatalysis, isolated active sites

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