

Active sites and mass/charge transport engineering in carbon-based catalysts for electrochemical CO₂ reduction reaction

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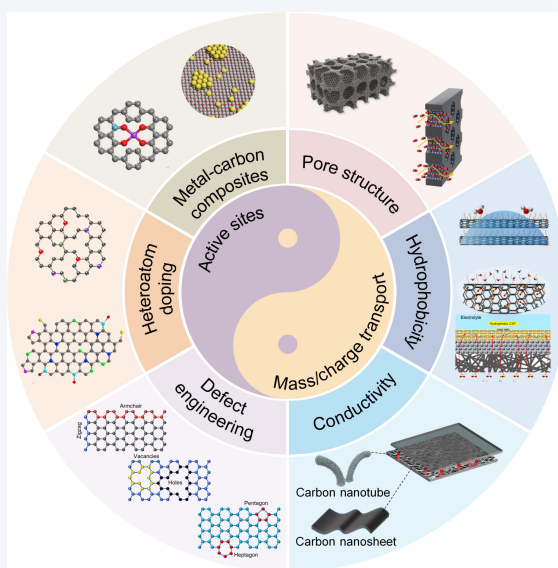
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ABSTRACT: The electrochemical CO₂ reduction reaction (CO₂RR) offers a dual benefit: closing the carbon cycle, while simultaneously storing renewable energy in chemical bonds. Carbon-based catalytic materials, as exceptional electrocatalysts, exhibit excellent conductivity, robust stability, tunable surface functionality, and unique capability to construct metal–carbon synergistic interfaces. In CO₂RR, carbon-based catalytic materials stand out double critical functions among series roles: (i) active site engineering governing intrinsic activity, and (ii) mass/charge transport dictating effective active sites utilization. Synergistic optimization of these elements constitutes the “catalytic activity–transport kinetics” binary model for performance enhancement. This review dissects active sites design via defect engineering, heteroatom doping, and metal–carbon composites, coupled with mass/charge transport engineering through electronic conductivity modulation, surface hydrophobicity control, and hierarchical porosity optimization. We further critically examined the challenges and opportunities in CO₂RR, with a focus on the integrated design bottlenecks constraining high-performance catalyst development. By integrating these dual engineering paradigms, structure–performance correlations were established to guide the rational design of carbon-based CO₂RR catalysts.

KEYWORDS: carbon-based catalysts, electrochemical CO₂ reduction, active sites, mass/charge transport



1 Introduction

The relentless rise in atmospheric CO₂ levels constitutes a pressing global challenge, leading to climate warming, ocean acidification,

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and ecosystem disruption [1–3]. In response, a spectrum of CO₂ mitigation strategies has been developed, spanning from direct CO₂ capture and storage [4–6] to various conversion pathways, including thermo- [7, 8], photo- [9, 10], electro- [11, 12], and biocatalysis [13, 14]. Among these approaches, electrochemical CO₂ reduction reaction (CO₂RR) stands out due to its capability to convert CO₂ into value-added chemicals and fuels under mild conditions, while directly utilizing renewable electricity for sustainable operation [15–18]. To date, a wide range of electrode materials have been explored for electrochemical CO₂RR, including pure metals (e.g., Cu, Ag, Au, Sn, and Bi) [19–22], metal compounds (e.g., oxides and sulfides) [23–25], metal-organic

frameworks (MOFs) [26–28], alloys [29, 30], and various carbon-based materials [31–34]. However, many of these materials suffer from drawbacks such as high cost, limited selectivity, or poor long-term stability. In this context, carbon-based catalysts have garnered significant attention for their abundant availability, excellent electrical conductivity, chemical stability, tunable surface and electronic properties, and their ability to form composites with metal species [35, 36].

Structural design of carbon-based catalysts has remained central to enhancing CO₂RR performance. Thus far, significant advancements have been achieved through various structural engineering strategies, including defect engineering [37–39], heteroatom doping [40, 41], and pore structure adjusting [42, 43]. In parallel, the well-developed porous architecture, abundant defects, and diverse heteroatom functionalities of carbon-based materials offer numerous anchoring sites for metal nanoparticles (NPs), clusters, and single atoms, facilitating the construction of carbon-metal hybrid catalysts that synergistically integrate the merits of both components [44–47]. However, current research efforts remain largely focused on optimizing catalytic performance by tuning single or a limited set of structural parameters. This reductionist approach has resulted in an incomplete understanding of how multiple structural factors collectively influence performance, and the potential synergistic effects arising from their interplay remain largely unexplored. Moreover, considerable discrepancies exist across studies regarding the primary factors governing catalytic activity. Addressing these challenges requires establishing clear structure–performance correlations, identifying the key determinants of catalytic behavior across different material systems, and systematically evaluating the synergistic interactions among multiple structural variables.

Based on a comprehensive review of current literature, the factors influencing catalytic performance can be broadly classified into two principal categories (Fig. 1). On the one hand, the formation, distribution, and electronic structure of active sites, achieved via defect engineering, heteroatom doping, and metal-carbon composites, govern the adsorption and activation of CO₂, as

well as the stabilization of key reaction intermediates. These factors collectively determine the intrinsic activity and product selectivity. On the other hand, mass/charge transport, including the movement of reactants, intermediates, and products within the catalyst matrix and across the electrode–electrolyte interface, critically determines the accessibility and utilization of active sites. Insufficient mass/charge transport may result in CO₂ depletion near the catalyst surface, accumulation of products, and local pH shifts, which collectively hinder reaction kinetics and potentially alter product selectivity. Notably, different structural parameters can serve as the decisive factors for catalytic performance in specific environments.

The performance of carbon-based catalysts in electrochemical CO₂RR is governed by a complex interplay of structural features. Specifically, the distribution of active sites governs local concentration gradients and thus mass transfer efficiency; the electronic structure dictates the interfacial electric field, directly modulating charge transport kinetics; while the microporous architecture concurrently influences both the accessibility of active sites and the pathways for mass transfer. Consequently, maximizing catalytic efficacy demands a holistic approach that integrates active sites engineering with the strategic management of mass/charge transport. Most reviews traditionally focused on active sites design in isolation, often overlooking mass/charge transport optimization and the intricate interplay between these two aspects. Therefore, a fundamental understanding of the structure–performance relationship, encompassing both the nature of active sites and the dynamics of mass/charge transport, is paramount for the rational design of high-performance carbon-based catalysts.

In this review, we provide a comprehensive overview of structural design strategies for carbon-based catalysts in electrochemical CO₂RR, with a focus on active sites and mass/charge transport. We begin by analyzing the catalytic mechanisms to identify the structural parameters that influence catalytic performance. Next, drawing upon both experimental and computational studies, we review recent progress in the engineering of active sites and mass/charge transport in electrochemical systems, and address the key challenges and unresolved issues in these areas. Finally, we highlight the interconnectedness of these two aspects and propose future directions for the integrated design of high-performance carbon-based electrocatalysts. Through this dual-focused perspective, we aim to inspire novel design principles that transcend traditional boundaries and accelerate progress toward practical CO₂ conversion technologies.

2 Mechanism of electrochemical CO₂RR

Electrochemical CO₂RR occurs at the cathode–electrolyte interface within the cathodic half-cell, where CO₂ is reduced via proton-coupled electron transfer (PCET) to generate hydrocarbons or other valuable products following the general reaction: $x\text{CO}_2 + n\text{H}^+ + ne^- \rightarrow \text{product} + y\text{H}_2\text{O}$ [48, 49]. Characteristically, the overall CO₂ reduction process generally involves three key steps [48, 50, 51]: (1) diffusion of CO₂ molecules from the bulk electrolyte to the electrode surface and their subsequent capture by active sites (chemisorption process); (2) coupling of CO₂ with electrons and protons, and further reaction of intermediates with electrons and protons, resulting in the cleavage of C–O bonds and the formation of reduction products (activation and products formation process); and (3) desorption of the target products from the active sites, followed by their diffusion away from the electrode surface

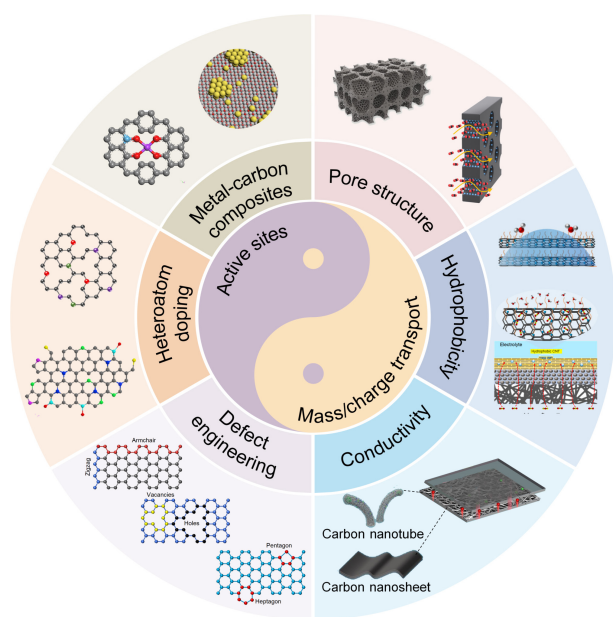
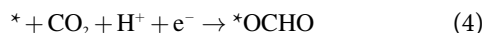
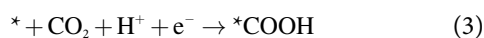
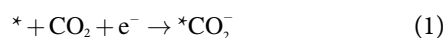


Figure 1 The rational design of carbon-based catalysts for electrochemical CO₂RR from the perspectives of active sites and mass/charge transport.

(products separation process). In recent years, extensive research has been conducted on PCET processes in electrochemical CO₂RR. Although the precise reaction pathways remain under debate, a substantial body of theoretical and experimental research has been devoted to proposing and elucidating potential mechanism for electrochemical CO₂RR.

Based on the current literatures, we summarized the major reaction pathways for electrochemical CO₂RR and illustrated them in Fig. 2. This schematic encompasses key mechanistic steps, including CO₂ activation, PCET, desorption, C–C coupling, and CO insertion. In the activation step, the linear CO₂ molecule adopts a bent configuration with electron redistribution, which facilitates the weakening of the C=O bond and primes the molecule for subsequent reduction (Eqs. (1)–(4)) [52]



Upon activation, CO₂ can form three principal intermediates and one nucleophilic agent [53–55]: When the C of CO₂ binds, $* \text{CO}_2^-$ (Eq. (1)) and $* \text{COOH}$ (Eq. (3)) are formed, with $* \text{CO}_2^-$ further protonated to yield $* \text{COOH}$; when the O of CO₂ binds to the catalyst, the $* \text{OCHO}$ species is generated (Eq. (4)); and when the redox transformation occurs, driven by potential-dependent changes in the oxidation states of active metal species, $* \text{H}^-$ is produced (Eq. (2)). $* \text{H}^-$ can not only participate in the hydrogen evolution reaction (HER) side reaction but also act as a nucleophile, attacking the C of CO₂ to generate $* \text{COOH}$ or $* \text{OCHO}$ intermediates. The $* \text{OCHO}$ intermediate, through additional PCET, leads to HCOOH, marking one of the primary pathways for

HCOOH formation [56, 57]. Catalysts exhibiting relatively strong affinity for $* \text{OCHO}$ tend to favor this reaction route. Alternatively, the $* \text{COOH}$ intermediate can be further reduced and dissociated to produce $* \text{CO}$ and H₂O [1]. The generation of the $* \text{CO}$ intermediate is particularly significant, as it serves as a pivotal branching point for the formation of various products [58, 59]. Notably, the adsorption energy of $* \text{CO}$ on the catalyst surface is a decisive factor influencing product selectivity. According to the Sabatier principle, optimal catalytic performance requires a balanced binding energy between the active sites and key intermediates: If the interaction is too weak, intermediates desorb prematurely, minimizing conversion; if too strong, product desorption is hindered, leading to sites blockage and possible catalyst poisoning. For instance, weak $* \text{CO}$ binding favors its direct desorption as CO, whereas excessively strong binding results in accumulation of $* \text{CO}$ intermediates, which can suppress further reduction and promote competing reactions such as HER. Therefore, tuning the adsorption strength of $* \text{CO}$ is critical for steering the reaction toward C₁ via multi PCET process and C₂₊ products via both PCET and C–C coupling [60, 61].

In addition to the creation of active sites, mass/charge transport processes play a decisive role in determining the overall catalytic performance. The accessibility of active sites is governed not only by their intrinsic activity, but also by the efficient diffusion of CO₂, protons, reaction intermediates, and products within the catalyst structure and across the electrode–electrolyte interface [62]. Insufficient mass/charge transport can result in local depletion or accumulation of key species, leading to concentration gradients, pH changes, and diminished catalytic efficiency. Therefore, rational catalyst design must integrate both active sites engineering and mass/charge transport optimization to achieve superior CO₂ reduction performance.

3 Active sites engineering

Carbon materials, such as graphene, carbon nanotubes (CNTs), and advanced porous carbon, generally possess excellent electrical

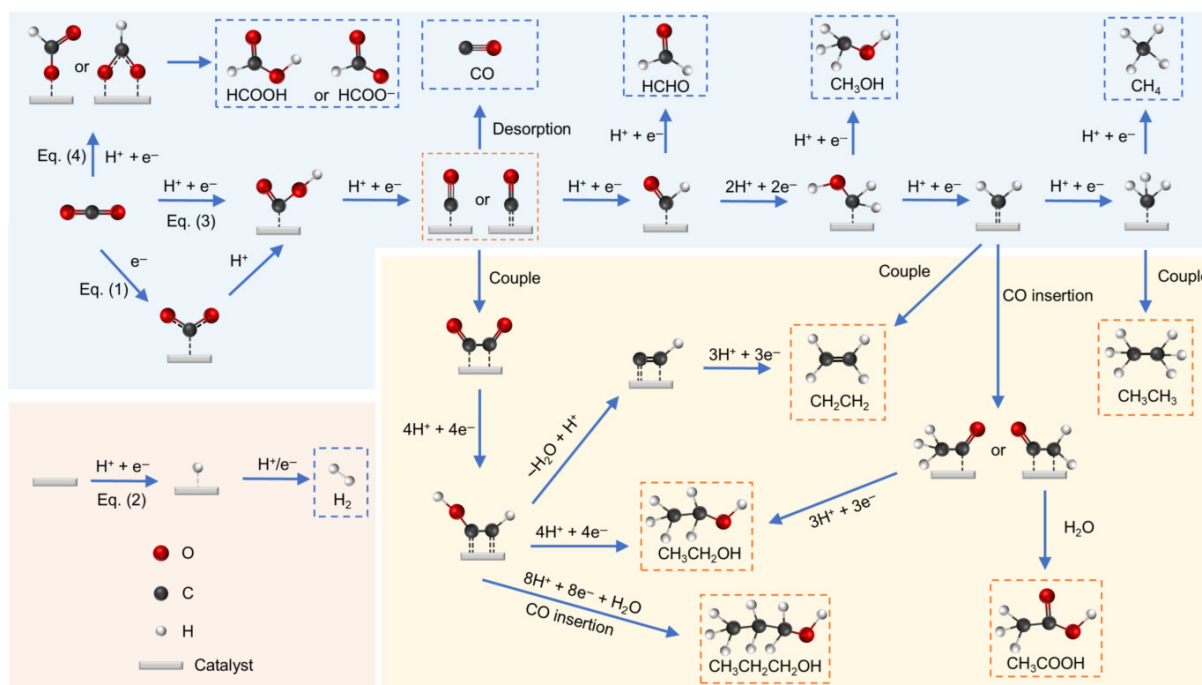


Figure 2 The general pathways of electrochemical CO₂RR to main C₁ and C₂₊ products.

conductivity, chemical stability, and well-developed pore structures, making them attractive candidates for electrocatalytic applications [38, 63]. However, in their unmodified state, pristine carbon materials typically exhibit limited intrinsic activity for electrochemical CO₂RR due to the absence of abundant active sites and weak interaction with CO₂ molecules [61, 64]. The inert nature of sp²-carbon framework results in high overpotentials, low current densities, and poor product selectivity. To surmount these limitations, advanced modification strategies have been extensively explored.

Defect engineering, encompassing the deliberate introduction of vacancies, edge sites, and topological defects, effectively tailors the electronic structure and generates highly reactive centers [65, 66]. Concurrently, heteroatom doping through incorporation of elements such as N, B, and S modulates the local coordination environment and redistributes charge density, thereby facilitating enhanced CO₂ adsorption and activation [40, 41]. Beyond these modifications, carbon materials inherently offer superior electron mobility, diverse porous architectures, strong resistance to chemical degradation, and adaptable surface functionalities. These properties facilitate effective charge transport, ample exposure of catalytic sites, and sustained structural stability during reactions. Such characteristics establish carbon materials as an excellent support for immobilizing catalytically active species. The integration of metal nanoparticles, clusters, or atomically dispersed single metal atoms onto carbon substrates yields metal-carbon composites that capitalize on synergistic interactions between metallic active sites and the conductive carbon matrix [67–69]. This strategic combination not only amplifies catalytic activity and selectivity but also significantly improves durability, positioning metal-carbon composite as a highly promising platform for efficient and sustainable electrochemical CO₂RR. Recognizing that testing conditions and performance metrics differ among studies, we present in Table 1 a comprehensive overview of main catalysts featuring distinct types of active sites, thereby facilitating a more direct and insightful comparative analysis.

3.1 Defect engineering

Carbon materials used as catalysts inherently contain various types of intrinsic defects. Although defects are often perceived as imperfections that compromise the material's ideal structure, in the context of electrochemical CO₂RR, these defects can play a beneficial and even indispensable role. Intrinsic defects in carbon materials modify the electronic environment of adjacent carbon atoms, potentially creating catalytically active sites that enhance the adsorption and activation of CO₂ molecules [66, 70, 71].

As shown in Figs. 3(a)–3(c), the main intrinsic defects found in carbon materials include edge sites, vacancies, holes, and topological distortions [72, 73]. Edge defects are commonly observed in finite-sized graphene sheets and carbon nanotubes, where the termination of the lattice exposes carbon atoms bearing unsaturated bonds, resulting in significantly enhanced chemical reactivity relative to the basal plane. Within the framework of the graphitic hexagonal lattice, these edge sites are conventionally classified into two distinct types: zigzag and armchair edges. Vacancy and hole defects originate from the absence of carbon atoms within the lattice, creating unsaturated sites that induce localized changes in electron density and thereby enhance interactions with CO₂ molecules and reaction intermediates. Specifically, a vacancy defect refers to the removal of one or a few carbon atoms, whereas a hole defect involves the elimination of a larger region of carbon atoms, resulting in a hierarchical pore structure that includes micropores, mesopores, and macropores. Topological defects are characterized by the presence of non-hexagonal carbon rings within the otherwise hexagonal graphene lattice, which induces lattice strain and curvature that modulate the electronic properties and generate chemically active sites. During various synthesis processes, distortions of the carbon network give rise to diverse non-hexagonal topological structures, including pentagons, heptagons, octagons, Stone–Wales defects, and dangling bonds, all of which contribute to the complexity and reactivity of the carbon framework [74].

The presence and density of these defects can be tuned by manipulating synthesis conditions or applying post-synthesis

Table 1 Summary of testing conditions and CO₂RR performance of main catalysts with different types of active sites

Catalyst type	Catalyst material	Cell type	Potential (V vs. RHE)	Product	FE (%)	<i>J</i> (mA·cm ⁻²)	Ref.
Defect engineering	Defective N-doped carbon	H-cell	−0.7	CO	93.0	~ −1.4	[38]
	Fe single-atom catalysts rich in intrinsic defects	H-cell	−0.6	CO	96.9	~ −9.1	[39]
	Intrinsic defect-rich graphene-like porous carbon embedded with single-atom Fe–N ₄ sites	H-cell	−0.75	CO	90.0	~ −16.5	[70]
	Nitrogen-removed mesoporous carbon	H-cell	−0.6	CO	80.0	−2.9	[77]
	Defective N-doped carbon spheres	H-cell	−0.6	CO	94.5	~ −1.0	[78]
Heteroatom doping	O-substituted porous C ₂ N frameworks	H-cell	−0.6	CO	94.8	~ −2.8	[32]
	3D N-doped graphene nanoribbon networks	H-cell	−0.4	CO	87.6	~ −5.0	[94]
	Graphitic-N highly doped graphene-like carbon	H-cell	−0.72	CO	95.0	~ −9.1	[95]
	N, S co-doped carbon	H-cell	−0.6	CO	93.0	−5.2	[96]
	B, N co-doped graphite	Flow cell	—	CO	87.4	−150	[97]
Metal-carbon composites	Ni SA/CNs single-atom catalyst	H-cell	−0.68	CO	98.0	~ −12	[111]
	Co-coordinated phthalocyanines	H-cell	−0.7	CO	95.0	~ −8.6	[116]
	Asymmetric Cu–N ₂ single-atom catalysts	Flow cell	−1.45	CH ₄	83.5 ± 4	~ −33	[117]
	Single-atom Cu–S ₁ N ₃ catalysts	H-cell	−0.65	CO	100.0	~ −4	[118]
	NiCu dual-atom catalysts	H-cell	−1.2	CO	100.0	−18.2	[119]

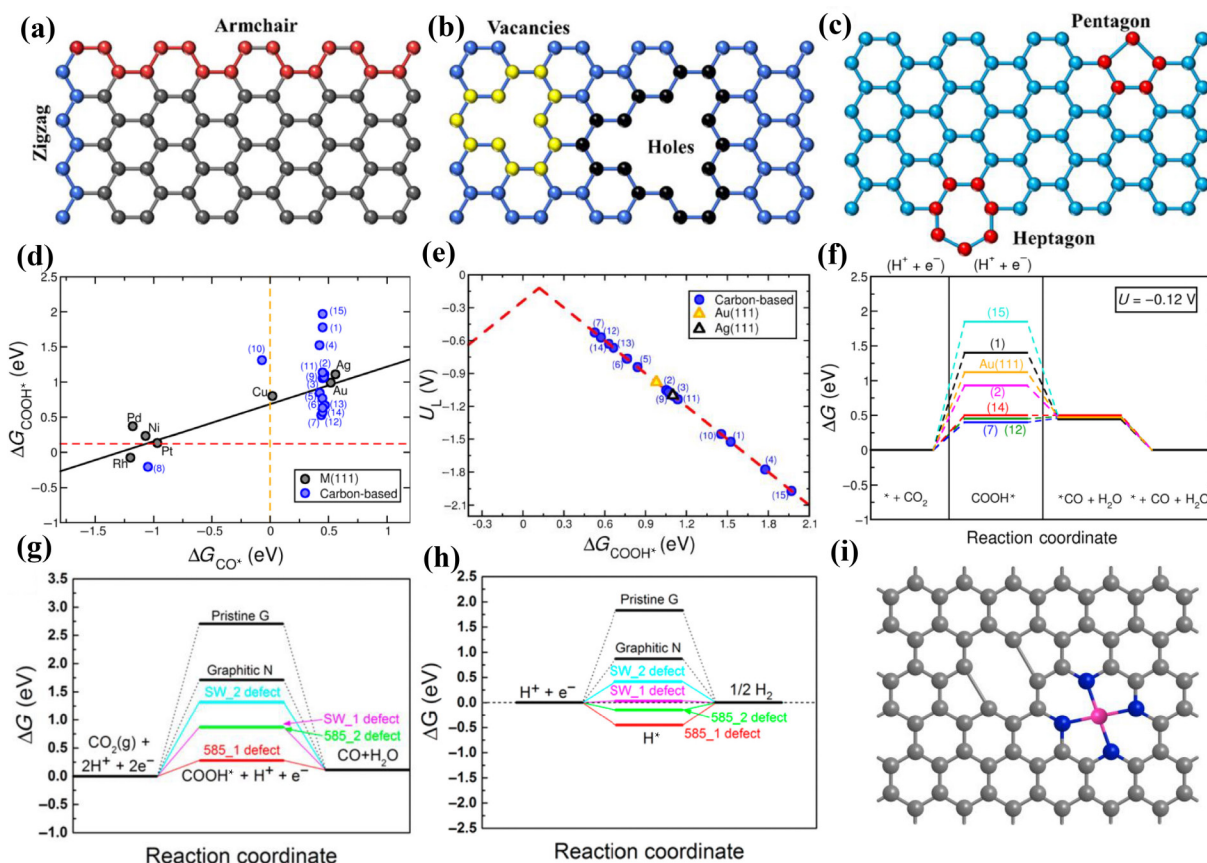


Figure 3 ((a)–(c)) Typical intrinsic defects in carbon-based materials: (a) edge defects, (b) vacancies and holes, and (c) topological defects. Reproduced with permission from Ref. [73], © Zhengzhou University 2022. (d) Calculated chemisorption energies of COOH^* vs. CO^* intermediates, (e) activity volcano, and (f) free energy diagram at various defects. Reproduced with permission from Ref. [76], © American Chemical Society 2017. ((g) and (h)) Free-energy diagram at (g) point defects (5–8–5) and (h) SW edge defect. Reproduced with permission from Ref. [77], © American Chemical Society 2018. (i) Structure of Fe–N₄ site-coupled “585” ring. Reproduced with permission from Ref. [39], © Elsevier B.V. 2024.

treatments. Techniques such as plasma etching, thermal annealing under controlled atmospheres, chemical oxidation, or ion bombardment are commonly employed to introduce or adjust the nature and concentration of defects [37, 65, 75]. Through these methods, it becomes possible to optimize the catalytic activity of carbon-based materials by generating an abundance of active sites that enhance CO_2 adsorption and mass/charge transport processes.

Several representative studies have highlighted the critical role of intrinsic defects in carbon catalysts for electrochemical CO_2 RR. Siahrostami et al. [76] employed graphene as a model system to construct a variety of defect sites and systematically investigated the chemical adsorption energies of key intermediates, CO^* and COOH^* , at these defect sites using density functional theory (DFT) calculations. By benchmarking against the (111) facets of transition metals (TMs), they observed that most defect sites exhibited similar adsorption energies for CO^* , while the adsorption energies for COOH^* varied significantly among different defects (Fig. 3(d)). Based on these findings, the authors proposed that the adsorption strength of COOH^* at defect sites serves as a critical descriptor governing the catalytic activity for the electrochemical reduction of CO_2 to CO . Notably, a series of defect types demonstrated higher catalytic activity than the Au(111) surface (Figs. 3(e) and 3(f)). This theoretical study provides valuable insights for designing defect-engineered carbon-based catalysts by elucidating the pivotal role of defect-specific adsorption characteristics in modulating CO_2 reduction performance. While DFT calculations provide valuable

mechanistic insights, it is important to recognize their inherent limitations, including the use of implicit solvation models that simplify the electrochemical environment, finite model sizes that may not capture the structural complexity of realistic catalysts, and the static nature of most calculations that overlook dynamic surface reconstructions under operating conditions.

In addition to theoretical calculations, experimental studies have also demonstrated the effectiveness of intrinsic defects in electrochemical CO_2 RR. Daiyan et al. [77] systematically varied the treatment temperature and number of treatments to progressively remove N atoms from N-doped mesoporous carbon, thereby pioneering how intrinsic defect sites influence on the electrochemical CO_2 RR performance of carbon-based catalysts. The mesoporous carbon sample treated three times at 900 °C exhibited catalytic behavior comparable to that of metal catalysts, achieving a FE_{CO} (FE = Faradaic efficiency) of approximately 80% and a j_{CO} of -2.9 mA/cm^2 at an applied overpotential of 490 mV vs. reversible hydrogen electrode (RHE). DFT calculations further identified point defects and Stone–Wales (SW) edge defect sites as the active catalytic centers responsible for this enhanced performance (Figs. 3(g) and 3(h)). Similarly, Wang et al. [78] employed thermal treatment to gradually remove N atoms from N-doped carbon spheres, concurrently generating carbon defects. Electrochemical measurements revealed a positive correlation between the electrochemical CO_2 RR performance and defect concentration, while an inverse correlation was observed with N content. The

sample treated at 1100 °C exhibited a remarkable FE_{CO} of 94.5% at a relatively low applied potential of -0.60 V vs. RHE. Further insights obtained through near edge X-ray absorption fine structure (NEXAFS) spectroscopy and DFT calculations elucidated that those octagonal and pentagonal defects involving sp^2 -hybridized carbon atoms, rather than coordinatively unsaturated edge defects with dangling bonds, were primarily responsible for the outstanding activity. These studies collectively highlight the critical role of defect engineering in optimizing carbon-based catalysts for efficient CO_2 electroreduction.

Intrinsic defect sites can also synergize with other metal or non-metal atoms to enhance electrocatalytic performance [38, 39, 70]. For example, Shen and colleagues [39] obtained a catalyst containing both Fe- N_4 sites and intrinsic carbon defect sites by high-temperature NH_3 etching of ZIF-8. This catalyst achieved a FE_{CO} of 96.9% at -0.6 V vs. RHE, with a maximum j_{CO} of 20.0 mA/cm^2 in an H-cell, which are significantly superior to catalysts containing only Fe- N_4 sites. Theoretical calculations suggest that this enhancement is attributed to the Fe- N_4 site-coupled “585” ring defects in the carbon matrix (Fig. 3(i)).

Although defect engineering offers promising improvements, the catalytic activity generally remains limited, and significant challenges persist in both the creation and precise characterization of intrinsic defects. Achieving precise control over defect type and density is difficult because many synthesis and treatment techniques produce a heterogeneous mixture of defects. This complexity complicates efforts to systematically correlate specific defect structures with catalytic performance. High-resolution characterization methods such as aberration-corrected transmission electron microscopy, scanning tunneling microscopy, and electron energy loss spectroscopy are essential for identifying and quantifying defects at the atomic scale, but these techniques are not universally accessible.

3.2 Heteroatom doping

Besides intrinsic defects, the catalytic performance can be optimized by introducing extrinsic defects into the carbon framework. Heteroatom doping represents an effective approach to creating such extrinsic defects, providing complementary advantages to intrinsic defect engineering. The incorporation of heteroatoms with different atomic radii, electron configurations, and electronegativities into the carbon matrix fundamentally alters the physicochemical properties of carbon-based electrocatalysts. Heteroatom doping disrupts the symmetry of the carbon lattice and induces localized charge redistribution, thereby modulating the electronic structure of the carbon framework and generating heteroatom-functionalized active sites [79–82]. These sites, formed through the synergistic interplay between the heteroatoms and adjacent carbon atoms, are widely recognized as the primary catalytic centers that facilitate key steps in electrochemical CO_2RR . Specifically, N, O, B, S, and P dopants have been demonstrated to enhance the adsorption and activation of CO_2 molecules as well as intermediates, thus lowering energy barriers and improving both activity and selectivity. Additionally, the introduction of heteroatoms can generate structural defects and increase the density of edge sites, further contributing to the overall catalytic efficiency. These modifications result in substantial improvements to the activity, selectivity, and stability of metal-free carbon catalysts for CO_2RR , as evidenced by numerous experimental and theoretical studies [83, 84].

N atoms, as neighboring elements to C in the same period of the periodic table, exhibit a slightly smaller atomic radius and a higher electronegativity compared to C atoms. Doping N into the carbon matrix can alter the electronic structure of neighboring C atoms due to its stronger electron-withdrawing ability. Moreover, the lone pair of electrons present in the outer shell of N can interact with the conjugated π -bonds within the carbon matrix, potentially leading to distortions in the carbon structure that further influence the electronic properties of C atoms [85]. Based on their bonding environment within a carbon matrix, N atoms can be categorized into four types: pyrrolic N, pyridinic N, graphitic N, and NO_x .

N doping is currently one of the most prevalent strategies for enhancing the performance of carbon-based electrocatalysts. The synthesis of N-doped carbon materials is typically achieved through *in situ* doping during precursor pyrolysis [81, 86–89] or via post-treatment methods such as thermal annealing in NH_3 or N-rich environments [34, 90]. Extensive research has demonstrated the significant impact of N incorporation on improving catalytic activity and selectivity for electrochemical CO_2RR . The specific types of N functional groups are closely correlated with the processing temperature, which governs their formation and relative abundances [91–93]. Identifying the active N species and elucidating their mechanistic roles are central topics in current research, as such knowledge not only clarifies the origin of catalytic activity but also guides the rational design and synthesis of highly efficient N-doped carbon catalysts.

Current studies suggest that the primary active sites in N-doped carbon catalysts are pyridinic N [90, 93, 94] and graphitic N, as well as the C atoms adjacent to graphitic N [92, 95]. Liu et al. [94] synthesized three-dimensional N-doped graphene nanoribbon networks (N-GRW) via pyrolysis of melamine and L-cysteine, and systematically tuned the composition of N functionalities by adjusting the ratio of N sources (Fig. 4(a)). Through a combination of electrochemical performance evaluation and DFT calculations, they demonstrated that pyridinic N plays a pivotal role in catalytic activity. Specifically, pyridinic N provides an optimal binding environment for the key intermediate $^*\text{COOH}$, facilitating its conversion from CO_2 and subsequent reduction to $^*\text{CO}$ (Fig. 4(b)). This favorable interaction reduces the energy barrier for the reaction, resulting in a remarkably low overpotential of 0.33 V vs. RHE. Li et al. [95] systematically controlled the N functionalities in carbon catalysts by varying the pyrolysis temperature of dicyandiamide and phthalocyanine (Pc) precursors. Their study revealed that the sample treated at 1000 °C exhibited outstanding selectivity, achieving a 95.0% conversion of CO_2 to CO. DFT analysis indicated that the C atoms adjacent to graphitic N species serve as the principal active sites for the CO_2RR in the NG-1000 catalyst. These findings highlight the critical influence of both the type and local environment of N dopants, particularly graphitic N and its neighboring C atoms, in optimizing the electrocatalytic performance of N-doped carbon materials for CO_2RR (Fig. 4(c)). To date, controversy remains regarding the precise nature of the active sites, as multiple N species, including pyrrolic N, oxidized N, and various edge configurations, often coexist within the carbon matrix. This coexistence complicates the identification and attribution of catalytic activity to specific N functionalities, and further research is required to clarify the mechanistic roles of each type of N group in CO_2 reduction.

In addition to N, the incorporation of other heteroatoms (O, B, S, and P) and multi-atom co-doping have also been explored to

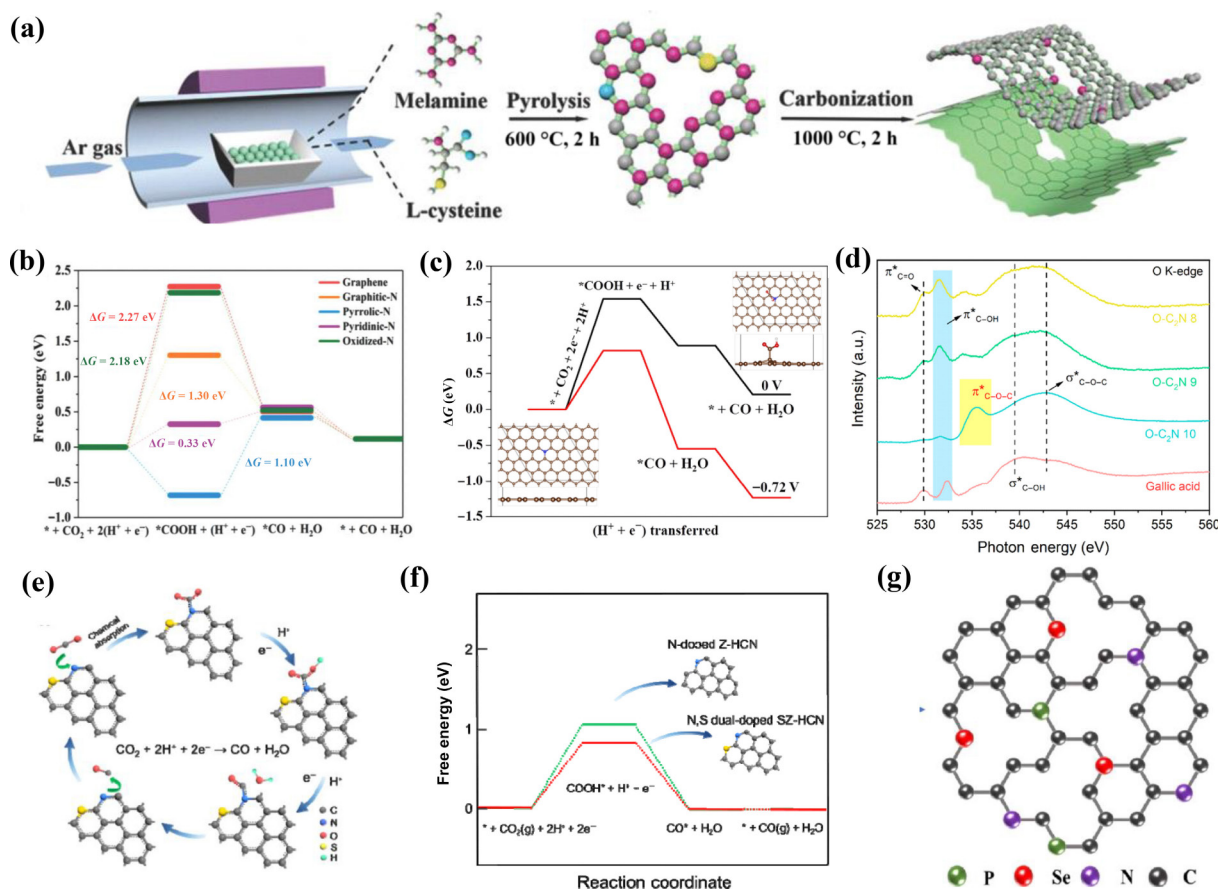


Figure 4 (a) The synthesis processes of N-GRW and (b) free energy diagram of CO₂RR on N-GRW catalysts. Reproduced with permission from Ref. [94], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2018. (c) Free energy diagram for CO₂RR to CO on NG-1000 catalyst. Reproduced with permission from Ref. [95], © Li, J. J. et al. 2021. (d) O NEXAFS spectra of the O-C₂N. Reproduced with permission from Ref. [32], © Wiley-VCH GmbH 2025. (e) Proposed mechanism and (f) calculated free energy diagram of CO₂ on SZ-HCN catalysts. Reproduced with permission from Ref. [96], © Dalian Institute of Chemical Physics, the Chinese Academy of Sciences 2020. (g) The molecular structure diagram of SePNC. Reproduced with permission from Ref. [64], © Elsevier B.V. 2024.

enhance the catalytic performance of carbon-based catalysts [32, 64, 96–101]. Wang et al. [32] developed O-substituted porous C₂N frameworks (O-C₂N) by pyrolyzing gallic acid and dicyandiamide, successfully introducing distinctive C–O–C functionalities into the carbon structure. By modulating the carbonization temperature, they were able to control the abundance of single-bonded C–O–C groups, with higher temperatures, specifically 1000 °C, yielding a greater concentration and dispersion of these moieties (Fig. 4(d)). Electrochemical evaluation revealed a positive correlation between the abundance of single-bonded C–O–C configurations and enhanced CO₂-to-CO conversion efficiency. These findings provide important mechanistic insights into how O incorporation, particularly through well-dispersed C–O–C units, contributes to improved CO selectivity in O, N co-doped carbon catalysts. Yari et al. [97] synthesized B, N co-doped graphite materials via pyrolysis of Cl-B-SubPc, and demonstrated that the synergistic interaction between B and N dopants plays a crucial role in stabilizing the CO_2^* intermediates during electrocatalysis. This B–N synergy not only enhances the adsorption and activation of CO₂ but also effectively suppresses the competing hydrogen evolution reaction.

Moreover, the co-doped structure promotes C–C coupling processes. Li et al. [96] prepared N, S co-doped carbon materials (SZ-HCN) with a high surface area by pyrolyzing N-containing polymers and sulfur powder, followed by ZnCl₂ activation. These dual-doped catalyst exhibited remarkable activity for the

electrochemical reduction of CO₂ to CO, achieving a FE of approximately 93%. DFT calculations further revealed that the co-doping of N and S significantly lowers the Gibbs free energy barrier for the formation of the key COOH* intermediate, compared to single N doping (Figs. 4(e) and 4(f)). Feng et al. [64] synthesized ternary-doped porous carbon electrocatalysts (SePNC) by co-pyrolyzing C, N, P, and Se precursors through a two-step process. SePNC exhibited outstanding CO selectivity, achieving a FE of 94.8%, with only 5.2% H₂ as a byproduct. The authors attributed this exceptional catalytic performance to the synergistic effects of N, P, and Se dopants (Fig. 4(g)), in conjunction with the catalyst's high specific surface area. These factors collectively enhance the active site density and optimize the electronic structure, thereby facilitating efficient CO₂ reduction and high CO selectivity.

The electrocatalytic reduction of CO₂ on heteroatom-doped carbon materials has attracted significant attention due to its potential for sustainable fuel and chemical production. However, a major challenge in this field is the ambiguous understanding of catalytic active sites. Multiple forms of active sites, including various dopant configurations, defects, and edge sites, often coexist within the same catalyst, leading to considerable debate regarding their respective roles in CO₂ reduction. This complexity hampers the establishment of clear structure–activity relationships. To resolve these controversies, it is essential to combine advanced *in situ* characterization techniques with theoretical modeling, allowing for

real-time identification and analysis of active sites under operating conditions. Constructing model catalysts with isolated or well-controlled dopant sites can help clarify their specific catalytic functions. Overall, integrating experimental and computational approaches will be the key to uncovering the true nature of active sites and guiding the rational design of more efficient CO₂ electrocatalysts.

3.3 Metal-carbon composite

Although metal-free carbon-based catalysts typically possess excellent electrical conductivity, well-developed porous structures, and abundant and tunable surface functional groups, they generally exhibit relatively low catalytic activity and produce limited product value in CO₂RR. In contrast, metal catalysts usually offer higher catalytic activity, but they often suffer from poor dispersion, limited stability, and lower electrical conductivity [102, 103]. By combining metals with carbon materials, these complementary properties are expected to be integrated. The carbon support helps to disperse and stabilize metal active centers, enhances overall conductivity, and provides a robust framework to prevent metal aggregation and degradation. Meanwhile, the metal sites contribute high activity for efficient CO₂ conversion. Furthermore, the strong electronic interactions between carbon and metal can modulate the electronic structure of active sites, further optimizing both activity and selectivity [48, 104].

According to current research, metal species in metal-carbon composite catalysts can be classified as metal nanoparticles [105–108], clusters [45, 109, 110], or atomically dispersed metals [46, 111–114] based on their size. These composite catalysts, especially atomically dispersed catalysts, are among the most popular research directions in the field of electrochemical CO₂RR. Since Zhang et al. [115] first introduced the concept of single-atom catalysts (SACs) in 2011, SACs have rapidly ascended to the forefront of catalysis research, owing to their uniformly distributed active sites with well-defined configurations and exceptional catalytic properties. In particular, atomically dispersed metal species anchored onto carbon supports have garnered significant attention as highly promising candidates for electrochemical CO₂RR. Recent research efforts are increasingly directed toward the rational design of these catalysts by tuning critical parameters, including the choice of metal, its coordination environment, and the characteristics of the carbon substrate, to maximize both activity and selectivity.

Through precise control over the dispersion of metal atoms and modulation of their electronic structures via interactions with tailored surface functional groups on the carbon matrix, researchers sought to enhance CO₂ conversion efficiency and selectively drive the formation of value-added products. These strategies, combined with ongoing advances in the engineering of carbon supports to optimize porosity, conductivity, and stability, continue to push the boundaries of SAC performance in CO₂RR. Chang et al. [116] synthesized a series of well-defined TM-N₄ (TM = Fe, Co, Ni, Cu, and Zn) catalysts by integrating transition metal-based phthalocyanines with Vulcan XC-72 carbon powder. They systematically compared the electrocatalytic performance of these catalysts for electrochemical CO₂RR to CO under identical potentials. Their results demonstrated a clear trend in CO selectivity, following the order of Co-Pc > Ni-Pc ≫ Fe-Pc > Cu-Pc > Zn-Pc, with the CO partial current density of Co-Pc nearly three orders of magnitude higher than that of Zn-Pc. Furthermore, DFT calculations revealed that the free energy difference between

*HOCO and *CO could serve as a reliable descriptor for CO₂RR activity across various TM-Pc catalysts. A strong linear correlation was observed between the DFT-predicted values and the experimental results over the entire potential range investigated (Figs. 5(a)–5(c)), highlighting the predictive power of this theoretical approach.

Modulating the coordination number of metal atoms, altering the type of coordinating atoms, or introducing bimetallic sites are effective strategies for further enhancing the electrocatalytic performance of SACs. Wu et al. [117] synthesized a Cu single-atom catalyst with unsaturated coordination (CuSA-N₃/C) via hydrothermal carbonization of CuCl₂·2H₂O and formamide. Unlike conventional Cu-N₄ coordination environments, the Cu-N₂ sites in this catalyst enabled efficient electrocatalytic reduction of CO₂ to CH₄. Notably, the FE_{CH₄} increased with rising system pressure, reaching an impressive maximum value of 83.5% ± 4% under elevated CO₂ pressure (Figs. 5(d)–5(f)). This work highlights the significant impact of unsaturated coordination environments on tuning product selectivity in SACs. Chen et al. [118] developed SACs with Cu-S₂N₃ coordination motifs (Cu-S₂N₃/Cu_x) by employing sulfur powder, CuCl₂·2H₂O, and glucose as precursors, followed by NH₃ etching (Fig. 5(j)). Cu-S₂N₃/Cu_x exhibited remarkable electrocatalytic performance for CO₂ reduction to CO, achieving a FE_{CO} of 100% at –0.65 V vs. RHE and maintaining FE_{CO} values above 90% within the potential range of –0.55––0.75 V vs. RHE. This performance significantly surpassed that of the analogues with Cu-N₄ (FE_{CO} of 54% at –0.7 V vs. RHE) configurations. The asymmetric Cu-S₂N₃ atomic interface on the carbon basal plane provided an optimized binding energy for the key *COOH intermediate, relative to the Cu-N₄ site. Additionally, the adjacent Cu_x species facilitated the protonation of *CO₂– by accelerating water dissociation and supplying *H to the Cu-S₂N₃ active centers. This work underscores the importance of heteroatom doping and interfacial engineering in enhancing the catalytic efficiency and selectivity of single-atom catalysts for CO₂ electroreduction (Figs. 5(g) and 5(h)). Yao et al. [119] prepared dual-atom catalysts (DACs) featuring both Ni-N₄ and Cu-N₄ coordination sites through the annealing of CuNi/ZIF-8 precursors (Fig. 5(j)). The coexistence of these distinct atomic moieties enabled effective electronic modulation, thereby enhancing the electrochemical CO₂RR with improved selectivity and catalytic activity (Fig. 5(i)). This approach demonstrates the potential of dual-atom site engineering for advanced electrocatalytic performance.

In summary, composite catalysts for electrochemical CO₂RR have attracted significant attention due to their potential for high efficiency and selectivity. Among them, atomically dispersed catalysts stand out owing to their maximized atomic utilization and unique active sites. However, the preparation of atomically dispersed catalysts is inherently complex, requiring precise control over precursor selection, coordination environment, and synthetic conditions to prevent aggregation and ensure uniform dispersion. Strategies such as heteroatom doping, unsaturated coordination engineering, and dual-atom site construction have been developed to optimize catalytic performance, but each introduces additional synthesis challenges. Moreover, interactions between different components in composite catalysts may lead to synergistic effects or, conversely, undesirable competitive reactions. Therefore, the rational design and scalable synthesis of atomically dispersed composite catalysts demand advanced characterization techniques and a deep understanding of structure–activity relationships. Future

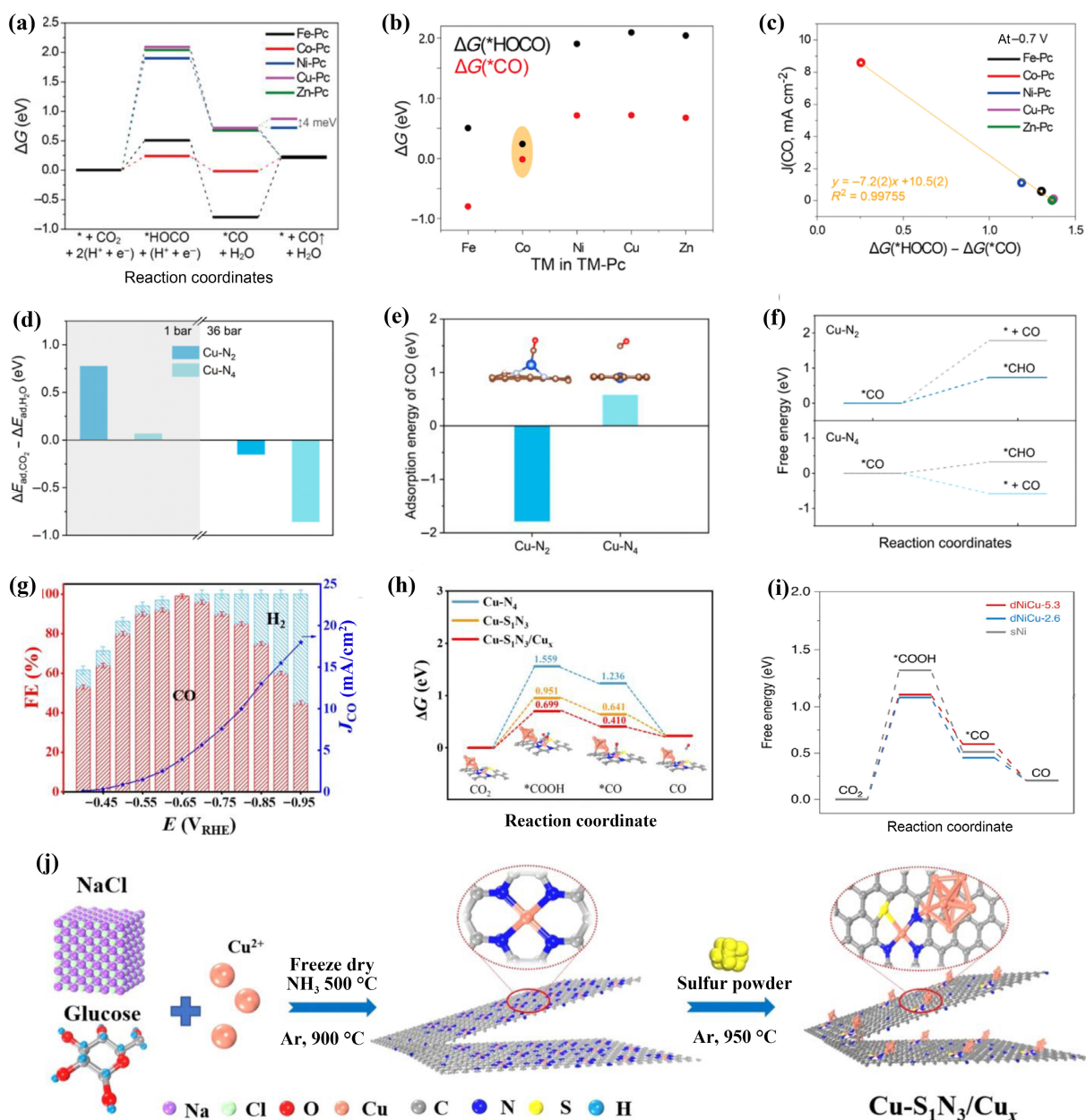


Figure 5 (a) Free energy diagram for CO₂RR at 0 V vs. RHE. (b) free energy of *HOCO and *CO with different TM-Pcs. (c) Free energy of *HOCO and *CO at -0.7 V vs. RHE. Reproduced with permission from Ref. [116], © American Chemical Society 2022. (d) Free energy of CO₂ and H₂O under 1 and 36 bar. (e) Adsorption energy of *CO. (f) Free energy of *CO hydrogenation and desorption. Reproduced with permission from Ref. [117], © American Chemical Society 2024. (g) FE_{CO} and j_{CO} of Cu-SiN₃/Cu_x. (h) Free energy diagram at 0 V vs. RHE on Cu-SiN₃/Cu_x, Cu-SiN₃, and Cu-N₄. (i) Free energy of CO₂RR on dNiCu-5.3, dNiCu-2.6, and sNi. Reproduced with permission from Ref. [119], © Yao, D. Z. et al. 2023. (j) Synthesis process of Cu-SiN₃/Cu_x. Reproduced with permission from Ref. [118], © Wiley-VCH GmbH 2021.

research should focus on elucidating these mechanisms and developing robust and controllable synthetic methodologies to facilitate practical applications in CO₂ conversion.

4 Mass/charge transport optimization

As discussed above, rational design of active sites can significantly enhance the electrochemical CO₂RR activity of carbon-based catalysts. However, in heterogeneous catalytic systems, catalytic performance is not solely dictated by the nature and density of active sites; efficient mass/charge transport processes are also critical factors influencing overall activity [62, 120].

The adsorption strength at the active site-intermediate interface

is governed by dual mechanisms: local reactant concentration (mass transfer control) and interfacial charge density (charge transfer control). Although recent research prioritizes active site engineering, neglecting concurrent mass/charge transport phenomena fundamentally limits holistic catalyst performance insights. The electrochemical CO₂RR inherently involves complex proton and electron transfer steps. Only when rapid and efficient transport of protons and electrons to the active sites is achieved can the catalytic centers be fully utilized, making kinetic processes pivotal for high catalytic efficiency.

Effective mass transport ensures that CO₂ molecules and protons can swiftly reach catalytic centers, minimizing concentration gradients and preventing local depletion, which could otherwise

hinder reaction rates. Simultaneously, robust electron transport pathways within the catalyst framework and at the catalyst–electrode interface are essential for fast electron transfer, supporting the catalytic cycle and lowering overpotential. Detailed analysis of current catalyst structures reveals that parameters such as pore structure (including specific surface area [121–123] and pore size distribution [42, 43, 124, 125]), surface hydrophilicity/hydrophobicity [91, 126], micro-morphology [95], and electrical conductivity [91, 127] are the primary factors that govern proton and electron transport. To experimentally assess the mass/charge transport properties discussed above, a range of well-established characterization techniques are available. Table 2 summarizes the most commonly used methods for evaluating pore structure, wettability, and electronic conductivity in carbon-based CO₂RR catalysts.

4.1 Mass transport

Efficient mass transfer processes, especially at high potentials, ensure that CO₂ and protons can rapidly reach the active sites, while intermediates and products can be quickly removed from the catalyst surface, which not only enhances the utilization of catalytic sites but also helps maintain high reaction efficiency and selectivity, preventing unwanted side reactions and catalyst deactivation [128]. Poor mass transport can lead to the accumulation of intermediates or products, causing local depletion of reactants and blocking active centers, which ultimately reduces catalytic activity. The rational design of catalyst structures, such as increasing surface area, optimizing pore size, adjusting hydrophilicity or hydrophobicity, and designing micro morphologies, is essential for improving mass transport properties. By addressing mass transport limitations, it is possible to fully exploit the catalytic potential of electrocatalysts and promote efficient, selective, and stable CO₂ reduction.

Regulation of pore structure represents one of the most extensively explored strategies for enhancing mass transport efficiency in electrochemical CO₂RR. Among these strategies, increasing the specific surface area is widely recognized as an effective means to maximize the exposure of active sites [129–132] and accommodate a higher density of catalytic centers [111, 133, 134], which is essential for improving catalytic activity. Furthermore, precise control over pore size distribution enables the formation of well-defined transport channels within the electrode, thereby facilitating the efficient diffusion of reactants, intermediates, and products [135–138].

For instance, Zhang et al. [87] synthesized hierarchically porous carbon catalysts via the co-pyrolysis of phenolic resin and varying proportions of ZIF-8. Among the series, the catalyst prepared with 30% ZIF-8 (designated as ZNMC-30) exhibited the highest specific surface area (Fig. 6(a)). This pronounced porous structure enabled ZNMC-30 to possess the greatest density of exposed active sites, which in turn contributed to its superior FE (Fig. 6(b)). This example highlights the critical role of optimizing pore structure and surface area in enhancing the catalytic performance for CO₂

electroreduction. Hursan et al. [42] employed o-phenylenediamine as a C and N source and utilized monodisperse silica nanoparticles as templates to fabricate N-doped carbon (N-C) materials. By carefully tuning the average diameter of the silica templates, they achieved precise control over the pore sizes, producing N-C samples with nominal pore diameters of 13, 27, and 90 nm (denoted as NC-13, NC-27, and NC-90, respectively) (Fig. 6(c)). Their experimental results demonstrated that the selectivity for CO₂ reduction, relative to the hydrogen evolution reaction, increased by approximately threefold upon introducing porosity into the carbon matrix, with the optimal performance observed for a pore size of 27 nm. This work provides compelling evidence that the distribution and size of pores within carbon-based catalysts play a pivotal role in governing the efficiency and selectivity of electrochemical CO₂RR.

Similarly, Jia et al. [124] and Yang et al. [31] optimized Fe-N-C catalysts (Fig. 6(d)) and metal-free catalysts, respectively, by tailoring their pore size distributions. They conducted systematic studies to elucidate how variations in pore structure within both catalysts influence mass transport characteristics during electrochemical CO₂RR. Furthermore, they analyzed gas diffusion behaviors within pores of varying sizes (Figs. 6(e)–6(g)), employing coupled lattice Boltzmann method and discrete element method (LBM-DEM) simulations. Their computational studies provided in-depth insights into how pore size distribution modulates gas transport at the microscale. Despite these advances, significant challenges remain in the precise engineering of catalyst porosity and in establishing clear structure–performance relationships that can directly guide catalyst design for optimized electrochemical CO₂RR.

The hydrophilicity or hydrophobicity of carbon-based catalysts modulates the distribution of liquid and gas at the electrode interface, thereby influencing the mass transport pathways and rates of CO₂ and reaction products. In electrochemical CO₂RR, enhancing the hydrophobicity of the catalyst is generally effective in suppressing the competing HER and mitigating electrode flooding by water [91, 126, 139]. For example, Xiong et al. [139] engineered a single-atom catalyst with enhanced hydrophobicity by combining amino-substituted cobalt phthalocyanine (CoPc-NH₂), octadecylamine (ODA), and carbon nanotubes, resulting in the composite CoPc-CNT-ODA (Fig. 7(a)). The significantly increased water contact angle observed for CoPc-CNT-ODA confirms its improved hydrophobic character (Fig. 7(b)). CoPc-NH₂ exhibits the highest current density both at the scan rate and at different reaction time (Figs. 7(e) and 7(f)). The superior activity and stability can be directly attributed to the robust hydrophobic structure, which effectively suppresses electrode flooding and maintains active site exposure during operation (Figs. 7(c) and 7(d)). At present, there are relatively few studies focusing on the enhancement of catalytic performance by increasing catalyst hydrophobicity, and the underlying mechanisms remain insufficiently explored. Future research should prioritize the rational design of hydrophobic catalysts and systematically investigate how their wettability influences catalytic activity and stability.

Table 2 Summary of key characterization techniques for transport-related properties

Transport property	Characterization technique	Key measured parameter(s)
Pore structure	N ₂ , BET method	Specific surface area, pore volume, pore size distribution
Hydrophilicity/hydrophobicity	Contact angle goniometry	Static water contact angle, dynamic advancing/receding angles
Electrical conductivity	Four-point probe method	Sheet resistance, bulk conductivity
Charge transfer resistance	Electrochemical impedance spectroscopy (EIS)	Charge transfer resistance, Warburg impedance

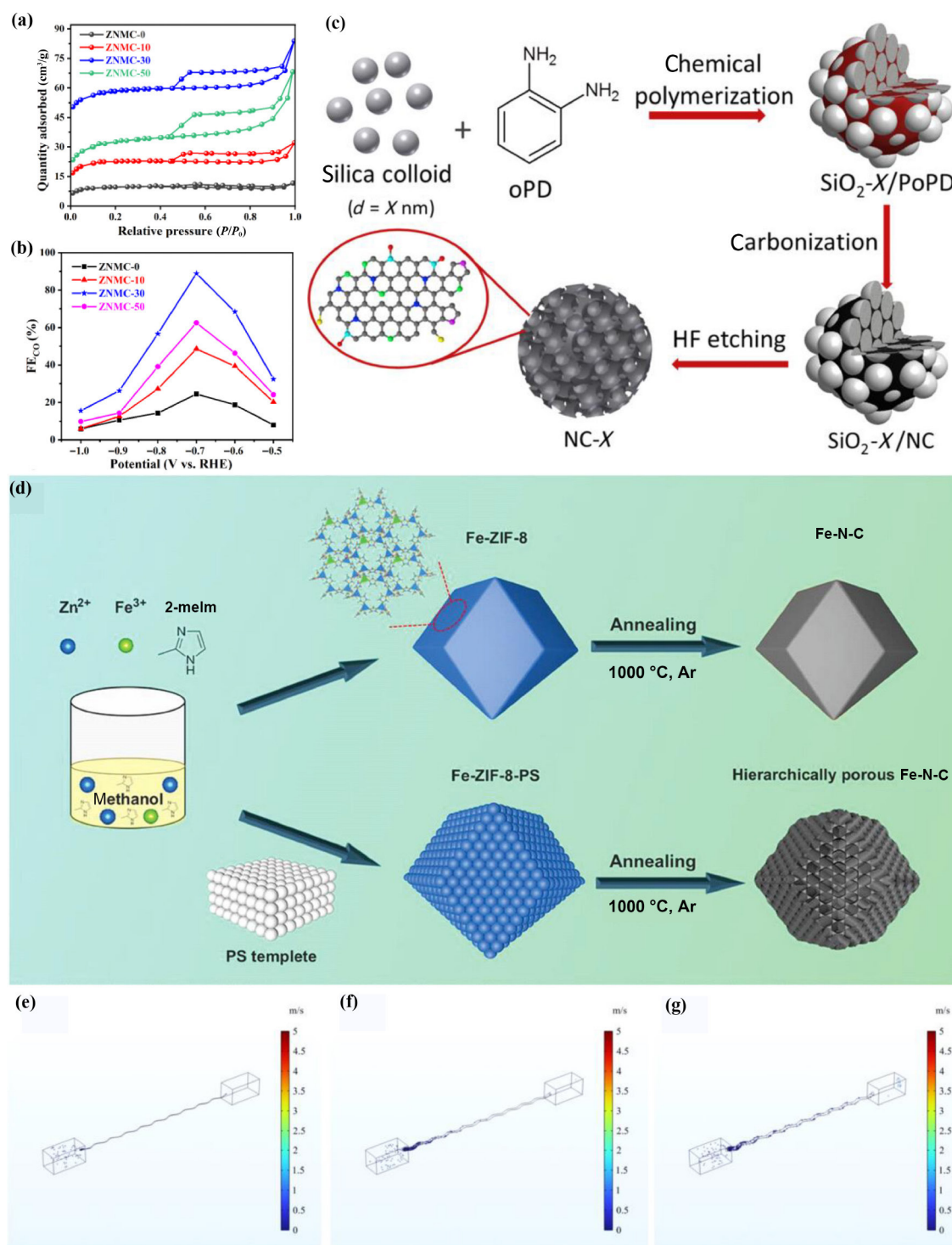


Figure 6 (a) N₂ adsorption-desorption isotherms and (b) FE_{CO} of ZNMCs. Reproduced with permission from Ref. [87], © American Chemical Society 2024. (c) Synthesis process of NC-X. Reproduced with permission from Ref. [42], © Hursán, D. et al. 2019. (d) Synthesis process of Fe-N-C. Reproduced with permission from Ref. [124], © Jia, C. et al. 2023. ((e)–(g)) The trajectories of CO₂ molecules in channels of (e) 0.7, (f) 3, and (g) 4 nm. Reproduced with permission from Ref. [31], © Elsevier B.V. 2025.

Carbon-based materials exhibit a variety of microscopic morphologies, such as carbon quantum dots, carbon nanotubes, graphene, and porous carbons with diverse structural features. In electrochemical CO₂RR, these distinct morphologies can create unique microenvironments that influence mass transport processes and, consequently, catalytic performance [140]. Although

numerous studies have intentionally or unintentionally discussed the impact of carbon catalyst morphology on transport and activity, the complex interplay of multiple structural parameters often complicates direct elucidation of the relationship between microstructure and catalytic behavior [141, 142]. As a result, systematic investigations specifically addressing how the

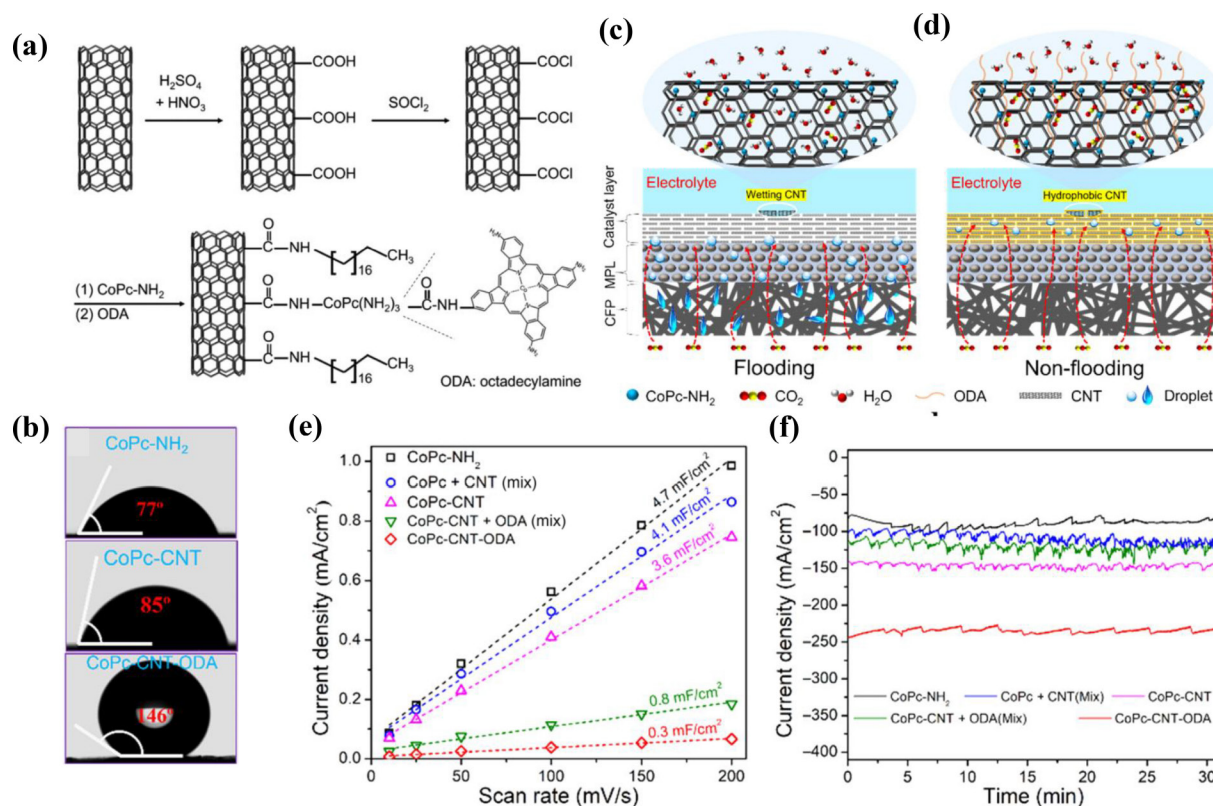


Figure 7 (a) Synthesis process of CoPc-CNT-ODA. (b) Contact angle of different catalysts. ((c) and (d)) The microenvironment and local three-phase interface of GDE with (c) pristine CNT and (d) CoPc-NH₂. ((e) and (f)) Current densities at (e) different scan rates and (f) different reaction time. Reproduced with permission from Ref. [139], © American Chemical Society 2023.

microscopic morphology of carbon-based catalysts governs their electrocatalytic performance remain limited.

4.2 Charge transport

In electrochemical CO₂RR, apart from the effect of mass transport on reaction kinetics, both the rate of electron transport within the electrode material and the efficiency of interfacial electron transfer between the electrode surface and CO₂ or its intermediates significantly impact catalytic performance, especially at low applied potentials [62, 127, 143, 144]. The electron transport within the electrode is largely determined by the electrical conductivity of the catalyst, whereas the electron transfer between active sites and reactant molecules is mainly influenced by the type and distribution of surface functional groups.

For example, Zheng et al. [107] enhanced the electrical conductivity of g-C₃N₄ by *in situ* growth of N-doped carbon nanotubes between g-C₃N₄ nanosheets and Ni species, forming an interconnected conductive network (Fig. 8(a)). This composite catalyst (TF-SA/NPs) exhibited a conductivity improvement of more than three orders of magnitude compared to pristine g-C₃N₄. In electrochemical CO₂RR, the TF-SA/NPs catalyst demonstrated a significantly higher FE_{CO} than other reference catalysts, as shown in Fig. 8(b), highlighting the critical role of carbon nanotube incorporation in boosting electronic transport and catalytic performance.

Liu et al. [145] synthesized P-doped onion-like carbons (P-OLC) via impregnation and chemical vapor deposition (CVD) methods, resulting in P-OLC-IP and P-OLC-CVD, respectively. P-OLC-IP contains only P-O functional groups, while P-OLC-CVD

incorporates both P-O and P-C functionalities, as shown in Fig. 8(c). The P-OLC-CVD catalyst exhibited markedly superior electrochemical CO₂RR performance compared to P-OLC-IP (Fig. 8(d)). This enhanced activity was attributed to the presence of P-C groups, which facilitate more efficient electron transfer between the catalyst and CO₂ molecules, thereby improving the overall electronic conductivity and catalytic effectiveness.

Previous studies have indeed demonstrated that the electrical conductivity of catalysts and the presence of surface functional groups independently influence electron transport and electron transfer, respectively. However, research in this area remains limited, and the underlying mechanisms are not yet fully understood. Future studies should focus on elucidating the structure-activity relationships between catalytic performance, conductivity, and functional groups through rational regulation of these parameters, and further explore their specific mechanistic roles.

5 Conclusions and perspectives

The rational structural design of carbon-based catalysts provides a promising pathway for boosting the efficiency, selectivity, and stability of electrochemical CO₂RR, thus contributing to practical carbon neutrality solutions and renewable electricity utilization. In this review, we systematically examined the dual aspects of catalyst design including active site engineering and mass/charge transport regulation, highlighting their respective roles and intricate interplay in determining catalytic performance. Key strategies, such as defect engineering, heteroatom doping, the creation of metal-carbon composites, and pore structure modulation, have significantly

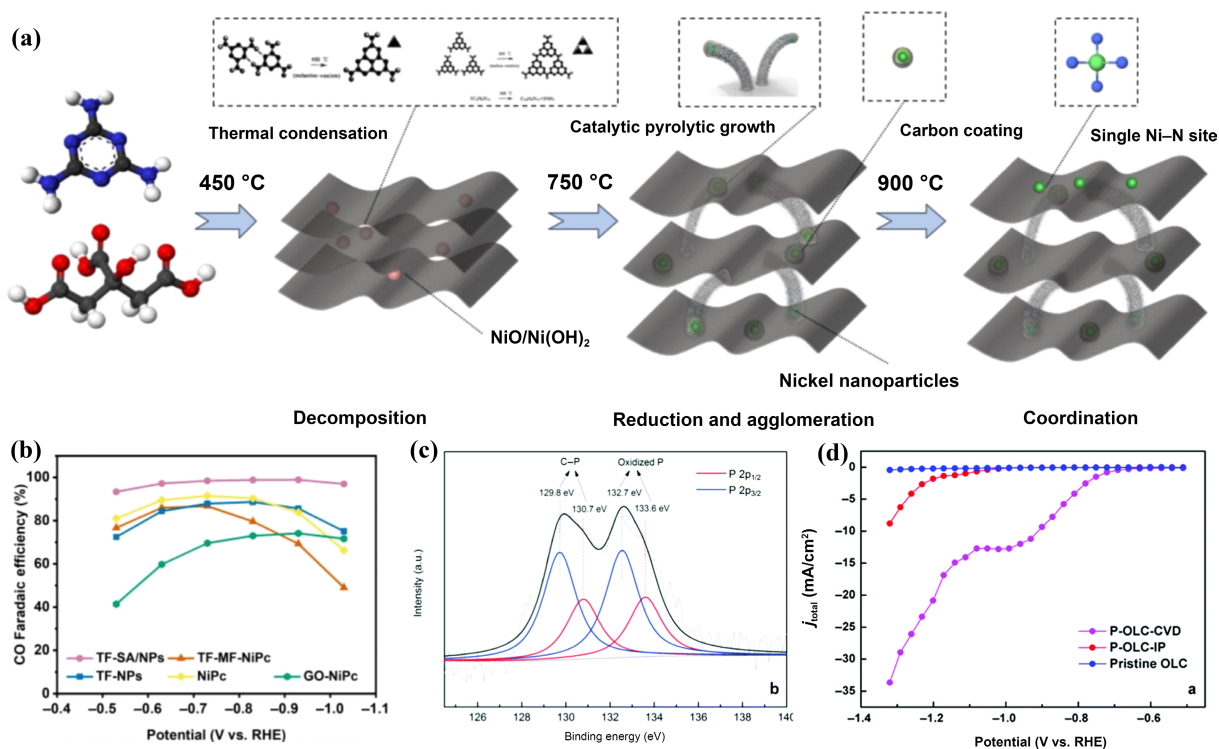


Figure 8 (a) Synthesis process of TF-SA/NPs. (b) FE_{CO} of the different catalysts. Reproduced with permission from Ref. [107], © Elsevier Inc. 2025. (c) P 2p X-ray photoelectron spectroscopy (XPS) spectra of P-OLC-CVD. (d) Linear sweep voltammetry (LSV) curves of OLC, P-OLC-CVD, and P-OLC-IP. Reproduced with permission from Ref. [145], © The Royal Society of Chemistry 2018.

advanced the understanding of structure–function relationships and promoted the construction of high-performance electrocatalysts. We hope to inspire new ideas for development of catalysts, thereby improving CO_2 conversion technologies.

Despite significant progress in developing CO_2 RR catalysts, several persistent challenges remain: First, most studies prioritize optimizing singular parameters while neglecting synergistic effects from coupled structural features. The lack of holistic design strategies impedes the identification of true performance-limiting factors. Second, the structural complexity of carbon-based catalysts, particularly those incorporating heteroatoms and metal species, hampers precise control over active site distribution and electronic properties. This necessitates broader adoption of advanced *in situ/operando* characterization and theoretical simulations to elucidate dynamic evolution of active sites and intermediates. Third, mass/charge transport limitations within catalysts and across electrode–electrolyte interfaces critically restrict active site accessibility and local reaction environments. Rational engineering of hierarchical porosity, surface wettability, and electronic conductivity is thus essential for efficient reactant diffusion and charge transfer.

Looking forward, several research directions merit particular attention:

(1) Integrated multi-variable design: Future efforts should move beyond the regulation of single parameters to embrace integrated strategies that simultaneously optimize active site chemistry, pore structure, and transport properties. This may be achieved by combining advanced synthesis methods, such as template-assisted assembly, atomic layer deposition, and molecular self-assembly, with precise control over composition and morphology.

(2) Mechanistic elucidation: A deeper mechanistic understanding of CO_2 RR is critical on carbon-based catalysts. *In situ*

characterization techniques (e.g., X-ray absorption, Raman, and infrared spectroscopy) and multiscale modeling can provide valuable insights into reaction pathways, active site evolution, and mass/charge transport phenomena under working conditions.

(3) Heteroatom and metal synergy: The rational incorporation of multiple heteroatoms (N, S, P, B, etc.) and the controlled loading of metal species can generate unique electronic structures and active sites, potentially yielding synergistic effects that surpass the sum of individual components. Systematic studies on the roles and interactions of different dopants and composites are needed to guide catalyst design.

(4) Scalability and practical application: For industrial implementation, the scalability, cost-effectiveness, and long-term durability of carbon-based catalysts must be considered. Developing scalable synthesis routes, optimizing electrode architectures for flow cells, and conducting comprehensive techno-economic and life-cycle assessments will be vital for bridging the gap between laboratory research and real-world applications.

(5) Interdisciplinary collaboration: Progress in this field relies on close collaboration between chemists, material scientists, and engineers. Such synergy will foster innovation in catalyst synthesis, mechanistic studies, device integration, and system optimization.

In summary, the ultimate goal is to realize robust, cost-effective, and high-performance carbon-based electrocatalysts for CO_2 RR through the integration of multi-level design strategies and advanced scientific tools. Achieving this vision will accelerate the practical deployment of electrochemical CO_2 reduction technologies.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. K. Y.: Conceived the theme and framework, writing manuscript. D. D. Z., S. Q. C., and L. H. W.: Literature search. B. L.: Conceptualization, H. X. L.: Methodology, investigation. X. R. W.: Data curation, formal analysis. W. H. W.: Project administration, supervision, manuscript review, and funding acquisition. H. N., J. S. Z., and M. B. W.: Manuscript review and editing, project administration, and funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

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