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Optimizing the Electrocatalytic Selectivity of Carbon Dioxide Reduction Reaction by Regulating the Electronic Structure of Single-Atom M-N-C Materials

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Electrochemical carbon dioxide reduction reaction (CO₂RR) is an efficient strategy to relieve global environmental and energy issues by converting excess CO₂ from the atmosphere to value-added products. Atomically dispersed metal-nitrogen-doped carbon (M-N-C) materials are superior catalysts for electrocatalytic CO₂RR because of the 100% atomic utilization, unsaturated coordination configuration, relatively uniform active sites, and well-defined and adjustable structure of active centers. However, the electrochemical CO₂RR is a great challenge due to the process involving protoncoupled multi-electron transfer with a high energy barrier, which leads to unsatisfactory selectivity to the targeted product, especially for C2 products (e.g., C₂H₄ and C₂H₅OH). Here, the authors systematically summarize effective means, including reasonable selection of isolated metal sites, regulation of the coordination environment of isolated metal atoms, and fabrication of dimetallic single-atom sites for attaining optimal geometric and electronic structures of M-N-C materials and further correlate these structures with catalytic selectivity to various C1 (e.g., CO and CH₄) and C2 products in the CO₂RR. Moreover, constructive strategies to further optimize M-N-C materials for electrocatalytic CO₂RR are provided. Finally, the challenges and future research directions of the application of M-N-C materials for electrocatalytic CO₂RR are proposed.

1. Introduction

The exploitation of fossil fuels has promoted economic development and improved people's quality of life. However, the continuous consumption of fossil fuels has exacerbated the deterioration of the environment, since the burning releases a large amount of CO_2 and destroys the CO_2 balance in the environment. The increase in CO_2 has brought about a serious greenhouse effect, destroyed the ecological balance, and risen the sea level due to the melting of glaciers.^[1]

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202111504.

DOI: 10.1002/adfm.202111504

Therefore, reducing the concentration of CO_2 in the atmosphere has become an urgent problem to be solved. However, in industry, fossil fuels are still needed to provide energy, and therefore it is necessary to reduce the concentration of CO₂ in the atmosphere from the capture, storage and conversion of CO₂.^[2] The effective conversion of CO2 into carbonbased chemicals and fuels has good prospects.^[3] In recent years, electrocatalytic carbon dioxide reduction reaction (CO₂RR) has made much progress.^[4–7] In CO_2RR , CO_2 can be reduced to carbon monoxide, methane, methanol, formate, and ethanol, which are widely used in industry. The use of green electricity by electrocatalysis under mild conditions has become one of the main methods of CO₂ conversion. The electrocatalytic CO₂RR provides a good way for the conversion of electrical energy to chemical energy, which can be regarded as a form of renewable energy storage.^[8]

Until now, electrocatalytic CO_2RR faces many problems since the CO_2 gas as the reactant has relatively stable prop-

erties. Hundreds of millivolts of overpotential are required to activate the C=O bond with high bond energy. In addition, the hydrogen evolution reaction (HER), which is a side reaction, will occur concomitantly at higher overpotentials and affect the selectivity of CO₂RR. The CO₂RR is slow in kinetics involving a complex multi-proton process.^[9] The catalytic activity of CO₂RR is closely related to reaction intermediates. The adsorption energy of the intermediate on the active site determines the reaction rate. Therefore, a suitable catalyst will greatly help to improve the catalytic activity and selectivity of CO₂RR.^[10]

Carbon materials are widely used in electrocatalysis filed because of their high conductivity and large specific surface area. Carbon materials can be modified to construct atomic metal-nitrogen-doped carbon (M-N-C) with unique electronic and geometric structures. Atomic M-N-C materials have the following advantages. I) The utilization of metal atoms can be maximized. II) The density of effective active sites can be significantly increased. III) The central metal atom shows a low coordination environment, which favors the enhancement of electrocatalytic activity. IV) The unique electronic structure ADVANCED SCIENCE NEWS_____





Figure 1. a,b) Reaction pathway for C1 and C2 products.

favors the improvement of catalytic selectivity.^[11–17] Due to its excellent characteristics, it has been continuously developed in electrocatalytic CO₂RR in recent years.

Although there are some reviews on single-atom catalysts for the CO₂RR, few reviews focus on the structure-selectivity relationship of single-atom M-N-C materials. To guide further research of electrocatalytic CO₂RR on M-N-C materials, we summarized the synthesis methods of M-N-C materials and the CO₂RR mechanism, focusing on improving the CO₂RR catalytic performance of M-N-C materials by adjusting the central metal atom, coordination environment, and bimetal single atom active sites. Finally, the challenges and future development direction of M-N-C materials for electrocatalytic CO₂RR are also put forward.

2. Mechanism of Electrocatalytic CO₂RR

Electrochemical CO_2RR involves multi-electron/proton transfer processes. The catalytic hydrogenation reaction of CO_2 occurs on the cathode surface. By transferring 2, 4, 6, and 8 electrons of CO₂, the products of CO₂RR mainly involve C₁ (CO, HCHO, HCOOH, CH₃OH, and CH₄) and C₂ (C₂H₄ and CH₃CHO/C₂H₅OH) products (**Figure 1**a,b).^[8] The major half-reactions and the corresponding standard potential (vs RHE) of CO₂RR products are listed in **Table 1**.

In the process of CO₂RR, CO₂ is first assimilated on the active site to generate *CO2-, and the intermediates are subsequently formed by proton or electron transfer steps. Finally, the products are desorbed at the electrode.^[18] During the reaction, the transfer of an electron from CO_2 to produce $*CO_2^-$ is considered the rate determining step for most catalysts because a high energy barrier is required to initiate the process, and the reactivity of *CO₂⁻ is the key factor controlling the distribution of ultimate products.^[19,20] In addition, various catalytic pathways at higher overpotentials always produce different products that affect the selectivity. Most of studies have shown that catalysts should be designed to facilitate the activation of CO2 by adjusting the geometry and electronic structure.^[21,22] Highly efficient CO2RR electrocatalysts can bind with intermediates with appropriate strength and significantly inhibit the competitive HER.^[23]

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Table 1. The standard potential of CO2RR products.

Reaction	E ⁰ (V vs RHE)	Product	
$\overline{\text{CO}_2 + e^- \rightarrow \text{CO}_2^-}$	-0.19	-	
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.12	Formic acid	
$\mathrm{CO}_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{CO} + \mathrm{H}_2\mathrm{O}$	-0.1	Carbon monoxide	
$\mathrm{CO}_2 + \mathrm{6H^+} + \mathrm{6e^-} \rightarrow \mathrm{CH_3OH} + \mathrm{2H_2O}$	+0.03	Methyl alcohol	
$\mathrm{CO}_2 + 4\mathrm{H}^+ + 4\mathrm{e}^- \rightarrow \mathrm{C} + 2\mathrm{H}_2\mathrm{O}$	+0.21	Graphite	
$\mathrm{CO}_2 + 8\mathrm{H}^+ + 8\mathrm{e}^- \rightarrow \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O}$	+0.17	Methane	
$2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	+0.11	Acetic acid	
$2\text{CO}_2 + 10\text{H}^+ + 10\text{e}^- \rightarrow \text{CH}_3\text{CHO} + 3\text{H}_2\text{O}$	+0.06	Acetaldehyde	
$\mathrm{CO_2} + 12\mathrm{H^+} + 12\mathrm{e^-} \rightarrow \mathrm{C_2H_5OH} + 3\mathrm{H_2O}$	+0.09	Ethyl alcohol	
$\mathrm{CO}_2 + 12\mathrm{H}^+ + 12\mathrm{e}^- \rightarrow \mathrm{C}_2\mathrm{H}_4 + 4\mathrm{H}_2\mathrm{O}$	+0.08	Ethylene	
$\mathrm{CO}_2 + 14\mathrm{H}^+ + 14\mathrm{e}^- \rightarrow \mathrm{C}_2\mathrm{H}_6 + 4\mathrm{H}_2\mathrm{O}$	+0.14	Ethane	
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	+0.1	Propyl alcohol	

2.1. CO Generation Mechanism

In CO₂RR, C1 and C2 products can be obtained by reducing CO₂ based on the applied potential. Among them, CO is one of the most common two-electron transfer products, which can be used in the Fischer–Tropsch process to produce synthetic liquid fuels.^[24] The following is the reaction pathways on atomic M-N-C catalysts:

$$CO_2 + * + H^+ + e^- \rightarrow *COOH \tag{1}$$

$$CO_2 + * + e^- \rightarrow *CO_2^- \tag{2}$$

 $*CO_2^- + H^+ \to *COOH \tag{3}$

$$*COOH + H^+ + e^- \rightarrow *CO + H_2O$$
⁽⁴⁾

$$*CO \rightarrow CO + *$$

where * is the surface-active site of catalysts.

At the M-N₄ site, CO is easily generated with high selectivity. For example, Cao et al. used a self-sacrificial template method to prepare a Ni/NCT catalyst with hierarchical pores,^[25] which showed high selectivity, activity, and Faraday efficiency of CO (FE_{CO}: 98%) for the CO₂RR. In addition, when the applied voltage was -1.0 V, a large turnover frequency (TOF) (9366 h⁻¹) and CO current density (34.3 mA cm⁻²) can be achieved. Xu et al. designed a carbon-supported N-anchored Zn single-atom catalyst (ZnN_x/C) ,^[26] which had a highly effective performance for CO₂RR with initial potential as low as 24 mV, a high TOF of 9969 h⁻¹, and 95% FE_{CO} at low potentials. X-ray photoelectron spectroscopy (XPS) revealed that the Zn-N_x site serves as the main active site. Density functional theory (DFT) calculations further revealed the CO2RR mechanism at different sites of the ZnN_r/C catalyst. In the first step of activating CO₂ to form *COOH, different energy barriers needed to be overcome. Zn-N₄ (0.662 eV) required smaller free energy barrier than N₄-C (1.754 eV) and Zn-C (2.070 eV) sites. In the second step, the adsorbed *CO was formed, and the energy barrier at the Zn-N₄ site was 0.052 eV, followed by CO desorption. In the process of reducing CO₂ to CO, the step of forming *COOH was the speed determining step, and the Zn-N₄ site exhibited high CO₂RR catalytic activity (Figure 2).

2.2. HCOOH Generation Mechanism

Formic acid (HCOOH), as a product of the two-electron CO_2RR , has a minor obstacle. With the development of CO_2RR catalysts, formic acid or formate is a potential commercial product.^[27,28] Studies have shown that p-zone metals (Sn, Sb) anchored onto nitrogen-doped carbon materials can well catalyze CO_2 to generate formic acid or formate. Wallace et al. used electrospinning technology and pyrolysis process to synthesize a Sn-anchored N-doped carbon nanofiber catalyst, which can efficiently catalyze CO_2 to form formate with the FE of 62%.^[29]



(5)

Figure 2. XPS spectra for a) N 1s and b) Zn 2p in ZnN_x/C . c–e) The proposed CO_2RR pathways on carbon supported N₄, Zn-C₄ and Zn-N₄ active site, respectively. f) The free energy diagrams. Reproduced with permission.^[26] Copyright 2018, Wiley-VCH.



The strong electronic interaction between single-atom Sn and N-doped carbon materials can increase the bonding strength of the CO2⁻⁻ intermediate, thereby promoting the conversion of CO₂ to HCOOH. Through experiments and theoretical calculations, Xie et al. found that atomically dispersed positively charged Sn can stabilize CO₂* and HCOO* intermediates, so that the process of CO₂ activation and protonation can spontaneously proceed. In addition, N doping can reduce the rate of formate formation. The energy barrier of the step is reduced by about 1.15 eV.^[30] They used electrochemical in-situ Fourier transform infrared (FTIR) spectroscopy analysis to speculate the reduction mechanism on the atomically dispersed positively charged Sn and N co-doped graphene as follows:

$$CO_2 + * \to CO_2 * \tag{6}$$

$$\operatorname{CO}_2 * + e^- \to \operatorname{CO}_2^{-} *$$
 (7)

 $\operatorname{CO}_2^{-} * + \operatorname{HCO}_3^{-} + \operatorname{e}^{-} \to \operatorname{HCOO}^{-} * + \operatorname{CO}_3^{2-}$ (8)

$$HCOO^{-} * \to HCOO^{-} + *$$
⁽⁹⁾

Li et al. designed a single-atom material (Sb SA/NC) with Sb-N₄ sites, which exhibited high catalytic selectivity with FE_{HCOOH} as high as 94.0% at -0.8 V.^[31] They proposed a possible mechanism of CO₂RR on the surface of the Sb SA/NC catalyst. The CO₂ adsorbed on the catalyst surface accepted electrons and combined with hydrogen ions to form HCOO* intermediate, and then the HCOO* intermediate got electrons to form adsorbed HCOO⁻, which was finally desorbed from the catalyst surface. The formation of HCOO* is the speed determining step with a low energy barrier (0.21 eV) (Figure 3a,b). Wei et al. prepared a NiSn atom pair electrocatalyst (NiSn-APC) with bimetallic active sites and N₄-Ni-Sn-N₄ coordination configuration, which can promote the activity and selectivity of formate.^[32] Experiments and theoretical calculations confirmed that the existence of N₄-Ni-Sn-N₄ sites redistributed electrons, thereby lowering the generation energy barrier of the *OCHO intermediate, and enabling the speed control step to proceed spontaneously in thermodynamics (Figure 3c-f).

2.3. CH₃OH Generation Mechanism

Methanol is a high value-added product among CO₂RR products, but it needs a high energy barrier to produce $*CH_2OH$ or $*CH_3O$ intermediates in the reaction, and therefore there is still a great challenge in large-scale production of CH₃OH. Zhao et al. designed cobalt and nitrogen co-doped graphene with CoN₄ sites.^[33] They speculated that the best way to generate methanol at CoN₄ sites was CO₂ (g) \rightarrow COOH* \rightarrow CO* \rightarrow CHO* \rightarrow CH₂O* \rightarrow *OCH₃ \rightarrow CH₃OH, where the energy barrier for reducing CHO* to CH₂O* was 0.53 eV, which is the speed determining step. Wang et al. immobilized cobalt phthalocyanine on carbon nanotubes for CO₂RR with the efficiency of methanol generation of higher than 40%.^[34] Using DFT calculations, He et al. proposed that isolated copper-modified through-hole carbon nanofibers with Cu-N₄ sites can reduce CO₂ to methanol.^[35] The rate-limiting step was the conversion of CO₂ to COOH* intermediate. On Ni-N₄ sites and pyridine N structures, CO* desorption exhibited negative free energy, which is easier to produce CO on their surface, while CO* desorption was shown as positive free energy (0.12 eV) on the Cu-N₄ structure, and therefore the *CO intermediate was readily reduced to methanol. They further studied the conversion of *CO to methanol to explore the formation mechanism, and found that the *COH intermediate can be reduced to *CHOH or *C. DFT calculations showed that the free energy of C+ formation (~ 0.86 eV) was lower than the free energy of C* formation (~1.88 eV), suggesting that CO₂ is more easily reduced to CH₃OH instead of CH₄ on Cu-N₄ sites.

2.4. CH₄ Generation Mechanism

As one of the CO₂RR products, methane (CH₄) has the potential to replace fossil fuels in the future. At present, Au, Co and Cu-based materials are widely used in electrocatalytic CO₂RR to generate methane. Due to the high C=O bond energy and the complicated eight-electron transfer process, the activity and selectivity for the formation of CH₄ are low.^[36] Xin et al. designed Zn anchored in microporous nitrogen-doped carbon for CO₂RR, on which the Faraday efficiency of methane reached 85%.^[37] Using DFT calculations, the reaction process of CO₂ reduction to CH₄ was inferred. By comparing the free energy of *OCHO (0.46 eV) and *COOH (1.2 eV), the combination of oxygen and the *OCHO intermediate was more stable than the combination of carbon and *COOH. On the Zn-N₄ site, the rate-limiting step for the reduction of CO2 to CH4 was the transformation of *OCHOH to *CHO, and the energy barrier was 0.87 eV. After the quick control step, *OCH₂ and *OCH3 were generated, and then O was bonded to the active site. Finally, CH₄ was formed from the *OHCH₃ intermediate. Except the speed control step, all steps were exothermic. When an external voltage was applied, the energy barrier of each step was reduced. The results showed that single Zn atoms can inhibit the reduction of CO₂ to CO and promote the reduction to CH₄ (Figure 4a-c). Wang et al. connected cobalt phthalocyanine (CoPc) and zinc-nitrogen-carbon (Zn-NC) in series and found that the selectivity of CH4 was much higher than that on single component catalysts.^[38] By analyzing the charge density and state density, they concluded that CO2 reduction to CO had a high activity on CoPc. Therefore, CO₂ was first reduced to CO on CoPc, and the generated high-density CO diffused to the Zn-NC site for further transformation into CH₄. CoPc played a key role, not only generating high-density CO, but also improving the utilization of *H at the N site near Zn-N₄, thereby increasing the selectivity of CH₄ (Figure 4d,e).

2.5. C2 and C2+ Generation Mechanism

In general, C2 products like C_2H_4 , C_2H_6 or C_2H_5OH are obtained by dimerization or coupling of specific C1 intermediates at high local concentrations.^[39,40] It was found that CO₂ can be electro-reduced to C2 products on the metal Cu surface.





Figure 3. a) Proposed CO_2RR mechanism on Sb SA/NC. b) Calculated potential free energy diagrams for CO_2 electroreduction to formate. Free energy diagrams in CO_2RR for production of c) formate and d) CO. (e) In situ ATR-IR spectroscopy of CO_2RR over NiSn-APC. f) A proposed reaction pathway of CO_2RR on NiSn-APC. a,b) Reproduced with permission.^[31] Copyright 2020, Royal Society of Chemistry. c–f) Reproduced with permission.^[32] Copyright 2020, Wiley-VCH.

For example, Fontecave et al. synthesized a Cu-NC catalyst with CuN₄ active sites using pyrolysis technology. Under -1.2 V versus RHE, the Faraday efficiency of ethanol reached 55%, and the total Faraday efficiency of ethanol and ethylene products was as high as 80%. In addition, the catalyst is recycled, and the original material can be completely recovered after the reaction.^[41] Qiao et al. studied the reaction process of CO₂RR on the Cu-C₃N₄ structure. On g-C₃N₄ substrate, the d orbital of Cu can be moved to the Fermi level to adjust the electronic structure of Cu, thereby modulating the adsorption energy of reaction intermediates.^[42] In addition, in Cu-C₃N₄, Cu, and C have a unique dual-active-center synergistic catalytic effect, which plays an important role in the reduction of CO₂ to C₂H₅OH and C₂H₆. In the process of CO₂ reduction to CH₃CH₂OH, the first five protons transfer are the same. After the formation of *OCH₃ intermediate, it evolves together with the second *COOH $(*OCH_3 + *COOH \rightarrow *OCH_3 + *CO \rightarrow *OCH_3 + *CHO \rightarrow$ *OCH₃ + *CH₂O \rightarrow *OCH₃ + *CH₂OH \rightarrow *OCH₃CH₂OH).

Finally, the oxygen atoms adsorbed on the surface are protonated to form $\mathrm{H}_2\mathrm{O}.$

In addition to hydrocarbons and ethanol, Cu-based catalysts can also catalyze CO₂ to produce acetone. Chen et al. prepared a monoatomic copper encapsulated on nitrogen doped porous carbon. The Faraday efficiency of acetone was 36.7%.^[43] The best way of CO₂ to acetone on the Cu-N₄ active site was proposed by theoretical calculations, namely CO₂ \rightarrow COOH* \rightarrow CO* \rightarrow COCO* \rightarrow COCOH* \rightarrow COC* \rightarrow COCOH* \rightarrow COCH₃* \rightarrow COCOCH₃* \rightarrow COCOCH₃* \rightarrow COCOCH₃* \rightarrow COCOCH₃* \rightarrow CHCOCH₃* \rightarrow CH₂COCH₃*

3. Construction Methods of M-N-C Materials

Carbon materials with high conductivity, good stability and large surface area have attracted wide attention in recent years, and the introduction of single metal atoms into the carbon

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Figure 4. a) The reaction process of CO_2 reduction to CH_4 on $Zn-N_4$ -graphene. b) Free energy diagrams on $Zn-N_4$ -graphene. c) The most stable structure of each step. The free-energy profile and optimized configurations of intermediates in d) CO_2 electroreduction to CO, e) CO electroreduction to CH_4 over CoPc and ZnN_4 . a–c) Reproduced with permission.^[37] Copyright 2020, American Chemical Society. d,e) Reproduced with permission.^[38] Copyright 2020, Wiley-VCH.

materials can significantly improve their electrochemical properties.^[44] The strong interaction between metal atoms and supporting substrate provides favorable conditions for the stable fixation of the metal atoms. For most single metal atoms, they are anchored onto carbon materials by coordination with nitrogen atoms (M-N_x). Due to adjustable electronic structure and the exposure of active sites, M-N_x moiety can act as the reaction center. Owing to the unsaturated coordination and high surface energy of single atoms, they are easy to move and aggregate and eventually form clusters or nanoparticles. Therefore, the interaction between metal ions and the carrier needs to be considered for the synthesis of M-N-C catalyst with isolated metal ions. High surface area is required to accommodate more metal atoms, while a large number of defects help to anchor metal atoms.^[45]

So far, many methods have been proposed for preparing M-N-C catalysts, which are usually divided into top-down and bottom-up techniques. Conventional top-down techniques refer to the decomposion of regular precursors into small, irregular fragments, including thermal decomposition and etching.^[46] Bottom-up techniques include solvothermal, coprecipitation, chemical vapor deposition, and wet chemistry.^[16] Thereinto, solvothermal method and pyrolysis strategy have advantages in the synthesis of M-N-C catalysts with high loading of metal atoms. We will summarize five most common methods for

synthesizing M-N-C catalysts below, including pyrolysis, liquidphase exfoliation, electrochemical deposition, thermal synthesis and wet chemistry.

3.1. Pyrolysis Method

Pyrolysis is widely used in the synthesis of single-atom carbonbased catalysts, which is usually operated at temperatures ranging from 500 to 1000 °C, in N2, Ar, or NH3 atmospheres for the thermal decomposition of carbon materials or other precursors, such as graphene, carbon black, carbon nanotubes (CNT), metal-organic frameworks (MOFs), metal salt mixture, and template containing mixture, etc.^[47-51] Generally, metal nanoparticles are generated during pyrolysis, and the synthesized catalyst can be effectively removed by pickling with appropriate concentration. This synthesis method has the advantages of using cheap raw materials and simple operation. Kamiya et al. successfully synthesized Ni-N modified graphene by pyrolyzing metal complexes at 900 °C under Ar atmosphere. The introduction of Ni-N structure significantly enhanced the activity and selectivity for CO formation in CO2RR.[52] Strasser et al. synthesized a series of single-center N-coordination transition metal-doped nanoporous carbon materials by pyrolysis method. Both theoretical and experimental results showed that the combination of M-N_x and







Figure 5. Schematic illustration of synthesis of a) Fe/NG, b) Ni-NCB, c) NG-SAFe, d) C-AFC@ZIF-8, e) M-N-C, and f) Sb SA/NC. a) Reproduced with permission.^[57] Copyright 2018, Wiley-VCH. b) Reproduced with permission.^[57] Copyright 2019, Elsevier Inc. c) Reproduced with permission.^[60] Copyright 2020, Wiley-VCH. d) Reproduced with permission.^[65] Copyright 2017, Elsevier Ltd. e) Reproduced with permission.^[66] Copyright 2018, American Chemical Society. f) Reproduced with permission.^[31] Copyright 2020, The Royal Society of Chemistry.

the reaction intermediates improved catalytic CO_2RR activity.^[53] A nickel and nitrogen doped porous carbon catalyst (Ni-N-C) showed high CO yield at high current density and electrode potential.^[54] Tour et al. synthesized Fe atom-dispersed atomic nitrogen doped graphene (Fe/NG) using GO as a precursor (**Figure 5**a). The Faraday efficiency of Fe/NG in CO_2RR reached 80%. DFT calculations showed that Fe coordinated with four N sites was the active site, and Fe and N doping promoted the catalytic capacity of graphene.^[55] Wang et al. prepared defected Ni and N co-doped graphene (Ni-NG) by using layered GO nanosheets as a precursor. Highly dispersed Ni atoms improved the CO_2RR activity, and the maximum FE_{CO} was more than 95%.^[56]

Stacked carbon black carriers can block the diffusion path of gas, while nanoparticles on carbon black carriers can effectively promote the diffusion of CO_2 to ensure high local concentration of reactants. There are defects and oxygen-containing functional groups on the surface of carbon black with high surface area, which can adsorb metal cations in aqueous solution. Wang et al. synthesized high-performance atomic nickel and nitrogen co-doped catalyst (Ni-NCB) using commercial carbon black as the carrier (Figure 5b). The FE_{CO} was close to 100% at current densities up to 100 mA cm⁻².^[57] Sun et al. obtained a Ni-N-C catalyst (Ni/NC), on which the FE_{CO} reached 96.5%. Jiang et al. prepared nitrogen-doped carbon nanotubes (MSA-N-CNTs) with high metal load up to 20 wt% by multi-step pyrolysis technology, which showed high activity and selectivity

in CO₂RR.^[58] Chen et al. synthesized atomic Ni- and nitrogencodoped carbon materials by pyrolysis method, which were in situ encapsulated on carbon nanotubes (Ni@NCNT), showing FE_{CO} > 90% at a certain wide potential.^[59] Based on current studies, inherent defects are unified with other active sites, which can be produced by high temperature pyrolysis. Wang et al. prepared porous defect-rich carbonitrides (DNG-SAFE) with iron and nitrogen co-doping (Figure 5c). Defects and Fe-N₄ promoted the catalytic performance of DNG-SAFE in CO₂RR, over which the FE_{CO} can reach 90%.^[60]

MOFs with synthetic diversity and modifiers are widely concerned for synthesizing M-N-C catalysts by pyrolysis method. Because MOF-derived nanoporous carbon materials can retain the morphology of their precursors, the obtained M-N-C catalysts would possess porous pores and high specific surface area.^[61–63] Hu et al. prepared Fe-N-C catalyst by pyrolyzing irondoped Zinc (Zn) 2-methylimidazolium ester (ZIF-8) framework at 900 °C in N2 atmosphere, which showed excellent CO2RR catalytic activity with a low overpotential ($\eta = 80$ mV) for CO generation. The Fe sites showed fast CO₂ absorption and weak CO absorption.^[64] Bao et al. obtained C-AFC@ZIF-8 catalyst with atomically dispersed Fe-N sites by pyrolysis of surface functionalized ZIF-8 and ammonium ferric citrate (AFC) (Figure 5d). The activity of C-AFC@ZIF-8 in CO2RR increased with increasing the number of Fe-N sites.^[65] Daasbjerg et al. obtained MNC materials by pyrolysis of organic precursors and www.advancedsciencenews.com





Figure 6. Schematic description of synthesis of a) Co-PPy-C, b) CoTPP-cov, and c) CoPc-py-CNT. a) Reproduced with permission.^[80] Copyright 2018, Elsevier B.V. c) Reproduced with permission.^[81] Copyright 2018, Elsevier B.V. c) Reproduced with permission.^[82] Copyright 2019, Elsevier B.V. c)

silica templates. NaOH etching was used to remove silica and H_2SO_4 washing was used to remove metal particles (Figure 5e). The FE_{CO} on Ni-NC reached 93%, higher than Fe-NC and Co-NC.^[66] Zhang et al. synthesized Sb SA/NC with Sb-N₄ sites by pyrolysis method (Figure 5f), which could be used to efficiently generate formic acid in CO₂RR (FE = 94.0%).^[31]

In addition, pyrolysis temperature affects the structure of catalysts. On the one hand, the density of inherent defects increases with the increase of pyrolysis temperature; on the other hand, the nitrogen coordination number gradually decreases with the increase of pyrolysis temperature. The defect with suitable density and M-N_x can significantly improve the catalytic performance for the CO₂RR.^[26,67,68] Wang et al. obtained defect-rich porous carbon with Fe-N₄ sites by optimizing pyrolysis temperature, at which the FE_{CO} reached 90%.^[60] Amal et al. prepared Ni@NCH catalyst by pyrolyzing Ni-polydopamine (Ni-PDA) spheres at different temperatures (800–1000 °C). At 800°C, the main active site in Ni@NCH was Ni-N₄, which changed to Ni-N₂ and then to Ni-C₄ with increasing temperature gradually.^[69]

3.2. Liquid-Phase Exfoliation Method

Liquid-phase exfoliation is widely used in the treatment of layered structures, and the stripping effect can be significantly improved by ultrasonic and plasma. In addition, the pH value of solution, reaction temperature, surfactant and solution type will affect the morphology and properties of the obtained materials.^[70,71] Lamellar organic structures can be exfoliated to obtain larger surface area and effective active sites. Lan et al. designed a covalent organic framework (M-TTCOFS) with metalloporphyrin-tetrathiofulvarene.^[72] After stripping, the thickness of Co-TTCOF nanosheets is only 5 nm, on which the FE_{CO} can reach 99.7% at -0.8V. Theoretical calculation shows that Co-TTCOF has the lowest energy barrier (0.73 eV) in the CO₂RR velocity control step.^[73]

3.3. Electrochemical Deposition Method

Electrochemical deposition is the process of depositing conductive/semiconductor material onto a substrate via an electric field and redox reaction, which has been widely used in the preparation of nanostructured electrocatalysts.^[74–76] Using electrochemical deposition, the structure, size, and shape of electrocatalysts on conductive materials can be controlled by changing bath composition, pH, temperature, and current density. It is a simple and efficient method with the advantages of economical process, few synthetic steps, high conversion rate, and simple operation. Ma et al. bridged Cu NW to Bi NSs by



electrochemical deposition, and the obtained Cu NW-Bi NS array electrode showed good CO₂RR catalytic activity, on which the FE_{formate} reached 87% at -0.86V.^[77] Tin-based catalysts usually reduce CO₂ to formic acid in electrocatalytic CO₂RR with a selectivity of more than 80% but low activity.^[78] Qiao et al. utilized the characteristics of tin-based catalysts to prepare copper-tin alloy catalysts on N-doped porous carbon cloth by electrochemical deposition. The Faraday efficiency of formic acid formation at a certain wide potential reached 90%, and the durability of formic acid formation exceeded 20 h.^[79]

3.4. Thermal Synthesis Method

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Thermal synthesis is generally carried out at 80-1000 °C under a pressure of 1-1000 Mpa in solution, which includes hydrothermal synthesis in aqueous solution and solvothermal synthesis in organic solvent. The reaction activity was significantly improved by molecular level reaction in solution. Thermal synthesis has the advantages of energy saving, easy control and low temperature operation. Lee et al. prepared metal-organic hybrid catalyst (Co-PPy-C) by solvothermal synthesis method (Figure 6a). The doped polypyrrole onto Co surface can reduce the adsorption capacity, accelerate the desorption, and improve the catalytic CO₂RR activity.^[80] Jiang et al. covalently connected cobalt tetrapenylporphyrin onto carbon cloth (CoTPP-cov), and there was a covalent bond between carbon electrode and CoTPP (Figure 6b). Compared with non-covalent support, the surface density of active sites in CoTPP-cov increased and the TOF increased by about $2 \times (\eta = 550 \text{ mV})$.^[81] Han et al. prepared a cobalt phthalocyanine-supported pyridine functionalized carbon nanotube catalyst (COPC-Py-CNT) by solvothermal synthesis (Figure 6c), which showed high activity, 98% selectivity to CO, and high TOF of 34.5 s^{-1.[82]} Liu et al. synthesized nickel phthalocyanine with tetra amino (NiTAPc) substituents by a simple solvothermal reaction, which showed high CO selectivity (99.8%). DFT calculations showed that the activity was related to the electron density of Ni site, which promotes the adsorption and activation of CO₂.^[83]

3.5. Wet Chemistry Method

Wet chemical method involves chemical reactions in liquid phase, including coprecipitation, impregnation, and chemical reduction. In general, wet chemical method is suitable for preparing single-atom catalysts with low load to avoid metal agglomeration. In addition, the carrier needs to contain rich oxygen-containing functional groups, which is conducive to metal anchoring.^[84] Kang et al. prepared single-atom iron catalysts by graphene-assisted wet chemical reaction, showing FE_{CO} over 90%.^[85] Yang et al synthesized covalent triazine framework (CTF-Cu), which supported copper atoms with CuN_2Cl_2 structure using impregnation method, displaying FE_{ethene} of 30.6%.^[86] Wang et al. synthesized a single-atom catalyst catalyst (CoPc@Fe-NC) with Fe-N sites and cobalt phthalocyanine (CoPc) by means of pyrolysis and impregnation, exhibiting FE_{CO} over 90%.^[87]

4. Adjusting the Electronic Structure of Central Metal Atoms in M-N-C Materials

The factors that affect the electronic structure of M-N-C materials can be divided into two aspects: the central metal atom and the surrounding coordination environment. By adjusting the type of the central metal element and the number of nitrogen ligands, and introducing other axial ligands or double-center metal active sites, the CO₂RR performance can be improved. The d orbital of the metal site is adjusted, which significantly affects its catalytic activity for electrocatalytic CO2RR.[88] In this section, we mainly discuss the influence of the electronic structure of M-N-C materials on electrochemical CO₂RR performance. The central metal atom in M-N-C materials plays an important role in electrocatalytic CO₂RR. The kind of metal species, electron configuration, number of d electrons, and energy level of d-orbital would influence the electrocatalytic activity and selectivity. Therefore, appropriate central metal atom should be selected to enhance the electrocatalytic performance, which includes Fe, Co, Ni, Cu, Zn, Sn, and Sb.^[48,55,89] These metal sites show good catalytic CO₂RR performance in M-N-C materials because their Gibbs free energy of CO₂RR is low.

4.1. Fe-N-C for CO₂RR

With the rise of monatomic catalysts, Fe-N-C materials are constantly designed and widely used in many fields, such as oxygen evolution reaction (OER), oxygen reduction reaction (ORR), biosensing, tumor, and so forth. Li et al. synthesized Fe-anchored N-doped graphene nanomaterials, which can simulate NADPH oxidase activity and have good biological functions.^[90] Li et al. obtained iron-nitrogen co-doped carbon nanoparticles by pyrolysis method, which has a broad application prospect in tumor therapy in vivo and in vitro.^[91] Due to the existence of π - π conjugated electrons between the substrate carbon material and coordinated N atoms, the delocalized π electrons are more easily transferred, which affects the fall of the d-band center and changes the electronic structure of Fe atom. The synergistic effect between Fe and N-C can effectively catalyze OER and ORR, showing low overpotentials in water decomposition.

The preparation of Fe-N-C materials is relatively simple, and the nitrogen sources generally use small molecules or polymers containing nitrogen.^[92] Usually, Fe and N exist in the structure in the form of a tetrocoordination configuration. Fe-N-C materials have a low starting potential in the catalytic reduction of CO2 to CO, and the Faraday efficiency exceeds 90% at a certain voltage.^[87] Fontecave et al. synthesized Fe-N-C materials with variable proportion of single-atom iron centers and iron-containing nanoparticles, and characterized them structurally and electrochemically to investigate the structural parameters ruling the selectivity toward CO₂ electroreduction.^[48] They identified isolated FeN₄ sites as the key catalytic species for the selective CO₂ reduction into CO under aqueous conditions. The $\ensuremath{\text{FE}_{\text{CO}}}$ on $\ensuremath{\text{Fe}_{\text{M}}}$ sites was 91%. Tour et al. synthesized atomic iron dispersed on nitrogen-doped graphene (Fe/NG) for CO2 reduction to CO. Fe/NG exhibited a low reduction overpotential and the FE_{CO} was 80%.^[55] DFT calculations indicated that Fe encircled by four N atoms





Figure 7. a) Schematic illustration of the formation of FeSAs/CNF-900. b) N_2 sorption isotherms and corresponding pore size distributions of FeSAs/CNF-900 and ZIF-8-C-900. c) TEM image. d) HAADF-STEM image. e) Aberration-corrected HAADF-STEM image and f) enlarged image. g) HAADF-STEM image and corresponding element mappings. Reproduced with permission.^[94] Copyright 2020, Elsevier B.V.

(Fe-N₄) inserted in nitrogen-doped graphene is the catalytic active site of CO₂RR. Hu et al. reported a catalyst with singleatom iron sites that produced CO at a low overpotential of 80 mV.^[93] Operando X-ray absorption spectroscopy (XAS) discovered that the active site was discrete Fe³⁺ ion coordinated with pyrrole nitrogen (N) atoms of the carbon carrier, which maintained its +3 oxidation state during electrocatalysis possibly by electron coupling to the conductive carbon carrier. Electrochemical data showed that adsorption of CO₂ and desorption of CO were more likely to occur on Fe³⁺ sites than on Fe²⁺ sites. Zhu et al. prepared mesoporous carbon nanoframe embedded with atomically dispersed Fe-N_x active sites.^[94] The Fe atoms were atomically dispersed in the nanostructure with metalloporphyrin-like Fe-N₄ configuration (Figure 7a). The N₂ sorption isotherms and transmission electron microscopy (TEM) images revealed that the exceptional hierarchically porous structure of FeSAs/CNF-900 had large mesopores and Fe species were highly dispersed (Figure 7b-g). Meanwhile, TEM, powder X-ray diffraction (PXRD) and X-ray absorption fine structure (XAFS) indicated that the dominant Fe species in FeSAs/CNF-900 should be considered as Fe-N_x sites. At -0.47 V, FeSAs/CNF-900 had the best selectivity to CO, and the maximum FE_{CO} can reach 86.9%. The results indicated that Fe-N_r might be an effective active site for CO₂RR.

Zeolite imidazolate frameworks (ZIFs) with a variety of nitrogen ligands and adjustable metal sites are widely used as precursors for the synthesis of M-N-C materials. In addition, different nitriding methods also have great influence on the catalytic capacity of the active site. Wang et al. found that an additional ammonia treatment process can improve the activity of ZIF-derived carbon material doped with Fe-N sites.^[95] Ammonia treatment promoted the sublimation of residual Zn and etching of the unstable carbon part to maximize the exposure of Fe-N active sites and optimize the fractional pore structure, thus improving the FE_{CO} and current density. Liang et al. presented a simple method for the synthesis of Fe-N-C catalysts with atomically dispersed iron sites from ZIF-8 (Figure 8).^[96] The metal sites were dispersed in C-FePc(CN)₈/ZIF-8, and there was no Fe aggregation. The Fourier transform extended X-ray adsorption fine structure (EXAFS) curves indicated the $Fe-N_x$ coordination and the absence of Fe-Fe coordination. C-FePc(CN)₈/ ZIF-8 displayed a reduction current density of -5.0 mA cm⁻² at -0.46 V, a turnover frequency (TOF) of 0.13 s⁻¹ and a FE_{CO} of 94%. C-FePc(CN)₈/ZIF-8 had stable selectivity and activity at low current density, but a significant decrease in CO selectivity and potential increase were observed at -5 mA cm⁻². DFT calculations revealed that desorption of CO on the Fe-N₄ (N) site was easy, indicating that the nitrogen-doped carbon matrix was

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beneficial to the stability of active sites. Deng et al. reported the preparation of multi-scale foamed carbon containing single iron atoms with the assistance of SiO₂ template.^[97] The FE_{CO} reached 94.9% at -0.5 V versus RHE in CO₂RR. Moreover, the activity of the catalyst can be maintained for more than 60 h due to the coordination of single-atom Fe with four nitrogen atoms in the carbon matrix.

For the catalytic reduction of CO_2RR on Fe-N₄ active sites, CO₂ can be catalyzed to CO. In addition, studies have shown that Fe(OH)₃ can selectively reduce CO₂ to acetic acid on N-C carrier. Arrigo et al. investigated the CO₂RR activity of Fe hydroxyl oxide nanostructures supported on O and N codoped graphite in CO₂ saturated 0.05 M KHCO₃ solution.^[98] They found that nanostructured iron (III) oxyhydroxide on nitrogendoped carbon displayed high Faraday efficiency (97.4%) and selectivity to acetic acid (61%) at low potential (-0.5 V vs silver/ silver chloride). XPS and theoretical calculations confirmed that the reduction of CO₂ to CH₃COOH was due to the chemical interaction between the iron in the ferrite and the pyridine N doped in the carbon carrier. The efficiency of Fe/N-C connection to produce CH₃COOH is about 61%, while Fe/O-C connection has a high selectivity to H₂ (up to 94.9%).

4.2. Co-N-C for CO₂RR

For the application of cobalt-based catalysts in CO₂RR, a large number of studies have focused on the macrocyclic ligands of cobalt, such as cobalt phthalocyanine (CoPc) and tetraphenylporphyrin cobalt (CoTPP) anchoring onto conductive carbon materials.^[99] In Co-N-C materials, the substrate has good electrical conductivity, and the FE_{CO} can be improved by adjusting the electronic structure of macroring ligand. When the CoPc was adsorbed to the graphite electrode, it can reduce CO₂ to CO in solution.^[100] Cheng et al. designed a cobalt porphyrin catalyst with covalent organic framework (COF), showing FE_{CO} of 90%.[101] Shui et al. synthesized N-doped porous carbon nanorods anchored with cobalt phthalocyanine, showing CO overpotential as low as 180 mV and FE_{CO} as high as 85.3%.^[102] Zhu et al. loaded cobalt phthalocyanine onto pyridine functionalized carbon nanotubes, exhibiting FE_{CO} above 98% and TOF up to 34.5 s^{-1.[82]}

The transition metal phthalocyanine has a great application prospect for CO₂RR. They consist of transition metal centers with adjustable oxidation states and macro-ring ligand frameworks that provide chemical stability and storage of reduction equivalents and/or protons. For single-atom cobalt, it plays a key role in regulating the electronic structure of materials. Rodionov et al. reported that perfluorinated cobalt phthalocyanine (CoFPc) fixed on carbon electrode can selectively electrocatalyze CO₂ reduction to CO in aqueous solution.^[103] At -0.8 V versus RHE, the FE_{CO} was as high as 93%. In addition, CoFPc had a good stability in a wide potential range from -0.9 to +2.2 V versus RHE. The introduction of fluorine substituent has a negative inductive effect, reducing the molecule to a Co(I) oxidation state, thus accelerating the first step of the catalytic cycle. The inductive effect of fluorine substituents reduced the affinity of CoFPc to CO, which made it less susceptible to poisoning.

Li et al. obtained an organic-inorganic hybrid material with high efficiency for CO₂RR by in situ polymerization of cobalt phthalocyanine onto carbon nanotubes (CoPPc/CNT).^[104] This synthesis strategy inhibited the aggregation of organic molecules, enlarged the electrochemically active surface area, and thus improved their physical and chemical stability (Figure 9a-e). CoPPc/CNT can selectively reduce CO₂ to CO with a Faraday efficiency of up to 90%, a TOFof 4900 h⁻¹ at $\eta = 0.5$ V, and a stability of more than 24 h. The calculated Gibbs free energy (ΔG) of the conversion of CO₂ to COOH^{*} on the CoPPc was 0.46 eV, and the conversion of COOH* to CO* was 0.05 eV. The adsorbed CO was spontaneously released on the surface of CoPPc ($\Delta G = -0.38$ eV). According to the Tafel analysis, the first electronic step is the rate-determining step. The sequential proton-electron transfer (SPET) steps of CO₂RR on CoPPc were studied (Figure 9f-k). In the first step of electron transfer, the central Co^{II} of CoPPc was reduced to Co^I, and the injected electrons were mainly in the Co-dz2 orbital, and some of them were in the C-pz orbital. The charge of Co^I in CoPPc⁻ (+0.86 |e|) is much lower than that of Co^{II} in CoPPc (+1.15 |e|), indicating that CO₂ reduction to CO on CoPPc has a high feasibility.

Mantiram et al. synthesized highly dispersed Co phthalocyanine as a model catalyst by supporting it on oxygen-functionalized carbon paper, showing a high TOF of CO₂RR at a low catalyst loading.^[99] As the dispersion level increased, the TOF increased by three orders of magnitude. In situ characterization confirmed that Co^I was in a static state in the process of CO₂RR, and the first reduction step Co^{II} to Co^I was irreversible.^[101] High CO₂RR rate was achieved on the cobalt phthalocyanine by adjusting the rate-limiting step from electron transfer to synergistic proton-electron transfer. Robert et al. prepared a novel cobalt phthalocyanine (CoPc2) with a trimethyl ammonium part and three tert-butyl groups attached to a phthalocyanine macro-ring,^[105] which showed high conversion of CO₂ to CO over a wide pH range of 4-14. Under alkaline conditions, it had 95% FE_{CO} , a good stability, and a maximum partial current density of 165 mA cm⁻² at -0.92 V versus RHE. Officer et al. successfully immobilized a highly soluble and steric hindered Co^{II} octaalkoxyphthalocyanine on chemically converted graphene (CCG/CoPc-A) using π - π stacking as a heterogeneous catalyst for CO₂RR.^[47] The alkoxy substitutions on CCG/CoPc-A complexes helped to inhibit the aggregation of phthalocyanine on graphene sheets, thus significantly improving the catalytic activity of individual phthalocyanine molecule. At an overpotential of 480 mV, the CO conversion rate was stable during 30 h, and the FE_{CO} reached 75%.

The strategy of using molecular catalysts to precisely control the structure of active sites has been successfully implemented for the reduction of CO₂ to CO.^[106] In addition to CO, the reduction products included methanol. At pH 12–13, the FE of CH₃OH increased from 0.3% to 14.3% when pure CO was used. CoPc was capable of electrically reducing CO₂ to CH₃OH in an aqueous medium through CO intermediates, and the total FE reached 19.5%. Kang et al. designed iminobipyridine cobalt (II) complex that can be used as a catalyst for CO₂RR, and the product was formate in acetonitrile with 80% Faraday efficiency. The addition of water promoted the formation of formate and reduced the formation of CO. The process of CO and formate formation had the same







Figure 8. a) STEM image of C-FePc(CN)₈/ZIF-8, and corresponding elemental maps. b) HAADF-STEM image. c) Fe K-edge XANES for different sample. d) Fe K-edge EXAFS spectra. Reproduced with permission.^[96] Copyright 2019, American Chemical Society.

intermediates, and the redox activity of the imino-bipyridine ligand could effectually delocalize the electron density from the CO midpoint to the ligand, thus reducing the electron content of CO center. DFT calculations suggested that large π -conjugated groups can act as stable intermediates through electron conjugation.

The catalytic efficiency and selectivity can be improved by adjusting the electronic structure of molecular complexes through functionalization. Cobalt(II)-tetrapenylporphyrin complex with pyridine was immobilized on the glassy carbon electrode, and the catalytic activity of carbon dioxide reduction was obviously improved.^[107] Han et al. developed a cobalt-based phthalocyanine catalyst supported on pyridine-functionalized carbon nanotubes.^[82] The catalyst had high activity and high selectivity to CO with TOF of 34.5 s⁻¹ at -0.63 V versus RHE and Faraday efficiency of higher than 98%. The pyridine group coordinated with CO increased the nearby electron density, which made the highly loaded CoPc more dispersed and improved the inherent activity of the CoPc group. The mechanism analysis showed that the rate of CO₂ electroreduction over CoPc was determined by the binding of CO₂ and the

synchronous electron transfer, while the axial pyridine coordination had no effect on it.

Metallic porphyrins have been used as electrocatalysts for CO₂RR due to their unique geometric structure and electronic structure. Leung et al. studied the aqueous phase reduction of CO₂ on cobalt porphyrins using DFT calculations, and determined the optimal structure and harmonic vibrational frequencies of the low electron state of cobalt porphyrins, which are potential intermediates in the reduction reaction.^[108] The ground state of [CoP]+ was a non-planar wrinkled structure, showing a triplet state with the smallest Co-N distance (1.947 Å). Then they used first principles to calculate the two-electron multi-step electrochemical reduction of CO2 to CO on cobalt porphyrin in water.^[109] It was revealed that water can stabilize the binding of cobalt porphyrin with CO₂, and [Co^IPCO₂]²⁻ and [Co^{II}PCOOH]⁻ were the significant intermediates. The results showed that the electron transfer between the polymerized porphyrin catalyst and the gas diffusion electrode is probably the rate-limiting step. Lin et al. combined catalytic cobalt porphyrin units into covalent organic frameworks (COFs) to provide a highly active, stable and selective catalyst for the electrochemical

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Figure 9. a) Schematic illustration of the synthetic process of CoPPc/CNT. b) SEM image. c) TEM image. d) HAADF image. e) EDS elemental mapping. f,g) Co-N bond lengths. h–j) Co-C bond lengths (Å). k) Proposed mechanistic scheme for the CO₂ RR on CoPPc. Reproduced with permission.^[104] Copyright 2017, Elsevier Inc.

reduction of CO₂ to CO in water.^[101] Transmission between the metal and COF lattices allows the cobalt midpoint to have a more delocalized electronic structure, which is a networked solid simulation of the behavior of non-innocent ligands in molecular systems. Yang et al. connected catalytic cobalt porphyrins to MOFs and fabricated them into thin films covering conductive substrates (**Figure 10**a–c).^[110] The system has been proven to be active, selective and stable for CO generation, and the catalytic performance is the highest at the initial layer thickness, which provides the conditions for the balance of charge transfer, mass transfer and active site density (Figure 10d–j).

Using high selectivity of organic molecular catalysts and the advantages of large surface area and high conductivity of carbon nanomaterials, coupling cobalt porphyrin with carbon nanomaterials is a good strategy. Daasbjerg et al immobilized cobaltmeso-tetraphenylporphyrin (CoTPP) on carbon nanotubes, and the electrocatalytic capacity of CO_2RR was significantly enhanced.^[111] The FE_{CO} was >90% in the water medium at low overpotentials, which was mainly due to the specific environment generated by the water medium at the catalytic site of the immobilized catalyst. It promoted the adsorption and further

reaction of CO₂. Peng et al. designed a highly conjugated system to facilitate electron transfer, using in situ Sonogashira coupling reaction to support acetylene-linked Co(II) porphyrin conjugated polymer (PCP) onto ornament functionalized carbon nanotubes(CoCoPCP/CNTs).^[112] By adjusting the central site of the porphyrin unit to optimize the electrocatalytic performance, the FE_{CO} reached 94% with a TOF of 2.4 s⁻¹ at an overpotential of 0.44 V. The experimental results verified that the high CO partial current density of CoCoPCP/CNTs was due to the exposure of more CO active sites and the promotion of electron transfer by hybridization with CNTs, which enhanced the conductivity and inherent electrocatalytic activity of CO₂RR (Figure 11a-d). The two Co centers differed slightly in the charge of Mulliken and Hirshfield, and the spin densities of Mulliken and Hirshfield were very close. At both Co sites, the formation of *CO was exothermic step, while the formation of *COOH and desorption of CO were endothermic steps. DFT calculations showed that the catalytic performance was better when both types of Co centers were used as active sites. Because the formation of *COO at one Co site reduced the electron density at the other Co site associated with charge transfer inside the CoCoPCP, which would





Figure 10. a) Adjustable MOF structure. b) The organic building units. c) The functional CO₂ electrochemical reduction system. d) Voltammogram trace of the MOF catalyst. e) As the scan rate was systematically increased in a CO₂-saturated electrolyte. f) The electrochemical waves increased in magnitude proportional to the square root of the scan rate. g) The MOF catalytic performance was maximized at a starting layer thickness of 50 ALD cycles. h) The selectivity for each product was tested over a potential range of -0.5 to -0.9 versus RHE. i) The steady-state current density for product quantification. j) A one-electron reduction from CO₂ to the CO₂ rate-limiting step. Reproduced with permission.^[110] Copyright 2015, American Chemical Society.

hinder the adsorption of CO_2 at the second Co site (Figure 11e). Figure 11f showed the mechanism of CO_2RR on CoCoCP/CNTs. The electrons were firstly transferred from carbon nanotubes to CoCoCP. Due to the rapid transfer of intramolecular charge from Co-a to Co-b site, Co(II) was reduced to Co(I) at the Co-b site. Co(I) triggered the adsorbed CO_2 molecule and *COOH intermediate was formed through proton coupled electron transfer process. Successively, *COOH was transformed to *CO intermediate, and finally *CO intermediate was desorbed from the Co center to generate CO.

Beside Co-porphyrin compounds, Co-corrole was also investigated in CO_2RR . Roy et al. synthesized cobalt(III) triphenylphosphine corrole complex. During the reduction of cobalt(III) to cobalt(I), the axial ligands fell off one after another, and the square cobalt(I) complex was obtained. Due to electronrich and nucleophilic d⁸ metal central cobalt(I) with its two electrons filling the antibonding dz² orbital, the orbital had a high affinity with the electrophile. Cobalt(I) can therefore act as an active site for CO₂RR. They designed a series of immobilized cobalt A₃-corrole catalysts and demonstrated that the Co-corrole selectively catalyzed CO₂ to alcohols, formaldehyde, carboxylate, and hydrogen at a low overpotential (–0.8V vs RHE). In neutral medium, the FE of ethanol can reach 48%.

4.3. Ni-N-C for CO₂RR

Many studies have shown that introducing Ni into N-C materials can significantly improve the catalytic ability of CO₂RR. Theoretical calculations showed that the introduction of Ni

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Figure 11. a) Specific CO current density. b) C_{dl} values. c) Tafel plots. d) EIS plots. e) Free energy diagrams. b) Proposed mechanism for the CO₂RR on CoCoPCP/CNTs. Reproduced with permission.^[112] Copyright 2021, Elsevier B.V.

single atom can reduce the reaction energy barrier.^[113] In addition, the transition metal Ni showed higher activity and selectivity in the catalytic production of CO from CO₂.^[53,114,115] When single-atom Ni was targeted at carbon materials, Ni can show the maximum atomic utilization, and further enhance the catalytic performance of CO₂RR.^[116] Qiu et al. synthesized Ni single-atom catalysts with different contents of N coordination, on which the current density of CO generation reached 18.2 mA cm⁻² and the Faraday efficiency reached 94.8%.^[117] Wang et al. synthesized single-atom Ni-N-C materials with Ni-N₄ coordination structure, on which the FE_{CO} reached 98%.^[118]

The modulation of electronic structure can facilitate the reaction, and the strong chemical bonds between individual metal atoms and the substrate can increase the stability. In addition, single metal atom with unsaturated coordination environment acts as the active site, which can improve the catalytic performance. Li et al. designed a MOF-assisted catalyst containing single Ni sites (Ni SAs/N-C) through an ion exchange method.^[119] In CO₂RR, the turnover frequency of single Ni site reached 5273 h^{-1} , the FE_{CO} was >71.9%, and the current density was 10.48 mA cm⁻² at 0.89 V versus RHE. The increase in the number of surface-active sites would lead to the decrease in the adsorption energy of CO at single Ni sites and the increase in the electronic conductivity were attributed to the improvement of the reduction performance of CO₂ by Ni SAs/NC. Wu et al. successfully constructed a catalyst with abundant Ni-N4 sites by using a topological chemical transformation strategy.^[116] This method favored retaining the Ni-N4 structure as much as possible and effectively reducing the agglomeration of Ni atoms, thus affording rich active sites for the catalytic reaction

(Figure 12a-f). The presence of Ni-N₄ structure makes the catalyst display outstanding electrochemical reduction activity and selectivity for CO_2RR . The FE_{CO} was more than 90% in the potential range of -0.5 to -0.9 V. The high activity and selectivity of Ni-N₄-C were studied by DFT calculations (Figure 12g-h). In the reaction process, the potential limiting step on Ni-N₄-C and N-C was the formation of the intermediate COOH*. When Ni-N₄ sites were introduced, the formation energy of COOH* decreased, and the generation of CO was accelerated, showing higher catalytic activity. In CO2RR, the generation of H2 is the main competitive reaction. According to previous reports, the selectivity of CO₂RR can be reflected by the difference of thermodynamic limit potential between CO₂ reduction and H₂ generation $(U_{L}(CO_{2}) - U_{L}(H_{2}))$, where $U_{L} = -\Delta G_{0}/e$.^[120,121] The more positive the calculation result is, the higher the selectivity is. It was theoretically and experimentally confirmed that the Ni-N₄ structure can reduce the energy barrier of CO₂ reduction and accelerate the charge transfer, thus improving the activity and selectivity of CO₂ conversion to CO.

Wang et al. used atomically dispersed Ni atoms in graphene nanosheets for the formation of CO by CO_2RR .^[56] At an overpotential of 550 mV, the Ni monatomic catalyst showed high CO selectivity (FE = 95%) and good stability. The CO desorption barrier and H* adsorption energy at atomic Ni and Co sites were compared by thermodynamic calculation. Atomic Ni sites showed a lower desorption barrier, indicating that the resistance of CO poisoning on Ni sites was stronger than atomic Co sites, while the HER activity of Co was stronger than that of Ni. It was further concluded that atomic Ni catalysts have better selectivity in CO_2RR than atomic Co catalysts. Liu et al. loaded isolated high-density monovalent nickel onto N-doped graphene

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Figure 12. a) Schematic illustration of the topo-chemical transformation strategy. b,c) FT of the Ni K-edge EXAFS oscillations. d) TEM image of Ni-N₄-C (scan bar: 500 nm). e) HAADF-STEM image. f) Element mapping images. g) Calculated free energy diagram. h) Difference in limiting potentials for CO_2 reduction and H₂ evolution. Reproduced with permission.^[116] Copyright 2017, American Chemical Society.

and N,S-codoped graphene for CO2RR (A-Ni-NG and A-Ni-NSG).^[11] The electronegativity of pyridine N and S in the A-Ni-NG and A-Ni-NSG was lower than that of pyrrole N in Ni(II) Pc, which allowed the formation of Ni(I) atoms. The Fourier transformation of EXAFS spectrum confirmed the existence of Ni-N₄ structure in A-Ni-NG. The introduction of single-atom Ni increased the activity and selectivity for CO₂RR. At the applied potential of -1.0 V versus RHE, the A-Ni-NSG electrode can produce a high cathode current density (115 mA cm^{-2}), which corresponds to the mass activity of 1150 A g_{catalyst}⁻¹. A-Ni-NSG as a catalyst for CO generation showed a low initial overpotential of about 70 mV. At -0.5 V versus RHE, the FE_{CO} reached 97%. The Tafel slopes of A-Ni-NG and A-Ni-NSG in CO2RR were 108 and 114 mV dec⁻¹, respectively, which implied that the first electron transfer of the *COOH species was the ratedetermining step for CO generation. The TOF of A-Ni-NSG can attain 14800 h⁻¹ at an overpotential of 0.61 V and the activity can be maintained for more than 100 h. DFT calculations showed that the 1π orbital of the bent CO₂ molecule adsorbed on Ni(I) and the delocalization of the Ni 3d orbital resulted in the rise in the density of states round 3 - 6 eV beneath the Fermi level. The results illustrated that there existed the delocalization of unmatched electrons in the Ni $3d_{x2-y2}$ orbital and unprompted charge transfer from Ni(I) to C 2p orbital during the formation of CO_2^{δ} species, which contributed to the reduction of energy barrier in electrochemical CO2RR. Chen et al. used a semi-sacrificial template strategy to synthesize atomic Ni and nitrogen codoped hollow carbon spheres (SA-Ni/N-CS).^[122] The SiO₂/ polydopamine spheres can adsorb Ni²⁺ ions. After pyrolysis and leaching, polydopamine can be converted into hollow N-C spheres. The FE_{CO} on the SA-Ni/N-CS reached 95.1%. Theoretical calculations indicated that the reaction control step of CO₂RR catalyzed by SA-Ni/N-CS was CO₂ activation process with activation energy barrier of 2.16 eV. The atomic dispersion of Ni atoms and unique hollow sphere structure improved the CO₂RR performance.

4.4. Cu-N-C for CO₂RR

Among all transition metal catalysts reported previously, copper-based catalysts are the only ones that can reduce CO_2 to a variety of products with high Faraday efficiency, including C1 (CO, CH₄, and CH₃OH) and C2 (C₂H₄, C₂H₆, and CH₃CH₂OH). CO₂ can be reduced to CO at some Cu-N₄ sites, and the protonation process is more likely to occur when the coordination N is in the edge position to form *COOH.^[123] In contrast, the CO desorption structure on Cu-N₃ is very difficult since the energy barrier is very high, but the active site of Cu-N₃ has good selectivity to CH₄.^[124,125] At a relatively low overpotential, ethylene is inclined to generate on Cu(100) for CO₂RR, whereas methane is inclined to generate on Cu(211) and only a small amount of

ethylene can be generated.^[126] The reaction process generally takes place at the three-phase interface, and hence CO₂ adsorption and products desorption on the surface are the rate-controlled steps.^[127] The surface active site determines the electrocatalytic performance of CO₂RR. Exposure of central active copper sites as much as possible is an effective method to improve the selectivity and efficiency of electrochemical CO₂RR. Developing single atom metal catalysts is an important mean to improve catalytic activity due to their distinctive electronic structure and maximum atomic availability.^[17]

In addition, the C–C bond coupling reaction was enhanced by increasing pH value, further improving the selectivity of C2 products.^[126] Wei et al. synthesized a MOF-derived coppernitrogen-doped carbon catalyst, on which the Faraday efficiency of ethylene and ethanol was 11.2% and 18.4%, respectively. The single-atom copper-modified carbon nanotube catalyst synthesized by He et al. exhibited an efficiency of 44% in catalytic reduction of CO₂ to methanol.^[35] Fontecave et al. synthesized a monatomic Cu-anchored N-doped carbon material that was highly selective for ethanol in CO₂ electroreduction, with a Faraday efficiency of 55%.^[41]

In aqueous media, Cu catalysts showed high Faraday efficiency for hydrocarbon generation, including C2H4 and CH4. [128-131] Kusama et al. anchored crystalline copper phthalocyanine (CuPc) onto carbon black. CuPc/C was highly selective and stable for the electrochemical reduction of CO₂ to C₂H₄ with a Faraday efficiency of 25%.^[132] However, CuPc treated with sulfuric acid was not selective to the formation of C₂H₄ due to the lack of Cu sites. Liang et al. studied the catalytic activity of three copper complexes for the reduction of CO₂ to CH₄.^[133] Amongst them, Cu(II) phthalocyanine(CuPc) displayed high activity and selectivity for the formation of methane with a Faraday efficiency of 66% and a partial current density of 13 mA cm⁻² at -1.06 V versus RHE. Using in situ X-ray absorption spectra (XAS), it was found that CuPc underwent a reversible change in structure and oxidation state, and CuPc molecules were reorganized into metal Cu clusters with a size of about 2 nm, which catalyzed the conversion of CO₂ to CH₄. After releasing the negative electrode potential, the Cu nanoclusters were converted back to the primary CuPc structure. The reversible formation of Cu nanoclusters promoted the CuPc catalyst to have good activity for CO₂RR. DFT calculations showed that the recombination is reasonable and the reversibility is due to the robust divalent metal ion-ligand coordination in the molecular structure of CuPc and the little size copper clusters formed in the reaction states. Albo et al. studied the catalytic effect of four kinds of copper-based organic porous materials supported on gas diffusion electrode for CO₂RR.^[134] Due to relatively high surface area of the electrode and more exposed Cu catalytic centers, the catalyst showed a good catalytic performance for CO2RR, and the efficiency of CO₂ conversion to methanol and ethanol in the liquid phase was high. The results illustrated that the improved performance of electrocatalytic CO₂ reduction to alcohol can be attributed to the exposure of metal-organic porous materials at the unsaturated coordination site in the pore system. The paddle wheel motifs constructed from N donor ligands reserved the square plane coordination geometry round Cu^{II} atoms, resulting in exposed metal sites that are prone to interact with guest molecules in the entire porous network.

Depending on the characteristics of different copper sites, He et al. prepared isolated copper decorative through-hole carbon nanofibers (CuSAs/TCNFs).^[35] The Faraday efficiency of methanol generation in liquid phase can reach 44%. Cu single atoms with Cu-N₄ configuration were highly dispersed on the substrate, which can well improve the CO2RR performance (Figure 13a-f). CuSAs/TCNFs exhibited high Faraday efficiency, high partial current density of methanol (-93 mA cm⁻²) and good stability (>50 h). Using DFT calculations, they compared the activity of CO₂RR on CuSAs/TCNFs and Ni modified catalyst (Figure 13g-j). The rate-limiting step was the conversion of CO₂ molecule into COOH*. The Gibbs free energy at the Ni-N₄ site was 0.98 eV, lower than that at the Cu-N₄ site (1.17 eV). In the CO* desorption step, both Ni-N₄ (-0.21 eV) and pyridine N (-0.54 eV) showed negative free energy, indicating that CO was easily generated on the surface of these catalysts. The desorption free energy of *CO on Cu-N₄ was positive (0.12 eV), and this step required energy absorption, which makes the *CO intermediate further reduced to methanol, and it was not easy to release from the catalyst surface as CO product. In addition, only C1 was produced on CuSAs/TCNFs, because the dispersed Cu atoms blocked the C-C coupling pathway of *CO intermediate conversion to advanced products, thus increasing the amount of CO and CH₃OH in the reaction.^[4] By comparing the energy barriers (≈0.86 eV and ≈1.88 eV) of the reduction of COH* to CHOH* and C* on Cu-N₄ structure, it was confirmed that the selectivity to CH₃OH at single atomic Cu sites on CuSAs/TCNFs catalyst was higher than the selectivity to CH₄.

4.5. Zn-N-C for CO₂RR

Although transition metal Zn and Cu are the adjacent elements, the products on Zn-based catalysts and Cu-based catalysts are obviously different in catalytic CO_2RR . CO_2 was mainly reduced to CO and formate on Zn-N-C materials. For example, Zn/NC NSs showed excellent catalytic performance for CO_2RR , generating CO with a high current density of 50 mA cm⁻² and a Faraday efficiency of about 95%.^[135] Zhou et al. synthesized zinc-atom-dispersed nitrogen-doped layered porous carbon, showing FE_{CO} of 96%.^[136] Chen et al. found that the temperature could affect the selectivity of CO and formate on zinc-based catalysts, and higher temperature was favorable to the formation of formate.^[137]

Compared with catalysts based on extended structure, transition metal complexes have unique advantages of clear molecular structure and adjustable structure. Wang et al. synthesized a multiphase electrocatalyst zinc(II) 5,10,15,20-tetramesitylporphyrin (PorZn), which showed high selectivity and activity for the CO2RR.[138] At -1.7 V versus RHE, the FE_{CO} reached 95% and a TOF was 14.4 $\rm site^{-1}\ s^{-1}.$ In situ XAS analysis indicated that the Zn(II) center always maintained its oxidation state. In addition, the ligand in the PorZn complex has redox activity confirmed by chemical reduction, and the reduced intermediate product can react with CO₂. The zeolite imidazole framework (ZIF), composed of metal ions and imidazole ligands, has a variety of topological structures, high porosity, and excellent thermal and chemical stability.^[139] Bao et al. researched the effect of four imidazole ligands on CO2RR, and found that ZIF-8 showed the largest Faraday





Figure 13. a) XRD patterns. b) N ls spectra of CuSAs/TCNFs. c) Cu 2p spectra. d) XANES spectra at the Cu K-edge. e) FT at R space. f) Fitting for EXAFS data. g) Optimized atomic structures of CuSAs/TCNFs and proposed reaction paths for CO_2 electroreduction. h,i) Free energy diagram of CO_2 to CO. j) Illustration of CO_2 diffusion on two samples. Reproduced with permission.^[35] Copyright 2019, American Chemical Society.

efficiency (FE_{CO} = 81.0%) at -1.1 V versus RHE.^[140] The CO current density can reach 12.8 mA cm⁻² at -1.3 V versus RHE. In situ XAS and DFT calculations displayed that the central coordination site of imidazoline and Zn(II) in ZIF-8 were active sites for the CO₂RR, improving the Faraday efficiency and current density of CO.

The structure obtained by simultaneous anchoring of single atom zinc and nitrogen to graphene has good catalytic performance of CO₂RR. Liu et al. prepared a series of Zn-N-G electrocatalysts by high temperature pyrolysis and subsequent acid leaching.^[141] N and zinc were uniformly dispersed on the graphene matrix, and no metallic Zn particles were observed, suggesting that Zn was dispersed in the Zn-N-G-800 in an ionic chemical state (Figure 14a-f). The Faraday efficiency of Zn-N-G-800 for CO generation in the CO₂RR was 90.8% (η = 0.39 V vs RHE). The small $R_{\rm s}$ and $R_{\rm ct}$ values of Zn-N-G-800 indicated that it has good electrical conductivity and fast interfacial charge transfer rate in electrochemical reaction process. The Tafel slope value (118 mV dec⁻¹) of Zn-N-G-800 suggested that the formation of the initial single electron transfer step (HCO_2) for the adsorption of free radical intermediates was the chemical rate-determining step. They used DFT to calculate the energy barrier on the Zn-N₄-G catalyst and the desorption energy of CO*. By comparison, they found that in Zn-N₄-G, CO* was more easily desorbed to generate CO (Figure 14g). In Figure 14h, the difference of limit potential of CO2 reduction and hydrogen evolution reaction on Zn-N4-G and N-G catalysts was compared. The difference value of Zn-N₄-G was more positive, indicating that it had high CO selectivity, which confirmed that $Zn-N_x$ active site can reduce the formation energy barrier of COOH* and CO* intermediates.

4.6. Sn-N-C and Sb-N-C for CO₂RR

The interaction of metal Sn/Sb in p region and N-doped carbon has a catalytic effect on CO2RR. Sn and N doping can regulate the electronic structure of carbon and increase the electrical conductivity and chemical adsorption capacity. Sn and Sb catalysts can reduce CO₂ to formate and formic acid. Anchoring tin nanoparticles to graphene allowed the catalyst to readily give away electrons, facilitating the adsorption of CO₂ and CO2⁻⁻, which was easily reduced to formate.^[142,143] Wallace et al. designed an inexpensive Sn-modified N-doped carbon nanofiber mixed catalyst (Sn-CF1000) using direct electrospinning and pyrolysis techniques to catalyze CO₂RR in aqueous solution.^[29] At an overpotential of 690 mV, the Faraday efficiency of formate formation was 62%, and the current density was 11 mA cm⁻². At a low overpotential of 490 mV, the FE_{CO} can reach 91%. In Sn-CF1000 catalyst, Sn atom was coordinated with pyridine-N to form Sn-N structure as the active site of CO₂RR. The strong electron interactions between Sn active sites and the pyridine-N doped carbon enhanced the stability of CO₂⁻⁻, promoted the formation of COOH* intermediate on the Sn-N site, and thus improved the dynamics of CO generation. Xie et al. prepared positively charged $Sn^{\delta+}$ on N-doped graphene by rapid freeze vacuum drying and calcination.^[30] Rapid cooling of liquid nitrogen made Sn ions uniformly dispersed in the graphene oxide, and the thickness of the graphene was about 0.4-0.5 nm, close to a single layer (Figure 15a-g). At a potential of -1.6 V versus SCE, the Faraday efficiency of formate formation on the single-atom $Sn^{\delta+}$ and N-codoped graphene reached 74.3%. The TOF was 11 930 h^{-1} at -1.8 V versus SCE, and the catalyst showed good stability during over 200 h.

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2 Graphene **⊘**Zn 00 ON. C) C **Pyrolysis** Electrolysis Acid leaching Zn(Ac) Zn-N-G CO, reduction C h 200 nm e μm Zn-N₄-G N-G C h g Zn-N_-G N-G Free energy (eV) △P_{limit} (V vs.RHE) 2 -2 P_{limit}(CO₂RR) P Imit (HER) -3 AP CO+H,O *+CO. COOH. CO*+H.O Reaction pathway

Figure 14. a) Fabrication process for Zn-N-G and CO₂ reduction process. b) SEM image of Zn-N-G-800 electrocatalysts. c,d) TEM images. e) HRTEM image. f) HRTEM image and the corresponding elemental mappings. g) Calculated free energy diagram. h) Calculated limiting potentials for CO₂RR and HER. Reproduced with permission.^[141] Copyright 2018, Wiley-VCH.

Strong bonding interactions may result in highly delocalized charge densities in metal atoms with charge densities moving away from the metal atoms to adjoining atoms. The remaining charge density was asymmetrically distributed on the metal atoms, making the metal band has a positive charge (M^{δ^+}). The asymmetrically scattered charge density promoted electrons to adsorb CO₂. Sn^{δ^+} can effectively stabilize the intermediates CO₂^{--*} and HCOO^{--*}, so that the activation and protonation of CO₂ can be spontaneously carried out. The single-atom Sn^{δ^+} on N-doped graphene had more adsorption capacity for CO₂ than graphene, and the effective adsorption site was the Sn-N site (Figure 15h–j). The desorption process of HCOO^{--*} was the rate-limiting step (Figure 15k), and the desorption energy was relatively small (1.01 eV), indicating that HCOO^{--*} was prone to

be desorbed. The doping of nitrogen atoms led to longer bond length between Sn and HCOO⁻, thus facilitating the desorption of HCOO^{-*} from the Sn^{δ +} species. The catalytic activity of single-atom Sn^{δ +} on N-doped graphene can be improved by accelerating the rate-limiting step.

The bulk Sb shows low selectivity to formate, but anchoring Sb on graphene can be used as an electrocatalyst for reduction of CO_2 to formate. The increased catalytic activity is attributed to the strong electron interaction between Sb and graphene. Zhang et al. prepared Sb and N co-doped carbon nanosheets (Sb SA/NC), in which Sb and N formed a tetraporic structure to act as the active site for $CO_2 RR.^{[31]}$ DFT calculations revealed the mechanism of CO_2 reduction to formate on the Sb SA/NC catalyst. According to the calculated Gibbs free energy, it was

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Figure 15. a) TEM image of single-atom $Sn^{\delta+}$ on N-doped graphene. b) HAADF-STEM image and the corresponding element mapping. c–e) The enlarged HAADF-STEM images. f,g) The corresponding intensity profiles along the line X–Y in (d) and (e). h) CO₂ adsorption isotherms i) CO₂ TPD spectra. j) Electrochemical in situ FTIR spectra of the single-atom $Sn^{\delta+}$ on N-doped graphene at the potentials of –1.6 V versus SCE. k) Calculated free energy diagrams. Reproduced with permission.^[30] Copyright 2019, Wiley-VCH.

more favorable to generate HCOO* on Sb SA/NC (0.21 eV), while COOH* pathway to generate CO and competing reaction HER both showed higher energy barrier and were difficult to take place.

5. Adjusting the Coordination Environment of Central Metal Atom in M-N-C Materials

According to the ligand field theory, center metal atom surrounded by different ligands has an impact on its electronic d orbit. The intensity of the interaction between metal atom and ligands decides the rise or fall of different d orbits on the level, and therefore, the electronic structure and catalytic performance of M-N-C materials can be modulated by tuning the ligands around central metal atom. The electronic environment of the central metal atom can be optimized by constructing different metal-nitrogen coordination numbers, regulating the type of ligands and the carbon base plane environment, and constructing bimetallic single-atom sites. Various reduction products can be obtained by using the number of coupled electrons and protons in CO_2RR .

5.1. Adjusting the Number of Ligands

In M-N-C materials, when the central metal atom is transition metal element, the nitrogen coordination number can be more than four,^[144,145] and the four nitrogen coordination is not always favorable to $\rm CO_2 RR.^{[146-149]}$ Other nitrogen coordination numbers, such as M-N₂,^[150] M-N₃,^[151] and M-N₅,^[12] have good catalytic effect on $\rm CO_2 RR.$ Wang et al. used a co-deposition strategy

of Fe was transferred to the p_x and p_y orbitals of N atom, which decreased Fe-CO π back-donation, resulting in a comparatively weak adsorption of CO at the FeN₅ site. Therefore, the generation of CO at the FeN₅ site has higher selectivity (Figure 16c–f).

In cobalt-centered M-N-C materials, the reduction of N coordination atom will produce multi-unoccupied 3d orbitals for Co atoms, which are conducive to the adsorption of CO_2 and boosting the reduction rate of CO2. Compared with catalysts with Co-N₄ sites, the catalysts containing Co-N₂ sites showed higher activity and selectivity. Wu et al. studied single-atom Co catalysts with diverse nitrogen coordination numbers.^[153] The coordination numbers of isolated Co atoms (Co-N₄, Co-N₃, and Co-N₂) were controlled by changing the pyrolysis temperature. HAADF-STEM images show that Co atoms were atomically dispersed even at 1000 °C (Figure 17a–g). In CO₂RR, the FE_{CO} was 94%, the current density was 18.1 mA cm⁻² at the overpotential of 520 mV, and the conversion frequency of CO formation can reach 18 200 h⁻¹. The adsorption potential of OH⁻ on the upper surface of Co-N₂ site was smaller than that at Co-N₄ site, suggesting that the adsorption of CO₂⁻⁻ was weaker at the former, which was conducive to the release of CO₂. DFT calculations indicated that the energy required forming $CO_2^{\bullet-*}$ at the Co-N₂ site was lower, and therefore, the electroreduction catalytic activity of CO_2 was higher at the $Co-N_2$ site (Figure 17h-k). Jiang et al. synthesized an atomically dispersed electrocatalyst with Co single-atom and N-functional group as the active sites for CO₂RR and HER.^[154] The catalyst exhibited a Faraday



Figure 16. a) Synthetic route towards single-atom FeN₄ and FeN₅ catalysts. b) Free energy profile. Local DOS of the c) FeN₄ and d) the FeN₅ with adsorbed CO. Partial charge density of e) the FeN₄ and f) the FeN₅ with adsorbed CO. Reproduced with permission.^[12] Copyright 2019, Wiley-VCH.

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to synthesize a single iron atom electrocatalyst with a monodis-

persed FeN5 active site on graphene.^[12] This strategy enabled

heme and melamine to be cross-linked at high temperature,

which successfully inhibited the accumulation of iron atoms on

graphene through thermal annealing (Figure 16a). The single-

atom iron electrocatalyst with FeN5 active site showed a high

Faraday efficiency of about 97.0% at a low overpotential (0.35 V).

The electrocatalytic performance on FeN5 was significantly better

than that on FeN4.^[152] In addition, the FeN5 catalyst exhibited

stability at -0.46 V during 24 h, and the FeN₅ configuration

remained unchanged on graphene. The free energy curve of the energy pathway from CO_2 to CO at the active sites of FeN_4 and

FeN₅ was plotted by DFT calculations as shown in Figure 16b,

showing that the free energy of the rate controlling step in the

conversion of CO_2 to CO at the two active sites was different. The adsorption energy of the rate controlling step at the active site of

FeN₅ was 0.77 eV (CO₂ \rightarrow *COOH), while the adsorption energy

at the active site of FeN₄ was 1.35 eV (*CO \rightarrow CO + *), indicating

that the conversion of CO₂ to CO was easier at FeN₅. The local

density of states (LDOS) and partial charge density were further

studied. In the energy window (-1.56 eV toward -0.82 eV), the

hybridization of Fe d_{xz} , d_{vz} orbitals and C p_{xz} , p_v orbitals was the

key reason for the π_{p-d} interaction. The distinctive electronic

structure of the active site of FeN5 was due to the interaction

between the potential pyrrolic N doped graphene and Fe. Bader

charge studies displayed that the oxidation state of Fe in FeN5

(+1.19 e) was higher than that in FeN₄ (+0.98 e). The d electron

S





Figure 17. a) The formation process of Co-N₄ and Co-N₂. b) SEM and c) TEM images of Co-N₂. d) Examination of the corresponding EDS mapping. e,f) Magnified HAADF-STEM images of Co-N₂. g) Corresponding SAED pattern of Co-N₂. h) Single oxidative LSV scans in N₂-saturated 0.5 M NaOH for different catalysts. i) EXAFS and j) CO specific current density for Co-N₂ and NH₃-treated Co-N₂. k) The Gibbs free energy diagrams. I) Top-view and side-view of CO₂ molecule adsorbed on Co-C₂N₂ sites with different configurations. a–k) Reproduced with permission.^[153] Copyright 2018, Wiley-VCH. I) Reproduced with permission.^[154] Copyright 2018, Wiley-VCH.

efficiency of nearly 100% and a high formation rate of about 425 mmol g⁻¹ h⁻¹ at 1.0 V for the CO₂RR. DFT calculations showed that C atoms in linear CO₂ molecules were more likely to bind to Co atoms, while two O atoms tended to be close to N atoms in Co-C₂N₂ sites (Figure 17l). The theoretical calculations and KSCN poisoning results showed that Co-C₂N₂ was the active site of CO₂RR, while the HER was slow at this site.

Different nitrogen species affect the species and selectivity of the products. Kang et al. designed a cobalt complex with large π -conjugated structure, where a single tridentate ligand creates more ligand sites, while the high steric hindrance of the large-

group diisopropyl prevents the polymerization of active hydride intermediates.^[155] The catalyst can reduce CO_2 to formate with a selectivity of 80%. The introduction of water in the reaction can promote the formation of formate. DFT calculations showed that Co^0 species was produced in the production of CO and formate. Moreover, imino-bipyridine ligand with redox activity can delocalize the electron density from the Co center to the ligand and reduce the electron content in the Co center, thus improving the selectivity of formate. Yang et al. designed amidate ligated pentadentate iron and cobalt catalysts for $CO_2RR.^{[156]}$ DFT calculations elucidated a ligand-assisted H₂ cracking mechanism

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Figure 18. a) XPS spectrum of N 1s for Ni_{SA}-N₂-C. b) Normalized Ni K-edge XANES spectra. c) FT-EXAFS spectra. d) EXAFS fitting and optimized model for Ni_{SA}-N₂-C. e) Proposed reaction paths for CO₂RR on Ni_{SA}-N₂-C. f) Free-energy diagram. Reproduced with permission.^[68] Copyright 2019, Wiley-VCH.

with ΔG of 23.3 kcal mol⁻¹. Chen et al. introduced atomically dispersed Co-N₅ sites on polymer-derived hollow N-doped porous carbon spheres, which showed high selectivity in CO₂ reduction to CO.^[157] Under a wide potential (-0.57 to -0.88 V), the FE_{CO} exceeded 90%. Theoretical calculations showed that the ΔG of the first reduction step of CO₂RR on Co-N₅/HNPCSs was -0.28 eV, and the structure of intermediate Co * species was similar with that in the CoPc. The ΔG of the first proton coupled electron transfer step was 0.31 eV, and the desorption free energy of CO increased by 0.16 eV compared with that of CoPc. The catalytic activity of Co-N5/HNPCSs in CO2RR was higher than that of CoPc. The results showed that the single-atom Co-N₅ site was the main active site for CO₂ activation and rapid production of key intermediate COOH* and CO desorption. The electronic localization function showed that the strong interaction between COOH and Co-N5 site makes it an effective site for CO2RR catalysis.

Metal anchoring in nitrogen-based macrocyclic compounds is beneficial to increase the redox activity of metal and the interaction with appropriate intramolecular hydrogen bonds, thus enhancing the catalytic capacity of $\rm CO_2RR.^{[158]}$ Jurss et al prepared a series of active macro-ring nickel complexes for $\rm CO_2RR.^{[159]}$ Experiments and theories displayed that the $\rm FE_{CO}$ was the highest (87%) when the central metal Ni was +2 valence, and Ni was coordinated with two N atoms in the structure. The macro-ring of the prepared catalyst increased the selectivity in $\rm CO_2RR$. This study showed that the interaction between the metal and the redox active ligand can determine the rate-determining step of the reaction. Jiang et al. introduced polypyrole (PPy) as a nitrogen source into the metal–organic framework and prepared single-atom catalysts with different nitrogen coordination numbers by controlling the pyrolysis temperature.^[68] The binding energy of Ni 2p_{3/2} in the single-atom catalyst with Ni-N2 site was 854.6 eV, indicating that the Ni was in a weak oxidation state. In Ni_{SA}-N_x-C (x = 2, 3, 4), the valence state of the Ni atom is between 0 and +2 valence. EXAFS fitting results revealed that the introduction of N effectively stabilized Ni atoms and prevented Ni atoms from agglomerating (Figure 18a-d). Among the three kinds of nitrogen coordination, the Ni_{SA}-N₂-C catalyst with two nitrogen coordination had the highest $\mathrm{CO}_2\mathrm{RR}$ activity, over which the FE_{CO} can reach 98% and the conversion frequency was as high as 1622 h⁻¹. DFT calculations illustrated that the rate-controlled step on the three catalysts is the formation of COOH* intermediate. For Ni_{SA}-N₂-C catalyst, the free energy of the ratedetermining step was 1.42 eV ($\Delta G_{\text{Ni-N3}}$ of 1.45 eV and $\Delta G_{\text{Ni-N4}}$ of 1.73 eV), which was the lowest, indicating that COOH* was more easily formed at the Ni-N2 site. Furthermore, the adsorption energy of CO* on the $\rm Ni_{SA}\text{-}N_2\text{-}C$ was low (0.47 eV), indicating that the release of CO* was easy. Both experiment and theoretical calculations confirmed that the Ni-N2 site of NiSA-N₂-C was highly active for CO₂RR (Figure 18e–f).

Li et al. synthesized a single-atom catalyst with Ni-N₃ active site (Ni SAs/NC),^[119] where Ni atoms were highly dispersed in nitrogen doped porous carbon, on which the FE_{CO} was more than 71.9% at $\eta = 0.89$ V, and the turnover frequency of Ni-N₃ active site was 5273 h⁻¹. The enhanced catalytic effect of Ni SAs/NC for CO₂RR may be attributed to the large exposure of active sites, the increase of electrical conductivity and the decrease of the adsorption energy of CO on the active site. The low interfacial charge transfer resistance on Ni SAs/NC accelerated the transfer of electrons from the electrode to CO₂, which ensured the formation of CO₂⁻⁻ radical anion intermediates.

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The low coordination of Ni-N3 active site can strongly bond with CO2⁻⁻, which promoted the electroreduction performance. Nakanishi et al. designed Co. Ni or Cu modified covalent triazine frameworks (CTF) with unsaturated 3d orbitals.^[160] The prepared Ni-CTF catalyst showed FE_{CO} of 90% at -0.8 V, higher than the corresponding metallic porphyrin. Theoretical calculations demonstrated that the free energy barrier formed by the adsorption of COOH in the first reduction step was reduced due to low coordination structure. Lu et al. first synthesized a single-atom catalyst with mixed coordination of nitrogen and oxygen atoms, and then used high temperature to remove Ni-O with weak interaction, and finally obtained Ni-N₃-V SAC with vacancy defect.^[161] The catalyst exhibited high current density (65 mA cm⁻²), high Faraday efficiency (>90%) and high turnover frequency $(1.35 \times 10^5 \text{ h}^{-1})$ at -0.9 V versus RHE for CO2RR. DFT calculations showed that the energy barrier of COOH* formation and CO desorption was reduced at the Ni-N₃-V site, and CO* was easily desorbed to form CO.

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Unsaturated M-N sites formed by reducing the coordination number of N can increase the bond M-N strength, thus reducing the reaction free energy of the rate-limiting step. Feng et al. designed an electrocatalyst (Cu-N2/GN) with highly dispersed and exposed Cu-N2 sites on graphene substrate, on which the maximum FE_{CO} was 81% at $-0.50~V.^{\left[162\right]}$ Theoretical calculations revealed that the free energy (U =0 V) of two sites (Cu-N₄ and Cu-N₂) during endothermic CO₂ capture was 0.408 and 0.295 eV, respectively. The results showed that the reaction free energy of CO₂ adsorbed on Cu-N₂ site decreased, suggesting enhanced activation of CO_2 at this site. The free energy from $*CO_2$ to *COOH and to *CO on Cu-N2 was 0.960 and 0.662 eV, respectively, suggesting that the strong Cu-N bond in the Cu-N₂ structure was conducive to the transfer of electrons from the Cu-N₂ site to *CO₂, hence promoting the formation of *COOH and *CO. The surface states of Cu-N₂ can be hybridized with the adsorbed states of H_2O , CO_2 , COOH and CO. DOS analysis showed a higher highest occupied molecular orbit (HOMO) at the Cu-N₂ site, indicating that electrons were easily transferred to reactants and intermediates at the Cu-N₂ site. Cu-N₂ structure can induce surface state hybridization, population redistribution, change of intermediate adsorption strength and change of potential barrier structure, thus optimizing the reaction path (Figure 19).

Kang et al. combined DFT calculations and experimental investigation to study the catalytic ability of Zn-NG catalyst with Zn-N₃ sites for CO₂RR.^[163] Because *OCHO adsorbent was produced in the process of pronation, the single-atom Zn coordinated with N and C in the Zn-NG catalyst cannot be used as the active site for CO generation, which was inconsistent with many studies. They found that the real active sites were C atoms bonded by Zn atoms, which had high activity. At the C_{NN} site, *COOH can be favorably formed. Without Zn atoms, *COOH was very stable, and the formation free energy of *COOH was -1.08 eV. When the applied voltage was greater than -1.29 V versus RHE, these sites played a certain role in CO₂RR. Zn atoms played an important role in CO₂RR.

5.2. Adjusting the Types of Ligands

In M-N-C catalysts, the nitrogen atoms bond to carbon, whose types include pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen, and oxidized nitrogen. Tour et al. demonstrated that pyridinic nitrogen and graphitic nitrogen dispersed in atomic Fe- and nitrogen-codoped graphene can improve CO selectivity in CO₂RR.^[55] Pyridinic nitrogen formed in the Fe-N₄ structure can improve CO₂ conversion, and graphitic nitrogen formed in nitrogen-doped graphene matrix can improve CO2 adsorption and increase CO₂ activation. At the Fe-N₄ site, *COOH was formed with coordinated proton-electron transfer, followed by a proton-electron transfer reduction process to produce CO*, and finally the weakly bonded CO* adduct was dissociated to produce CO. The process of forming *COOH was regarded as the rate controlling step, and the Gibbs free energy was 0.63 eV. The graphitic nitrogen formed by nitrogen doping on graphene matrix can promote the catalytic reaction. The catalytic activity of Fe-N₄ site was improved by reducing the energy barrier of the rate-controlling step to further accelerate the CO* desorption. DOS study confirmed the promotion effect of the FeN₄ by graphitic nitrogen, and the efficient formation of CO is a combination of Fe-N₄ site and nitrogen doping on the graphene surface.

For Ni-based single-atom catalysts, nickel coordinated to three pyrrolic nitrogen atoms showed good catalytic performance for conversion of CO₂ to CO. Sun et al. found that a small amount of Ni particles left in carbon nanotubes were easy to form thermally stable monatomic Ni after pyrolysis, and some of them formed NiN₃ structure (NC-CNTs (Ni)).^[164] The average valence state of Ni in NC-CNTs (Ni) was between 0 and +2, indicating that the electrons of Ni were attracted by the neighboring N atoms (Figure 20a-c). NC-CNTs (Ni) catalyst had high Faraday efficiency (over 90%) and turnover frequency (about 12 000 h⁻¹) for CO production at low overpotential, and the metal mass activity can reach 10 600 mA mg⁻¹, indicating that it was a highly efficient electrocatalytic CO₂RR catalyst. They used DFT to calculate the free energy values of *COOH formation in the first step reaction at three sites: Ni@N₃ (pyridinic) (-0.20 eV), Ni (111) (0.29 eV), and Ni@N₃ (pyrrolic) (1.09 eV). The low energy barrier for the formation of *COOH on Ni@N3 (pyridinic) and Ni (111) and the large amount of energy (1.08 and 1.19 eV, respectively) needed for CO desorption suggested that the two active sites were susceptible to *CO toxicity due to the difficulty of CO desorption. The desorption of CO at Ni@N₃ (pyrrole) site was exothermic ($\Delta G = -0.03 \text{ eV}$), implying that CO can be selectively produced at this site. At Ni@N₃ (pyrrolic) and Ni@N₃ (pyridinic) sites, the energy required for the formation of *COOH was more favorable than that for the formation of *H, indicating that CO₂RR was more likely to occur than HER. However, *H was more likely to form at Ni(111) site, indicating that this site was more suitable for hydrogen generation (Figure 20d-f).

Nitrogen at different locations has different effects on CO_2RR performance. Li et al. prepared atomic Fe-N₄ and Co-N₄ catalysts without metal nanoparticles.^[150] There are two kinds of nitrogen for metal coordination, edge nitrogen, and nitrogen in the substrate. The edge nitrogen was also connected to carbon atoms with dangling bonds (M-N₂₊₂-C₈ and





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Figure 19. a) DFT-based free energy profile. b) DFT-based free energy profile for the optimized Cu-N₂ and Cu-N₄ models during the CO₂RR under different applied voltages. c) DFT-based free energy profiles of water dissociation. d) The density of states of Cu-N₂ without and with CO₂ adsorption. DFT-based electron density of Cu-N₂ with e) H₂O, f) CO₂, g) COOH, and h) CO adsorptions. Reproduced with permission.^[162] Copyright 2019, Wiley-VCH.

M-N₄-C₁₀). The starting potential on Fe-N₂₊₂-C₈ and Co-N₂₊₂-C₈ in CO₂RR was –0.10 and –0.52 V, respectively, indicating that iron-based catalysts are more favorable for CO production. DFT calculations showed that the COOH dissociation step at the M-N₄-C₁₀ was an endothermic process requiring more than 1.0 eV of external heat, while the energy barrier to be overcome at M-N₂₊₂-C₈ was relatively small, which was beneficial to the CO₂RR. In addition, OH species was more inclined to adsorb to the edge carbon. With the breaking of C=O bond, OH was adsorbed to the carbon atom, while there was a suspended bond in the M-N₂₊₂-C₈ structure, which is beneficial to improve the thermodynamic and kinetic activity of CO₂RR.

In addition to nitrogen atoms, oxygen atoms, and some chain or ring structures also have certain effect on the electronic structure of M-N-C materials. Wu et al. developed a five-coordination iron-based catalyst that oxygen atoms occupy an out-of-plane coordination position perpendicular to the Fe-N₄ structure (Fe-N₄O) for the CO₂RR.^[165] At low overpotential (η = 470 mV), the FE_{CO} reached 96%, and the partial current density was –5.4 mA cm⁻². At –0.57 V versus RHE, the current can be maintained for more than 20 h, and the FE_{CO} was high in the range of –0.47 to –0.87 V versus RHE. The reduction of CO₂ to *COOH at Fe-N₄ active site was exothermic (0.05 eV), while the desorption of *CO to CO needed to overcome a higher energy barrier







Figure 20. a) Ni K-edge XANES. b) Ni K-edge Fourier transformed EXAFS spectra in the R space. c) N 1s XPS spectrum. d) Calculation models of Ni@N₃ (pyrrolic) and Ni@N₃ (pyridinic). e) Free energy diagram. f) Comparison of ΔG (*H) and ΔG (*COOH). Reproduced with permission.^[164] Copyright 2019, Wiley-VCH.

(1.74 eV), showing that *CO was not easy to release. However, the adsorption strength of CO at Fe-N₄O site was weak, which was conducive to the desorption of *CO to CO. The adsorption formation energy of H* at the Fe-N₄O site was 1.29 eV, which was much higher than that of Fe-N₄ (-2.99 eV). Therefore, Fe-N₄O site had an inhibitory effect for HER and absolute advantage in competition with HER even at higher potentials. Choi et al. studied the catalytic effect of three nickel-based catalysts on CO₂RR, namely Ni-N₄, tetraphenylporphyrin (N₄-TPP) and 21-oxatetraphenylporphyrin (N₃O-TPP),^[166] and found that the Ni(-Cl)-N₃O-TPP catalyst showed the highest catalytic activity. The results of spectroscopy and theoretical calculations showed that CO₂ can be activated by breaking the symmetry of ligand field. In CO₂RR, when the applied voltage was -0.6 V versus RHE, the Ni(II) in Ni-N₄-TPP was not favorable to the *COOH formation step, while the Ni(I) in Ni(-Cl)-N₃O-TPP can stabilize *COOH well, thus reducing the overpotential.

High local proton concentration of iron tetraphenylporphyrin (FeTPP) modified with substituted groups can increase activity and durability of CO formation for CO_2RR . Sun et al.

synthesized three Fe-based catalysts, Fe-pE, Fe-mF, and Fe-oE, by controlling the introduction of ester groups in the position of the para-position, meta-position and ortho-position, and found that their FE_{CO} in the CO_2RR was 84%, 65%, and 98%, respectively.^[167] DFT calculations showed that a low barrier for breaking C = O bond to form CO was required in an electron-rich system. Compared with the para-substituted and meta-substituted porphyrins, the ortho-substituted porphyrin was more electron-rich, and the Fe-oE structure showed higher catalytic activity in the CO2RR. Robert et al. modified carbon nanotubes by connecting iron porphyrins with covalent bonds.^[168] The catalyst exhibited high selectivity ($FE_{CO} = 95\%$) and high turnover (TOF = 178 h^{-1}) for CO formation at a low potential. Nocera et al. designed iron porphyrin modified by proton donor groups of sulfonic acid, which can effectively catalyze CO2RR and produce CO with Faradaic efficiency of more than 93%.^[169] Theoretical calculations illustrated that the introduction of the suspension group enhanced the activation of CO₂ at the central metal site. Chang et al. made use of synergistic effect to synthesize NADH functional mimics of biological

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redox cofactor,^[170] which can accelerate electron and proton transfer to enhance the activity of Fe-porphyrin catalyst. In addition, the catalytic reduction rate can be significantly increased by 13.4× in the electron-proton medium without breaking the high selectivity and proton reduction of CO₂ at Fe-TPP sites.

McCrory et al. anchored cobalt phthalocyanine onto a poly4vinylpyridine film (CoPc-P4VP film), which enhanced the catalytic activity and selectivity of CO2RR.[171] At -0.75 V versus RHE, the FE_{CO} was about 90%, and the turnover frequency was 4.8 s⁻¹. The good performance was attributed to the ability of single pyridine residue to coordinate with CoPc and the high concentration of uncoordinated pyridine residues in P4VP to boost the catalytic activity of CoPc. Marinescu et al. designed cobalt complexes with different side groups of secondary and tertiary amines to study the effect of ligands on CO₂RR.^[172] DFT calculations showed that side-chain secondary amines did not transfer protons directly to CO2, but combined to form acid molecules in the solution. These results indicated that uncoordinated side-chain amines enable the formation of hydrogen bond networks, which in turn facilitate the direct transfer of protons from acid to activated CO2. Han et al. obtained a cobalt-based catalyst with high activity for CO₂RR by covalently grafting cobalt porphyrin onto carbon nanotubes surface by substitution reaction.^[173] This strategy can improve the dispersion of the catalyst with high loading. The Faraday efficiency reached 98.3% at an overpotential of 490 mV, the total current density was 25.1 mA cm⁻², and the catalyst had good stability. The configuration can strengthen the interaction between the catalyst and the substrate and promote the transfer of electrons to the intermediate. Song et al. reported that two kinds of cobalt (III) porphyrins (CoPs) with opposite charges were self-assembled in aqueous solution and then pyrolyzed them at 350 °C.^[174] The CoPs lost part of their outermost groups and were tightly adsorbed on the carbon. At an overpotential of 430 mV, the FE_{CO} was 88% and the current density was 8 mA cm⁻². Low temperature pyrolysis can improve the interaction between CoPs and carbon carrier, which is beneficial to electron transfer and CoPs stabilization on the carbon.

McCrory et al. studied the change in the activity and selectivity of cobalt phthalocyanine encapsulated in the coordination polymer, and found that the pyridine group in poly 4-vinylpyridine changed the rate-limiting step of CO₂RR through the axial coordination with cobalt phthalocyanine complex, while the proton transfer of competitive hydrogen evolution reaction could be inhibited in proton transfer.^[175] Lan et al. embedded metallocene into a metal-organic framework with controllable porosity and metal sites (CoCp2@MOF-545-Co) by chemical vapor deposition,^[176] which showed good electrocatalytic performance for CO₂RR. At -0.7V versus RHE, the FE_{CO} was 97%. Due to the strong interaction between metallocene and metalloporphyrin, the adsorption energy of CO2 was significantly reduced. DFT calculations illustrated that metallocene can act as an electron donor and carrier, creating a continuous electron transport passage in the MOF, and improving the conductivity of the catalyst.

In addition, for catalysts with coordination of other groups in CO_2RR , CO_2 can be reduced not only to CO, but also to formic acid. Artero et al. reported a cobalt catalyst ([CpCo($P^R_2 N^{R'}_2$)I]I) that reduced CO₂ to formic acid at a fast rate and a low overpotential.^[177] In addition, it had high selectivity and almost no hydrogen and carbon monoxide produced in the CO₂RR. Leitner et al.

designed a kind of cobalt-based catalyst, which can selectively catalyze CO_2 into formic acid, formaldehyde and methanol with high selectivity under certain conditions. The formate Faraday efficiency can reach 96%, formaldehyde Faraday efficiency can reach 71%, and methanol Faraday efficiency can reach 99%.^[178]

5.3. Adjusting the Carbon Basal Plane

M-N-C catalysts are covalently connected to carbon bases. Therefore, the base carbon interacts with the d orbital of the active center atom. By regulating the electronic structure of base carbon materials, the electronic structure of the active center can be indirectly regulated.^[179] The electronic structure of the active center can be controlled by introducing heteroatoms on the carbon base plane. Sulfur- and fluorine-doped catalysts are studied in M-N-C catalysts. The influence of sulfur doping on the electronic structure of the central active site is mainly regulated by manufacturing defects. The reason for the formation of defects is that the radius of S is much larger than the radius of C and N. When S is doped into the structure, the spatial resistance of the integrity of the hexagonal carbon honeycomb frame is destroyed, so that defects are more likely to generate.^[180] Fluorine doping improves the electrocatalytic activity of catalyst by adjusting the electronic structure of N element, and promotes the charge transfer between N and CO₂ by enhancing the charge density of nitrogen species. Fluorine, as the most electronegative, can act as an electron donor. When fluorine atoms are doped into the carbon skeleton. The active site was activated by increasing the charge density to promote the catalytic capacity of the catalyst for CO₂RR.^[181]

In general, sulfur and fluorine elements are introduced into the carbon base plane through high temperature pyrolysis of thioacetamide, thiourea, potassium thiocyanate, sulfur powder, and polytetrafluoroethylene, etc. Compared with undoped catalysts, the catalytic performance of doped ones is generally improved. Li et al. synthesized Fe-NS-C materials with the help of copolymers, and adjusted the structure of carbon base plane and the electronic characteristics of Fe-N₄ at the active site by doping S atoms (Figure 21a).^[182] The doping of heteroatom S and N increases the micropores and surface area of carbon materials, increases the active sites and improves the utilization rate. Fe-NS-C catalyst exhibited good CO2RR catalytic activity, and the FE_{CO} reached 98% (η = 490 mV), and can maintain durability for up to 30 h. Three models were constructed using DFT calculations, that is, no sulfur doping, one sulfur doping, and two sulfur doping. When sulfur atoms are doped into carbon materials, vacancies are formed in the structure due to the radius mismatch. In CO₂RR, the formation of COOH* by proton coupled electron transfer is the speed control step. The introduction of sulfur atom reduces the energy barrier, which is 0.42 eV for Fe-N₄, 0.22 eV for Fe-N₄+1S and 0.19 eV for Fe-N₄+2S. By comparing the free energy barrier of the three catalysts in HER, the introduction of sulfur does not significantly affect HER. Sulfurdoped Fe-N₄ has a larger $U_{\rm L}(\rm CO_2) - U_{\rm L}(\rm H_2)$ ($U_{\rm L} = -G_0/e$), indicating that sulfur-doped Fe-N4 can enhance the selectivity of $Fe-N_4$ at the active site and exhibit a higher FE_{CO} . When $Fe-N_4$ is bonded to COOH, electrons in the iron center transfer to COOH*, and charge accumulation occurs on COOH*. The introduction of S will increase the Fermi energy of Fe 3d, and the







Figure 21. a) Illustration of the fabrication process for Fe-NS-C. b) Atomic structure of proposed Fe-N₄ and S-modified Fe-N₄ moieties. c) Free energy diagrams. d) Difference in limiting potentials between CO₂ reduction and H₂ evolution. e) Density of states for Fe 3d. f) Calculated adsorption energy of COOH* and Fe Bader charge. g) Different model structures. h) Calculated Gibbs free energy diagrams for CO₂-to-CO conversion. i) The difference between the calculated limiting potentials for CO₂ reduction and H₂ evolution, j) In situ ATR-IR spectra and k) the proposed reaction pathways of CO₂RR over Ni-SAs@FNC. a–f) Reproduced with permission.^[182] Copyright 2019, Wiley-VCH. g–k) Reproduced with permission.^[183]

strong driving force accelerates the electron transfer speed, thus increasing the adsorption of COOH* on the active site modified by S (Figure 21b–f). Zhao et al. synthesized a nickel monatomic catalyst doped with double heteroatoms by microwave induced plasma.^[183] S atom doping regulated the charge density of the unsaturated active site NiN₂, and there was structural evolution and S vacancy formation at high potential. The FE_{CO} was up to 97% at the coordination unsaturated NiN₂ site. Theoretical calculations showed that S doping and S vacancy caused by doping are beneficial to reduce the energy barrier in CO₂RR.

Introducing F atoms into the carbon base plane can increase the charge density of the surrounding carbon, which provide additional active sites for CO₂RR.^[184] Zhu et al. synthesized a nickel-rich nitrogen and fluorine co-doped single-atom catalyst (Ni-SAs@FNC) with a thickness of only about 1.25 nm using polymer-assisted pyrolysis.^[185] The introduction of F adjusted the electronic structure of Ni-N₄. Over a wide potential range, the FE_{CO} over Ni-SAs@FNC catalyst was about 95%. According to DFT calculations, the transformation of CO₂ into *COOH intermediate was the rate-determining step, and F doping reduced



the energy barrier of the rate-controlling step, which is due to the asymmetry of charge distribution caused by F doping. According to the PDOS diagram, F doping can make the d band of the central metal close to the Fermi level, increase the electron transfer speed and enhance the binding ability with the reaction intermediates. In addition, the charge density around Ni was increased by the difference of charge density, which is more conducive to charge transfer. In situ attenuated total reflectioninfrared spectroscopy (ATR-IR) under different applied voltages also indicated that the formation of intermediate *COOH was a speed control step (Figure 21g–j). Figure 21k shows the possible highly selective pathway of CO formation by CO₂RR. In conclusion, F doping regulates the electron configuration of the central active site, reduces the energy barrier for the formation of intermediate *COOH, and makes the reaction more likely to occur.

In addition to the regulation of the carbon base plane by heteroatom doping, functionalization of substituents around the central metal can also improve the catalytic activity.^[186,187] The introduction of substituents affects the environment of the metal center, and the electronic structure of the active center can be adjusted by induction.^[188] If the substituent is an electron donor, it can contribute electrons to the π -conjugated system of phthalocyanine, and the catalytic performance of the active site is improved due to the increase of electron density at the central site.^[189,190] Wang et al. reported the introduction of eight cyanide groups onto carbon nanotubes with uniform fixation of CoPc molecules. The introduction of cyanide groups promoted the formation of active cobalt sites and CO resolution, significantly improving the catalytic activity and selectivity of CoPc.^[13] Manthiram et al. proved that the introduction of electronic charge on the surface of the base of functional groups can improve the catalytic activity of immobilized cobalt porphyrin.^[191] When amino group and hydroxyl group act as substituents, they act as electron donors in the formation of p- π conjugation due to the existence of lone pair electrons in the 2p orbital of N or O. The N of amino group is less electronegative than that of O, and it has a stronger ability to donate electrons. Officer et al. used π - π stacking to fix cobalt (II) octanoxy phthalocyanines with high solubility and steric hindrance onto graphene. Alkoxy substitution reduced the aggregation of phthalocyanines and improved the utilization efficiency of active sites.^[47] Combining theoretical and experimental results, Liu et al. confirmed that NiPc with electron-donating groups can induce electron localization at metal active sites and significantly enhance CO2 adsorption and activation. When the current density was -400 mA cm⁻², the Faraday efficiency of NiPc with amino substituent group can reach 99.8%. Zhu et al. immobilized pyrrolidone nickel phthalocyanine (PyNiPc) on carbon nanotubes.^[192] PyNiPc presented a single molecule level dispersion, showing high activity and high selectivity. Subsequently, they used strong interactions to fix azides to nickel-phthalocyanine carbon nanotubes by chemical adsorption, which improved the catalytic performance of nickel phthalocyanine with near 100% FE_{CO}.^[193]

5.4. Constructing Bimetallic Single-Atom Sites

By introducing the same metal or different metal sites adjacent isolated metal sites, bimetallic single-atom sites can be constructed. The synergistic action of diatomic active sites can reduce the reaction barrier of CO_2 activation and enhance the adsorption of intermediates.^[194,195] Chen et al. found that Cu dimers can be stably embedded in porous C₂N layers due to strong hybridization between N 2p and Cu 3d orbits.^[196] Wu et al. studied the electrocatalytic performance of CO2RR on Cr-Cu metal dimers and nitrogen co-doped graphene using DFT calculations (M2N6-Gra).^[197] Figure 22a-d showed the favorable pathway of CO₂RR at the dimerized transition metal sites of Cr, Mn, and Fe. After CO₂ was adsorbed on the surface of the catalyst, *COOH and *HCOO were formed after protolysis in the first step. *HCOO was favorable at the site of Cr, Mn, Fe, and Cu dimers, and the stable structure was the combination of two oxygen atoms with the metal atoms on the surface of the catalyst. In Co₂N₆-Gra and Ni₂N₆-Gra, *COOH was formed in a favorable way because the free energy of *HCOO was higher than that of *COOH (Figure 22e-j). According to the calculated free energy, Cr₂N₆-Gra and Mn₂N₆-Gra had poor catalytic performance, while Fe₂N₆-Gra showed good selectivity and catalytic activity for CO₂RR, and there was a relatively high energy barrier for HER. For other transition metals, although the selectivity was good, the large overpotential made them exhibit poor catalytic activity in CO₂RR.

Due to unique orbital and geometric configuration of bimetallic active sites, the energy barrier in catalytic CO₂RR can be lowered. Zhang et al. prepared a series of electrocatalysts with double transition metal active sites using a covalent organic framework model for electrocatalytic reduction of CO₂ to CO.^[198] They studied Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn as active sites in M1/M2-N6 bimetallic-atom electrocatalysts (BACs) for CO₂RR and found that Fe/Zn-BAC had the lowest overpotential ($\eta = 0.05$ V) among them. The overpotential of CO formation was lower than that of HCOOH formation, indicating that the CO formation was more conducive. At Fe/Zn-BAC site, HER competed with CO₂RR, and CO₂RR was more favorable. With the increase of 3d transition metal atomic number, the overpotential increased gradually. In the volcanic peak plot, Fe/ Zn-BAC was located at the peak of the volcano, showing the best catalytic activity for CO₂RR (Figure 23a-h).

For modulating electronic structure of M-N-C materials, the central metal atom and the ligands play a very important role. Fe, Co, Ni, Cu, Zn, Sn, and Sb coordinated with nitrogen atoms can efficiently electrocatalyze CO_2RR . Among them, the central metal atom coordinated with four nitrogen atoms usually shows high catalytic performance, but M-N₄ is not always suitable for catalyze CO_2RR and some M-N₂, M-N₃, and M-N₅ configurations also show excellent catalytic performance for CO_2RR . In addition, the introduction of a new group on the four-coordinated central metal atom can improve the catalytic activity of CO_2RR to a certain extent due to the existence of electronic effects. **Table 2** shows the performance comparison of M-N-C catalysts for the CO_2RR .

6. Challenges and Perspective of M-N-C Materials for CO₂RR

6.1. Strategies for Optimizing M-N-C Materials for CO₂RR

6.1.1. Precise Control of Coordination Environment

The coordination environment mainly includes coordination number and coordination space, which plays an important role in regulating the electronic structure and geometric



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Figure 22. a) The most stable structures for the favorable pathway. (a), (b), and (c) are the formation of HCOOH via COOH on Cr_2N_6 , Mn_2N_6 , and Fe_2N_6 , respectively. d) The formation of HCOOH via HCOO on Fe_2N_6 . The numbers on top of each column are the transferred numbers. The free energy (eV) change of CO_2RR for C1 pathway on e) Cr_2N_6 -Gra, f) Mn_2N_6 -Gra, g) Fe_2N_6 -Gra, h) CO_2N_6 -Gra, j) Ni_2N_6 -Gra, j) Cu_2N_6 -Gra. Reproduced with permission.^[197] Copyright 2020, Elsevier Ltd.

configuration of active metal sites. The catalytic performance of $\rm CO_2RR$ can be improved by adjusting the valence state distribution of metal atom through changing the coordination environ-

ment. Generally, low N-coordination environment of metal atoms is favorable to catalyze CO_2RR, such as M-N_2, M-N_3, M-N_4, and M-N_5. In addition, the electronic configuration of active sites

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Figure 23. a–c) Free energy diagrams of CO₂RR and HER on Fe/M₂-BAC-COFs, respectively. b–d) The overpotentials of HCOOH (η^{HCOOH}) and H₂ (η^{H2}) as a function of the overpotential of CO (η^{CO}) on BAC-COFs, respectively. e) Color-coded diagram of the overpotential (η^{CO}) for BAC-COFs. f) The overpotential of CO₂RR to form CO (η^{CO}) as a function of the bonding energy of ΔG_{*COOH} - ΔG_{*CO} . g) The overpotential of CO₂RR to form CO (η^{CO}) as a function of the descriptor (Φ). h) The overpotential of HER to produce H₂ (η^{H2}) as a function of the descriptor (Φ). Reproduced with permission.^[198] Copyright 2020, Elsevier Inc.

can be modulated by introducing oxygen atoms along the axis of metal atoms, or introducing halogen atoms and chain groups. For example, Fe-N₄O and Ni(-Cl)-N₃O-TPP can efficiently catalyze the reduction of CO₂ to CO, and cobalt-based catalysts with side chains can reduce CO₂ to formic acid. Jiang et al. found that the selectivity

to CO on Ni SA-N₂-C catalyst with the lowest coordination number was much higher than Ni SA-N₃ and Ni SA-N₄, and the Faraday efficiency could reach 98% by optimizing the coordination number of Ni and N.^[68] Wang et al. reported that the FE_{CO} of catalysts with active sites of FeN₅ reached 97% at a low overpotential of 0.35 V.^[12]

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 Table 2. Comparison of CO₂RR performance of M-N-C catalysts.

Catalyst	Active site	Electrolyte	Product	FE (%)	TOF (h ⁻¹)	Ref.
Fe/NG	Fe-N ₄	0.1 м КНСО ₃	СО	80%	_	[55]
Fe–N–C	Fe-N ₄	0.1 м КНСО ₃	со	91%	-	[48]
Fe/N–C	Fe–N	0.05 м КНСО ₃	C–C coupling	97.4%	-	[98]
FeSAs/CNF-900	Fe-N ₄	0.5 м КНСО ₃	СО	86.9%	639 h ⁻¹	[94]
C-Fe30-N30/30	Fe–N	0.5 м КНСО ₃	СО	~ 90%	-	[95]
Fe-N-C	Fe-N ₄	0.5 м КНСО ₃	СО	94%	0.13 s ⁻¹	[96]
Fe–N ₄ /CF	Fe-N ₄	0.5 м КНСО ₃	со	94.9%	-	[97]
Fe-N-C	Fe-N ₂₊₂ -C ₈	0.5 м КНСО ₃	СО	93%	-	[150]
FePEGP	Fe-N ₄	MeCN	СО	98%	$1.4 \times 10~5~{ m s}^{-1}$	[89]
FeN ₅ Catalyst	Fe-N ₅	0.1 м КНСО ₃	со	97%	-	[12]
Co–HNC	Co-C ₂ N ₂	0.1 м КНСО ₃	CO/H ₂	100%	-	[154]
Co-N ₂ sample	Co-N ₂	0.5 м NaOH	со	94%	33 000 h ⁻¹	[153]
1 ^{MeCN}	Co-N ₃	MeCN	НСООМ	80%	-	[155]
CoPc–1.	Co-N ₄	0.5 м КНСО ₃	СО	94%	0.29 s ⁻¹	[144]
CoCoPCP/CNTs	Co-N ₄	0.5 м КНСО ₃	со	94%	2.4 s ⁻¹	[112]
CoTPP-CNT	Co-N ₄	0.5 м КНСО ₃	СО	>90%	2.75 s ⁻¹	וווח
CoPc–CN	Co-N ₄	0.1 м NaHCO ₃	СО	96%	4.1 s ⁻¹	[99]
CoFPc	Co-N ₄	0.5 м NaHCO ₃	СО	93%	2.1 s ⁻¹	[103]
CoPPc/CNT	Co–N₄	0.5 м NaHCO ₃	СО	90%	4900 hr ⁻¹	[104]
, CoPc–MWCNT	Co−N₄	0.5 м КНСО ₃	CH₃OH	19.5%	_	[106]
CCG/CoPc–A	Co−N₄	0.1 м КНСО ₃	co	~ 90%	~5 s ⁻¹	[47]
CoPc2	Co−N₄	0.5 м NaHCO₃	СО	95%	2.7 s ⁻¹	[105]
Co–N₅/HNPCSs	Co–Ns	0.2 м NaHCO₃	со	99%	480.2 h ⁻¹	[157]
SA-Ni/N-CS	Ni–N₄	0.5 м КНСО ₂	CO	95.1%	_	[122]
Ni–N ₄ –C	Ni–N₄	KHCO ₂	CO	90%	_	[116]
Ni–NG	Ni–N	0.5 м КНСО₂	со	95%	$2.1 \times 10.5 \text{ s}^{-1}$	[56]
A-Ni-NG	Ni–N₄	0.5 м КНСО₂	со	97%	14 800 h ⁻¹	[11]
NC-CNTs (Ni)	Ni−N₂	0.1 м КНСО₂	со	90%	12 000 h ⁻¹	[]64]
Ni SAs/N–C	Ni–N₂	0.5 м КНСО₂	со	71.9%	5273 h ⁻¹	[119]
CuPc/C	Cu−N₄	0.5 м KCl	C ₂ H ₄	25%	-	[132]
CuPc	Cu-N ₄	0.5 м КНСО ₂	CH4	66%	_	[133]
CuZnDTA	Cu-N ₂	0.5 м КНСО₂	CH₂OH	54.8%	_	[134]
CuZnDTA	Cu-N ₂	0.2 м КНСО ₂	C ₂ H ₅ OH	31.4%	_	[134]
CuSAs/TCNFs	Cu-N ₄	0.1 м КНСО ₃	CH₃OH	44%	_	[35]
ZIF-8	Zn–N	0.25 м К₂SO₄	co	81.0%	_	[140]
Zn-N-G-800	Zn–N4	0.5 м КНСО ₃	СО	91%	_	[141]
PorZn	Zn–N4	0.1 м ТВАРF₅ DMF/H₂O	СО	95%	_	[138]
Sn ^{δ+} /NG	Sn-N	0.25 м КНСО ₃	нсоон	74.3%	11 930 h ⁻¹	[30]
Sn–CF	Sn-N	0.1 м КНСО₃	со	91%	_	[29]
Sb SA/NC	Sb–N₄	0.5 м КНСО ₃	НСООМ	94%	_	[31]
CoPc	Co−N₄	0.5 м КНСО ₃	СО	99%	_	[199]
Cu-N-C-900	Cu–N	0.1 м КНСО ₃	CH₄	38.6%	_	[7]
[Fe ^{II} (qpy)(H ₂ O) ₂] ²⁺	Fe–N₄	ACN	CO	>95%	$3.3 imes 10 \ 4 \ s^{-1}$	[200]
Fe–N–C	Fe–N	0.1 м КНСО₃	CO	65%	_	[53]
Ni–N–C	Ni–N	0.1 м КНСО ₃	CO	85%	_	[53]
Ni/Fe–N–C	Fe/Ni–N₄	0.5 м КНСО3	CO	98%	7682 h ⁻¹	[195]
FeMn–N–C	Fe/Mn–N ₄	0.1 м КНСО ₃	CO	80%	-	[201]



6.1.2. Enhancing the Activity

The activity of M-N-C catalysts can be improved by three methods. One is to increase the inherent activity of the active site by adjusting electronic structure of the active site. The d orbital of the metal central atom can be effectively changed by selecting metal central atoms with suitable adsorption capacity and adjusting the coordination environment around the metal central atom.^[202] In addition, the construction of diatomic metal active sites can also improve the inherent activity of M-N-C materials. The synergy of metals can enhance the charge transfer ability, and can also adjust the position of the d band to lower reaction energy barrier.[195] Increasing singleatom site density is an efficient strategy to improve the activity. However, the increase in metal loading will reduce the distance between each single-atom site and cause the agglomeration of metal atoms. To prevent metal agglomeration, using high content of nitrogen in the synthesis can stabilize the metal atoms and reduce their agglomeration by forming M-N_x coordination. Finally, introducing single atoms on the supporting surface with unsaturated coordination or with defects can improve the activity of M-N-C catalysts.

6.1.3. Optimizing the Selectivity of CO₂RR

Over most M-N-C materials, CO2 is generally reduced to CO, while some Co-, Cu-, Zn-, Sn-, and Sb-based catalysts can reduce CO₂ to formic acid, methanol, or C2 products. For example, cobalt-based catalysts can reduce CO₂ to CO or CH₃OH, Sn, and Sb in the P region can reduce CO₂ to CO or HCOOH, and copper-based catalysts can reduce CO₂ to C2 products. The selectivity of the product in CO2RR can be determined by selecting appropriate central metal atom. The electron transfer and reaction path can be changed by tuning electronic structure of M-N-C materials. The difference of electronic structure has great influence on the CO₂RR energy barrier, thus affecting the selectivity. Suitable ligands of the central metal atoms can improve the selectivity of CO₂RR and the reaction path can be optimized by modulating coordination environment. For example, both Ni-N₄O and Fe-N₄O active sites have high selectivity for CO in CO₂RR. The selectivity to CO at -0.9 V on Ni-N₄O active site can reach 100%,^[202] and the selectivity to CO on porous carbon with Fe-N₄O sites can reach 96%.^[165] In addition, the CO selectivity on Ni(-Cl)-N₃O-TPP was 80%, while that on Ni-N₄-TPP was only 2% at -0.65 V. Theoretical calculations suggested that the destruction of the symmetry of the ligand field may be beneficial to the activity of the central metal nickel atom.^[137]

6.1.4. Improving the Stability

For evaluating catalyst stability, the retention of Faraday efficiency and current density at a constant potential over a period of time is an important index, while the activity is currently weakened due to the inactivation of catalytic sites or irreversible structural collapse. In laboratory stability tests, only a few dozen hours are generally adopted, and there is still a long way to go for commercial application. Low loading of single-atom metal can effectively reduce the agglomeration, and N-coordination can stabilize metal central atoms. Moreover, N-doping can introduce defect states around the Fermi level of graphene, and stable M-N-C materials can be appropriately obtained by adjusting the N-doping content. Stable coordination can prevent metal atoms from falling off, and relatively stable coordination environment can be formed by introducing large groups in the axial direction of the central metal atoms. In addition to the unstable nature of catalysts, the exfoliation of the catalyst from the electrode during the test also affects the stability. The catalyst can be in situ synthesized on graphite or metal electrode to effectively avoid the exfoliation. Wu et al. synthesized a singleatom catalyst with the active site of Co-N₂ by pyrolysis method. At -0.63 V, the FE_{CO} was almost unchanged after 60 h of reaction.^[153] Liu et al. reported that the activity of atom-dispersed nickel-anchored nitro-fossilized graphene catalyst remained 98% after 100 h of continuous reaction at high current density in catalytic CO₂RR.^[11]

6.2. Summary and Outlook

M-N-C materials with atomically dispersed metal sites are expected to replace precious metal catalysts for electrochemical CO_2RR due to their high-efficiency catalytic ability and low cost. Using electronic structure adjustment strategies, such as selecting a suitable central metal atom, changing the coordination environment of the central metal atom, and constructing bimetallic active sites, the adsorption behavior of reaction intermediates can be effectively adjusted and the energy barrier can be lowered. The selectivity can be controlled by tuning the energy barrier of the rate controlling step to achieve the target product.

Compared with metal oxides, single-atom catalysts show excellent catalytic performance in the field of electrochemistry. This review summarizes various single-atom catalysts used in the electrocatalytic CO₂RR. Although unprecedented progress has been made, the research on M-N-C materials still has certain problems and a lot of room for development. Due to the large surface free energy of M-N-C materials, the aggregation of single atomic sites may occur in the synthesis and electrochemical reaction, resulting in metal nanoparticles or clusters, which affect the catalyst activity. In order to avoid single atom aggregation, low metal loading is generally used, which limits the practical application of M-N-C materials. The development of metal single-atom catalysts with high loading capacity can substantially improve their catalytic activity and achieve largescale applications. Due to the proper distance between atoms and the strong interaction between metal atoms and the carrier, it is necessary to select suitable coordination complexes and carriers during the synthesis process. A complex with sufficient ligands ensures that a large number of single-atom active sites are loaded onto the carrier. In addition, the choice of carrier is also very important. Porous materials with large surface areas and defect sites are ideal carriers, which allow sufficient metal atoms to be loaded onto the carrier. Low temperature pyrolysis is usually used to avoid the aggregation of high loaded metals. At the same time, the existing synthesis strategies can be improved to maximize the aggregation of single atoms to synthesize M-N-C materials with high metal loading. In

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addition, it is difficult to control the type and location of single metal sites in synthesis, which inevitably leads to the formation of side reactions. It is still unclear whether the increase of catalytic performance comes from the regulation of metal active sites. Therefore, it is necessary to develop advanced controllable strategies for the synthesis of M-N-C materials.

In M-N-C materials, the characteristics of single atoms dispersed in the structure can be identified using existing characterization techniques (e.g., HAADF-STEM, AC-TEM, and XAS). However, the results obtained by these characterization methods are only local information and average statistics, and it cannot be concluded that the entire catalyst is atomically dispersed, and the current synthesis methods can hardly achieve 100% single atom dispersion. However, the local carbon structure near the central metal site cannot be accurately judged by the current existing characterization techniques, and thus the influence of the local carbon structure around the metal site on CO₂RR performance cannot be accurately evaluated. The theoretical models of DFT calculations cannot be well constructed based on the current clear system, which in turn affects the results of theoretical calculations.

In-situ XAS can offer valued dynamic information about active sites for CO₂RR. However, the cost of the equipment and operation technology of high complexity limit its wide application, and therefore, it is needed to develop easily acquired techniques for in situ characterization of single-atom sites for better understanding the reaction mechanism. Although there is difficult, people are constantly committed to the research of catalysis of single-atom catalysts for the CO₂RR, and we believe that the laboratory research results will be applied to industrial production in the future.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22075099).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon dioxide reduction, coordination environment, electronic structures, M-N-C materials, single-atom catalysts

> Received: November 11, 2021 Revised: January 10, 2022 Published online: February 9, 2022

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