Rational Design Strategies for Electrocatalytic CO_2 Reduction: From Nanostructured Metals to Metal-Free and Molecular Catalysts

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Abstract：The electrochemical CO_2 reduction reaction (CO_2RR) is a promising strategy for converting carbon dioxide into value-added fuels and chemicals using renewable electricity. This review summarizes recent advances in CO_2RR catalysts, focusing on metal-based nanostructured catalysts, metal-free catalysts, and molecular metal complex catalysts. Key design strategies, including nanostructure engineering, heteroatom doping, defect regulation, coordination-environment tuning, and framework optimization, are discussed in relation to catalytic activity, selectivity, and stability. Particular attention is paid to structure-performance relationships, reaction mechanisms, and product distribution. Major challenges, including limited selectivity, poor durability, competing hydrogen evolution, and difficulty in identifying true active sites, are also discussed. Finally, future perspectives for the design of efficient and stable electrocatalysts for practical CO_2 electrolysis are proposed.

Keywords: Electrochemical CO_2 reduction; CO_2RR; Electrocatalysts; Catalyst design strategies

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1 Introduction

Electrochemical CO_2 reduction (CO_2RR) is a promising strategy for converting CO_2 into value-added chemicals and fuels using renewable electricity, offering opportunities for carbon utilization, energy storage, greenhouse-gas mitigation, and reduced dependence on fossil resources.[1,2] Benefiting from the modularity of electrolysis devices, CO_2RR also shows considerable potential for flexible integration and large-scale industrial deployment.[3]

However, the practical application of CO_2RR is still limited by insufficient selectivity, inadequate catalyst durability, and high energy consumption. The formation of multi-carbon products involves complex reaction pathways and kinetically demanding C-C coupling steps, making catalytic performance highly dependent on the electronic structure and surface properties of electrocatalysts.[4,5] In addition, catalyst reconstruction and degradation during long-term operation can cause activity loss and product redistribution, while the competing hydrogen evolution reaction further decreases selectivity and overall energy efficiency.[3] To address these issues, extensive efforts have been devoted to catalyst design and system optimization. CO_2RR performance is governed not only by intrinsic catalyst properties, such as composition, morphology, particle size, and crystal structure, but also by extrinsic factors including applied potential, electrolyte composition, pH, CO_2 concentration, temperature, and pressure.[6–8] Therefore, the development of efficient CO_2RR systems requires the integrated regulation of catalyst structure and reaction conditions.[9–11]

In this review, recent advances in electrocatalytic CO_2 reduction are systematically summarized, with emphasis on catalyst design strategies, performance characteristics, current challenges, and future directions for efficient and stable CO_2 electrolysis systems.

2 Metal-based nanostructured catalysts

The electrocatalytic reduction of carbon dioxide (CO_2RR) is kinetically challenging because of the high stability and linear molecular structure of CO_2.[10,12] Bulk metal catalysts often suffer from low atomic utilization, limited active-site exposure, and insufficient mass activity.[13] Nanostructure engineering can improve catalytic performance by regulating surface atomic arrangement and electronic structure. Owing to their high surface-to-volume ratio and abundant active sites, nanostructured catalysts generally exhibit better activity and selectivity than bulk metals.[14]

In aqueous electrolytes, CO_2RR occurs at the gas-liquid-solid interface and competes with the hydrogen evolution reaction. The process involves CO_2 diffusion, adsorption, intermediate formation, and product desorption. Since the binding strength of intermediates strongly affects selectivity and efficiency, catalyst morphology, surface structure, and electronic properties must be carefully tuned according to the Sabatier principle.[15–17]

In this section, metal-based nanostructured CO_2RR catalysts are discussed in three categories: metal nanoparticles, metal oxide/sulfide nanomaterials, and bimetallic or alloy catalysts.

2.1 Metal nanoparticles (NPs)

Metal nanoparticles (NPs), including noble and non-noble metals, have been widely studied for CO_2RR because their tunable size, morphology, and surface atomic arrangement allow effective regulation of intermediate adsorption and catalytic selectivity.[18,19]

Au-based nanoparticles are representative catalysts for CO_2-to-CO conversion because their weak CO binding facilitates CO desorption.[20] Representative studies have shown that Au nanostructures can achieve high activity and CO selectivity under alkaline conditions.[21] Particle size and morphology strongly influence CO_2RR pathways: ultrasmall Au nanoparticles show enhanced activity, whereas in Cu-based catalysts, smaller particles tend to favor CO formation while larger ones are more selective toward C^{2+} products (Fig.

1a,b).[24-25]

Facet engineering also plays an important role. Pd (111)-dominated nanoparticles showed high CO selectivity, while Zn-based catalysts exhibited facet-dependent selectivity between CO formation and HER.[24,25] In addition, surface functionalization and support engineering can further improve selectivity and durability (Fig. 1c,d).[26,27]

Metal nanoparticles are promising for CO_2RR, but agglomeration, competitive HER, catalyst reconstruction, and limited long-term stability remain major challenges.

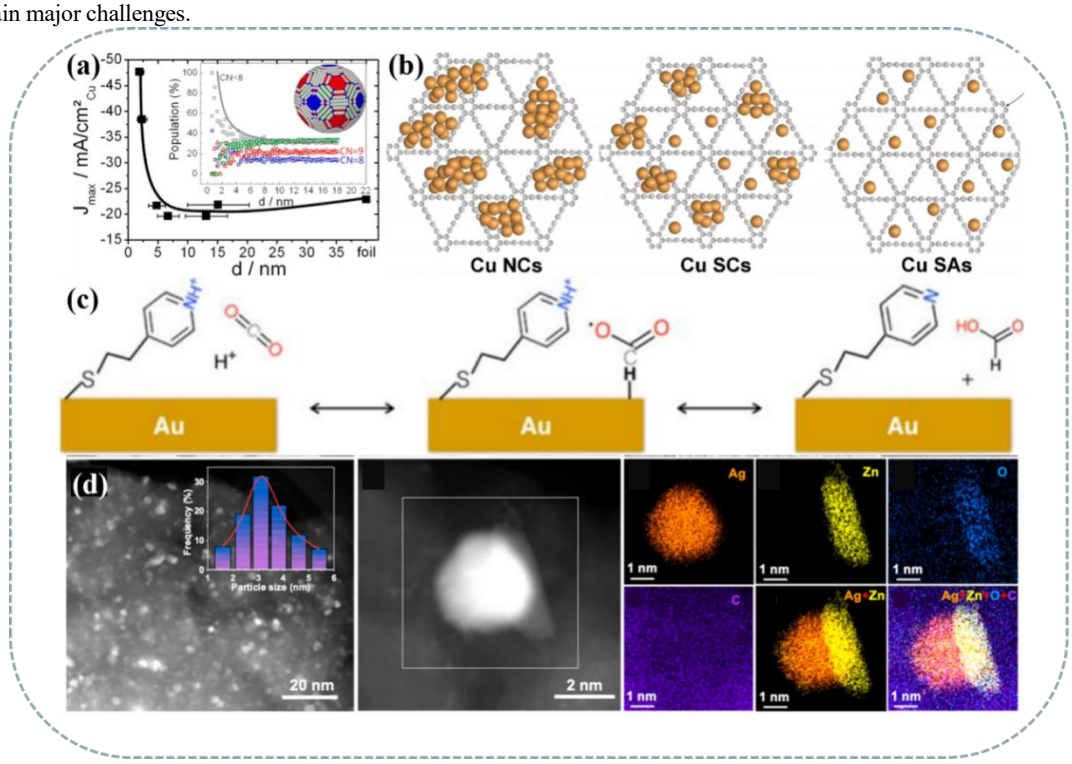

Fig. 1 (a) Faradaic current densities of Cu NPs with different sizes.[23] (b) Synthesis of Cu NPs, Cu clusters, and Cu SACs.[22] (c) Formate formation mechanism on a 4-pyridylethylmercaptan-modified Au surface.[27] (d) HRTEM image and corresponding EDS mapping of ZnO-Ag NPs.[26]

2.2 Metal oxide and sulfide nanomaterials

Compared with noble metals, non-noble-metal oxides have attracted attention for CO_2RR because of their low cost and tunable properties, although poor conductivity often limits their performance.[28,29] To overcome this drawback, heterostructure/carbon composite construction, electronic-state modulation, and defect engineering have been widely employed.

Representative studies showed that Sn-ZnO heterointerfaces enabled high CO selectivity and long-term stability (Fig. 2a),[30] while Mo-substituted ZnO enhanced CO_2RR activity and suppressed HER (Fig. 2b).[31] Defect engineering also played an important role: in SnO_2, in-situ-generated metallic Sn was identified as the active species for CO_2-to-formate conversion (Fig. 2c),[32] and in ZnO-based catalysts, defective structures and oxygen vacancies promoted CO_2 activation and improved syngas or CO production.[33,34] In addition, a CuO/C_eO_2 heterostructure promoted CO_2 adsorption and C-C coupling, while Nb-doped MoS2 showed much higher activity than pristine MoS2 (Fig. 2d,e).[35,36]

Metal oxide and sulfide nanomaterials are promising for CO_2RR, but conductivity, active-site identification, and long-term stability remain key challenges.

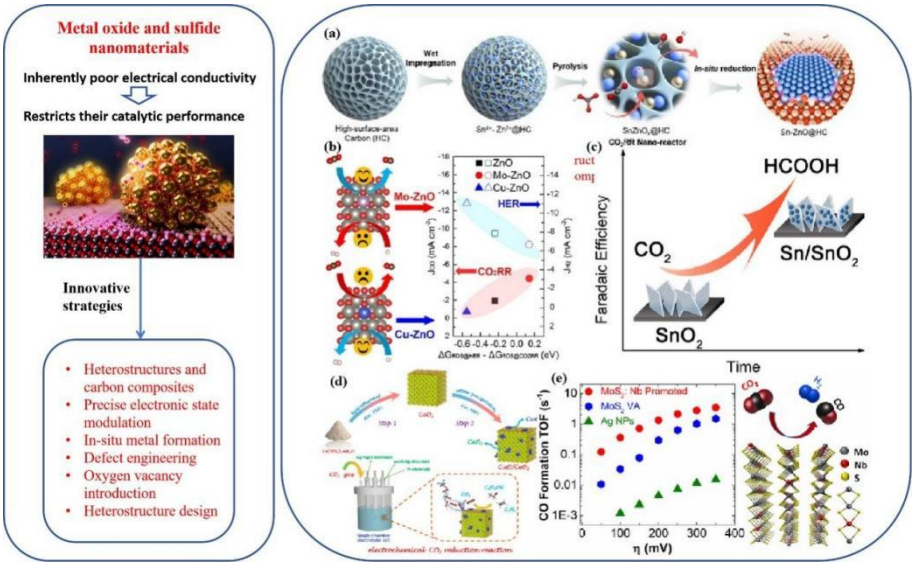

Fig. 2 (a) Synthesis of Sn-ZnO@HC materials.[30] (b) CO_2 electrolysis over Cu-ZnO catalysts. [31] (c) HCOOH production over Sn/SnO_2 catalysts.[32] (d) Synthesis of CeO_2 and CuO/CeO_2.[36] (e) TOF for CO production over MoS_2 catalyst.[35]

2.3 Bimetallic catalyst and metal alloy catalyst

Bimetallic and alloy catalysts have attracted increasing attention for CO_2RR because interactions between different metal components can regulate the local electronic structure of active sites, thereby affecting intermediate adsorption and product selectivity.[37,38] Compared with monometallic catalysts, they often show improved activity and selectivity owing to synergistic effects between different metal species (Fig. 3).

Pd-Cu catalysts are representative examples, with product distribution strongly dependent on metal composition: Cu_3Pd favored CH_4 production, whereas Pd_3Cu showed high selectivity for CO.[39] Other alloy systems, including PdCu and Cu-Zn, also exhibited enhanced CO_2-to-CO performance,[40,41] while Ag introduction into Cu-Zn alloys further promoted CO formation. Regulated Cu-Zn interfacial sites promoted C_2 product formation, and PtZn intermetallic nanoalloys showed structure-dependent selectivity for CO_2-to-CH_3OH conversion.[42,43]

Bimetallic and alloy catalysts are promising for CO_2RR, but catalyst stability, synthesis control, and long-term application remain challenging.

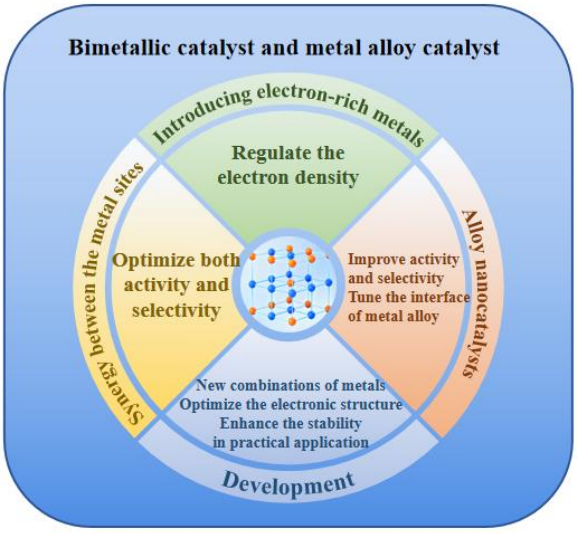

Fig. 3 Bimetallic and alloy catalysts for CO_2RR.

3 Metal-free catalysts

Metal-free catalysts have attracted increasing attention for CO_2RR because of their low cost, corrosion resistance, and tunable structures. Representative systems include heteroatom-doped carbon materials, COFs, g-C_3N_4, BDD, and homogeneous molecular catalysts. Among them, heteroatom-doped carbon materials have been most extensively studied, although the exact active sites and mechanisms remain unclear (Fig. 4).[44]

N-, B-, and P-doped carbon materials have shown good CO_2RR activity and selectivity.[45] Porous N-doped carbon enabled stable syngas

production, while B,N co-doped mesoporous carbon achieved high CO selectivity (Fig. 4a).[46,47] Ternary-doped carbon materials also showed high CO Faradaic efficiency and good durability.[48] In addition, intrinsic carbon defects can also serve as active sites, although the roles of different nitrogen species and oxygen-containing groups remain under debate.[49,50]

Other metal-free systems have also shown promise. COFs provide precise active sites and tunable pore structures, (Fig.4c).[51] g-C_3N_4 can be optimized through defect engineering and interfacial regulation, (Fig.4b).[52] and BDD exhibits surface-state-dependent catalytic behavior. (Fig.4d).[53] Homogeneous metal-free molecular catalysts also offer well-defined reaction pathways.[54]

Metal-free catalysts are promising for CO_2RR, but identifying true active sites, clarifying reaction mechanisms, and improving long-term stability remain key challenges.

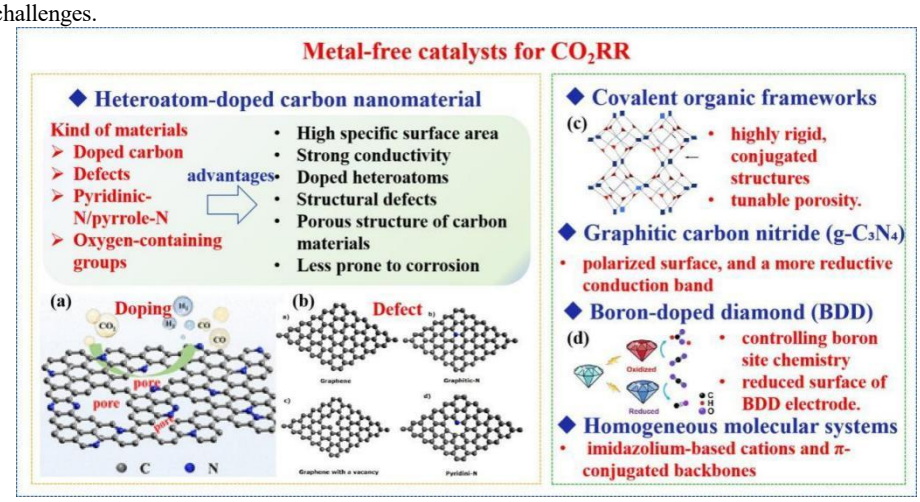

Fig. 4 Metal-free catalysts for CO_2RR: (a) Fabrication of porous N-doped carbon (PNC).[46] (b) Supercell model of defective graphene.[52] (c) Structure of COFs. (d) Reduced boron-doped diamond.[55]

4 Molecular metal complex catalyst

Metal complex catalysts, also referred to as molecular catalysts, have shown promising CO_2RR performance because of their well-defined coordination environments and tunable electronic structures.[56,57] Various molecular complexes have been explored for CO_2RR. Increasing macrocycle rigidity in nickel complexes improved CO selectivity (Fig. 5a),[58] Sn-PANI showed the best performance among metal-cation-doped polyaniline catalysts (Fig. 5b),[59] and transition-metal porphyrins exhibited metal-center-dependent selectivity, with Co-Pc showing the highest CO selectivity.[60]

MOFs are another important class of metal complex catalysts because of their high porosity and tunable structures, although low conductivity remains a major limitation. Conductive polypyrrole incorporation enabled PPy@MOF-545-Co to achieve a CO Faradaic efficiency of 98% at -0.8 V (Fig. 5c),[61] while ligand engineering improved MOF performance, as CALF20 showed 94% CO Faradaic efficiency (Fig. 5d).[62]

Metal complex catalysts, especially molecular complexes and MOFs, are promising for CO_2RR, but conductivity, structural stability, and long-term performance remain key challenges.

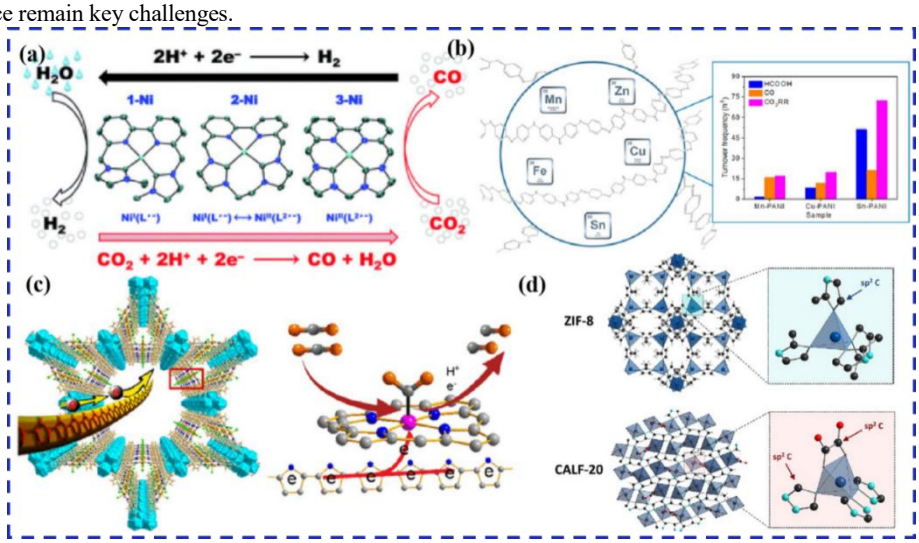

Fig. 5 (a) CO_2 electrolysis over nickel (II) catalysts.[58] (b) Polymer-metal complexes as emerging CO_2RR catalysts.[59] (c) Role of PPy in MOF-545-Co channels for CO_2RR.[61] (d) Structures of ZIF-8 and CALF20.[62]

5 Current Challenges and Future Outlook

Despite significant progress, the practical implementation of electrochemical CO_2 reduction still faces major challenges, including limited selectivity, insufficient durability, high overpotentials, and incomplete mechanistic understanding. Reactor design, mass transfer, product separation, and catalyst sustainability also hinder large-scale application.

Addressing these issues requires the integrated optimization of catalytic materials and electrolysis systems. Greater attention should be given to low-cost and recyclable catalysts, defect and interface engineering, advanced electrolyzers, and high-current-density reactors. Coupling CO_2RR with renewable energy, together with AI-assisted catalyst screening and in situ/operando characterization, may further accelerate catalyst development. With continued advances in catalyst design and electrolyzer engineering, CO_2RR is expected to play an increasingly important role in sustainable carbon conversion.

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