

Ligand and support engineering of metal nanoclusters for electrochemical CO₂ reduction

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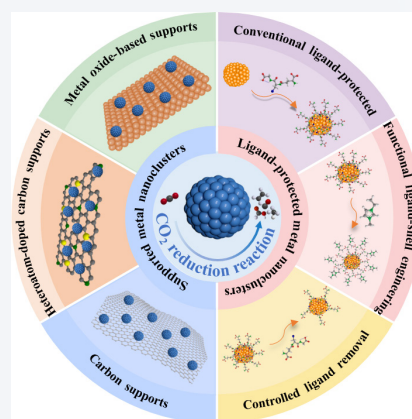
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ABSTRACT: Electrochemical CO₂ reduction reaction (CO₂RR) provides an attractive route for converting CO₂ into value-added fuels and chemicals using renewable electricity. However, its practical development is still hindered by thermodynamic stability and kinetic inertness of CO₂, the competing hydrogen evolution reaction, and the complex multielectron–proton reaction pathways. Atomically precise metal nanoclusters (NCs) have emerged as a distinctive class of CO₂RR electrocatalysts owing to their well-defined compositions, discrete electronic structures, abundant low-coordination metal sites, and highly tunable surface microenvironments. In this review, we summarize recent advances in ligand-protected and supported metal NCs for CO₂ electroreduction with emphasis on reaction mechanisms and structure–performance relationships. We first discuss reaction mechanisms obtained from atomically precise NCs as model systems for identifying active sites, key intermediates, and selectivity-determining steps. Then, ligand engineering for regulating the catalytic performance of NCs is highlighted, including conventional ligand protection, functional ligand engineering, and controlled ligand removal or reconstruction, which regulate electronic structures, cation accumulation, interfacial solvation, and local reaction environments. Subsequently, supported metal NCs are discussed by classifying support effects into conductive or defective carbon interfaces, heteroatom-doped carbon, and metal oxide/zeolite-based confined interfaces. Finally, we outline current challenges and future opportunities in precise synthesis, *operando* characterization, theoretical modeling, dynamic structural stability, and device-level evaluation, aiming to guide the rational design of next-generation nanocluster electrocatalysts for CO₂RR and beyond.

KEYWORDS: metal nanoclusters, CO₂ electroreduction, reaction mechanism, ligand engineering, metal–support interactions



1 Introduction

The continuous increase in CO₂ emissions has intensified global

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climate and energy challenges. Recent Global Carbon Budget assessments estimate total anthropogenic CO₂ emissions in 2025 to be approximately 42.2 billion tons, creating an urgent demand for sustainable technologies that can couple carbon utilization with renewable energy conversion [1]. The electrochemical CO₂ reduction reaction (CO₂RR) offers a promising route to convert CO₂ into value-added chemicals and fuels under relatively mild conditions, thereby providing a potential pathway toward a closed carbon cycle [2, 3]. However, the practical application of CO₂RR remains highly challenging, since CO₂ is thermodynamically stable and kinetically inert, while the hydrogen evolution reaction (HER)

competes strongly under cathodic conditions in aqueous electrolytes. Moreover, the formation of target products involves proton-coupled electron-transfer steps and a series of adsorbed intermediates with closely related binding energetics, making it difficult to simultaneously optimize activity, selectivity, and stability [4, 5]. Therefore, developing electrocatalysts with well-defined active sites and controllable interfacial microenvironments is crucial for moving CO₂RR research beyond empirical performance optimization toward mechanism-guided catalyst design [6–9]. These requirements make atomically precise catalysts particularly valuable, because catalytic behavior can be related to defined atomic and interfacial structures. However, it should be emphasized that atomic precision in the as-synthesized state does not necessarily imply that the initial nanocluster structure remains unchanged under electrochemical CO₂RR conditions. Actually, ligand-protected or supported metal nanoclusters undergo ligand dissociation, surface reconstruction, metal oxidation-state variation, interfacial charge redistribution, and support-induced structural evolution during operation. Consequently, many reported structure–performance relationships actually correlate well-defined pre-catalysts with reconstructed or partially reconstructed states, rather than directly revealing the intrinsic structure–function relationship of dynamic *in situ* active sites. This dynamic evolution constitutes a central challenge for nanocluster-based CO₂RR catalysis. The catalytically active structure must be understood as an evolving metal–core/ligand/support/interfacial system rather than as a static atomic structure. Resolving this issue requires *operando* characterization and theoretical modeling capable of tracking ligand stability, active-site exposure, metal valence changes, charge redistribution, and intermediate binding under realistic reaction conditions. These considerations make atomically precise metal nanoclusters particularly valuable model systems, since their well-defined initial structures provide a reliable reference for identifying the catalytic active sites generate or transform process during CO₂RR [10–12].

Over the past decade, metal nanoparticles, molecular complexes, single-atom catalysts, and metal oxides have been extensively investigated for CO₂RR [13–18]. These studies have revealed that catalytic performance is highly sensitive to composition, particle size, coordination structure, oxidation state, surface defects, and local reaction environments [19–21]. Among these catalyst systems, metal nanoclusters (NCs), typically located between single atoms and conventional nanoparticles, have recently emerged as a unique class of CO₂RR electrocatalysts. Owing to their atomically precise compositions, well-defined structures, discrete electronic states, abundant low-coordination metal sites, and tunable surface chemistry, metal NCs provide not only promising catalytic platforms but also ideal model systems for establishing atomic-level structure–performance relationships. Their molecule-like electronic structures and high fraction of exposed metal atoms enable the modulation of CO₂ activation, intermediate adsorption, charge redistribution, and product selectivity.

Despite these advantages, metal NCs are intrinsically susceptible to aggregation or structural reconstruction under electrocatalytic conditions because of their high surface energy [22–24]. Ligand protection and support immobilization have therefore become two major strategies for stabilizing NCs and regulating their catalytic behavior. In ligand-protected NCs, the ligand shell is no longer regarded merely as a stabilizing layer. Indeed, the ligand shell can actively participate in constructing the catalytic interface by

modulating the electronic structure of the metal core, local solvation, cation enrichment, and proton-transfer processes. In parallel, support engineering provides another effective route to improve the stability, conductivity, and interfacial reactivity of metal NCs through strong metal–support interactions, defect coordination, confined interfacial environments, and interfacial charge transfer. These two strategies provide complementary routes for converting the structural precision of NCs into controllable CO₂RR performance. Accordingly, organizing this review around ligand and support effects provides a direct link between structural stabilization and catalytic function.

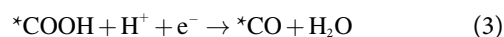
In this review, we summarize recent advances in ligand-protected and supported metal NCs for electrochemical CO₂ reduction, with particular emphasis on reaction mechanisms and structure–performance relationships. We first discuss ligand-protected NCs from the perspectives of conventional ligand stabilization, functional ligand-shell engineering, and controlled ligand removal/reconstruction. We then examine supported NCs by classifying support effects into carbon-based conductive and defective interfaces, heteroatom-doped carbon supports, and metal oxide/zeolite-based charge-transfer and confined interfaces. Finally, we outline current challenges and future opportunities in precise synthesis, *operando* characterization, theoretical modeling, dynamic stability, and device-level evaluation (Fig. 1). This Review aims to provide mechanistic insights and design principles for the rational development of next-generation nanocluster electrocatalysts for CO₂RR and broader energy electrocatalysis.

2 Fundamentals and reaction mechanism of CO₂RR on atomically precise metal nanoclusters

Atomically precise metal nanoclusters are ideal model systems for revealing the microscopic mechanism of CO₂RR and establishing structure–activity relationships, owing to their discrete electronic energy levels, well-defined geometries, high fractions of low-coordinated surface atoms, and tunable ligand environment. Depending on the target products, nanoclusters achieve highly specific catalytic pathway selection by tuning the electronic structure of active sites, adsorption energies of intermediates, and local microenvironment [25]. In this section, the reaction mechanisms of nanoclusters in CO₂RR are systematically discussed based on the product types including CO, HCOOH (or formate), and C₂₊ products. This product-based organization links elementary reaction steps to the catalyst-design variables discussed in the following sections.

2.1 Reaction pathway for CO

CO is a representative two-electron reduction product of CO₂RR, and its formation pathway can be described by the following steps (Eqs. (1)–(7), where * refers to the active site), in which the formation of the *COOH intermediate is generally the rate-determining step (RDS) of this reaction pathway (Eq. (2) or (4)) (Fig. 2(a)) [26, 27].



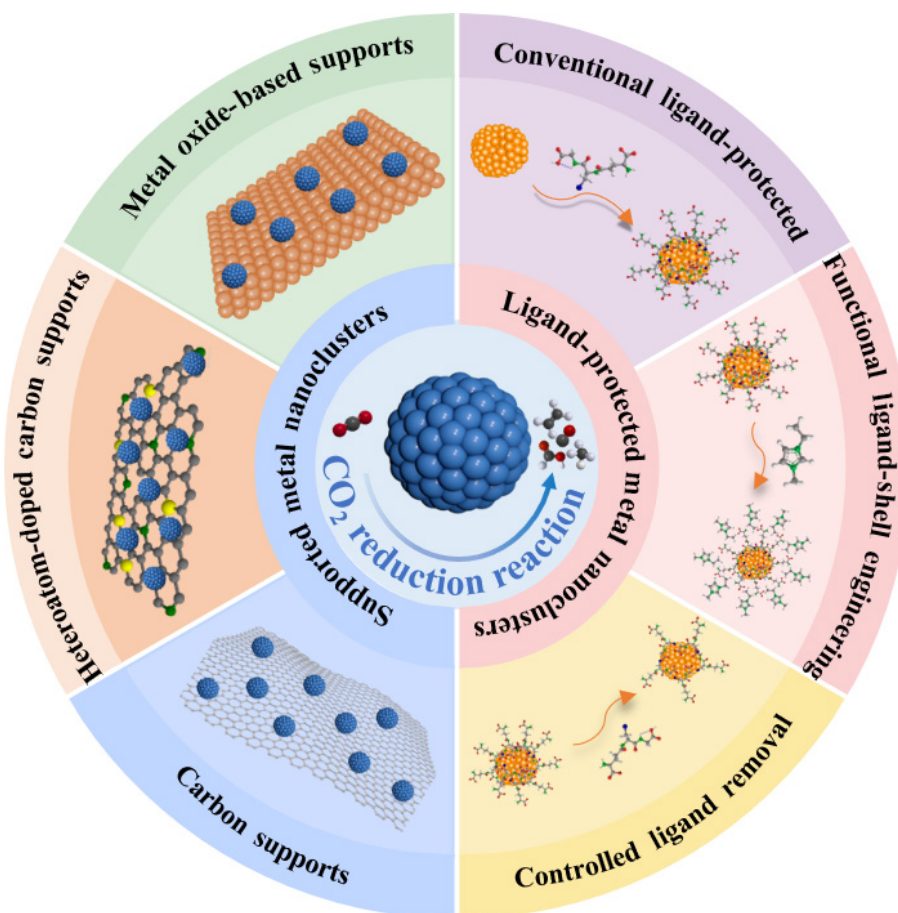


Figure 1 Schematic diagrams of ligand-protected and supported nanoclusters for CO₂ reduction reaction.



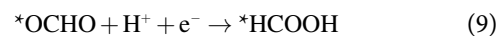
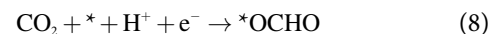
Equations (2) and (3) generally describe the pathway under acidic solution, Eqs. (4)–(6) are more relevant to neutral-to-alkaline conditions.

Au- and Ag-based nanoclusters are typical catalysts for efficient CO production because they can stabilize the key COOH intermediate while maintaining relatively weak CO binding, thereby facilitating CO desorption (Fig. 2(b)) [28–30]. Atomically precise Ag₂₅(IPBT)₁₈, Au₂₅(MHA)₁₈, and partially ligand-deficient Au₂₅(SR)₁₈ nanoclusters stabilize the critical *COOH intermediate and reduce its formation energy barrier via hydrophobic surface ligands, cation effects, and exposed Au active sites, respectively, thus steering catalytic selectivity toward CO generation [31–33]. It should be noted that the hydrophobic ligand shell of Ag₂₅(IPBT)₁₈ can also weaken the interaction between water molecules and the catalyst surface, lower the adsorption energy of the *CO intermediate, and facilitate CO desorption. Furthermore, unlike most Au-based clusters, the second electron-transfer step (Eq. (5)) serves as the RDS for Au₂₅(MHA)₁₈. Based on the thermodynamic and kinetic properties of the CO pathway, rational ligand

engineering strategies are proposed to improve CO selectivity. Hydrophobic alkyl or aromatic ligands isolate active sites from water to weaken *CO adsorption and increase CO desorption. Controlling ligand coverage produces ligand-deficient metal sites that lower the barrier for *COOH formation, and tuning ligand electron-donating/accepting effects adjusts the metal core electronic structure to balance *COOH and *CO binding and suppress competing HCOOH and C₂₊ pathways.

2.2 Reaction pathway for HCOOH (or formate)

The mechanistic pathway of HCOOH formation involves a two-electron and two-proton transfer process, with the formation of the *OCHO intermediate typically serving as the RDS (Fig. 2(c)). It can be described by the following elementary steps (Eqs. (8)–(10), where * denotes an active site)



The HCOOH pathway directly competes with CO formation during initial CO₂ activation, and the product selectivity depends on whether CO₂ binds to the catalyst through carbon to form *COOH (CO pathway) or oxygen atom to yield *OCHO (HCOOH pathway). Sn- or Bi-based metal sites with strong oxygen affinity

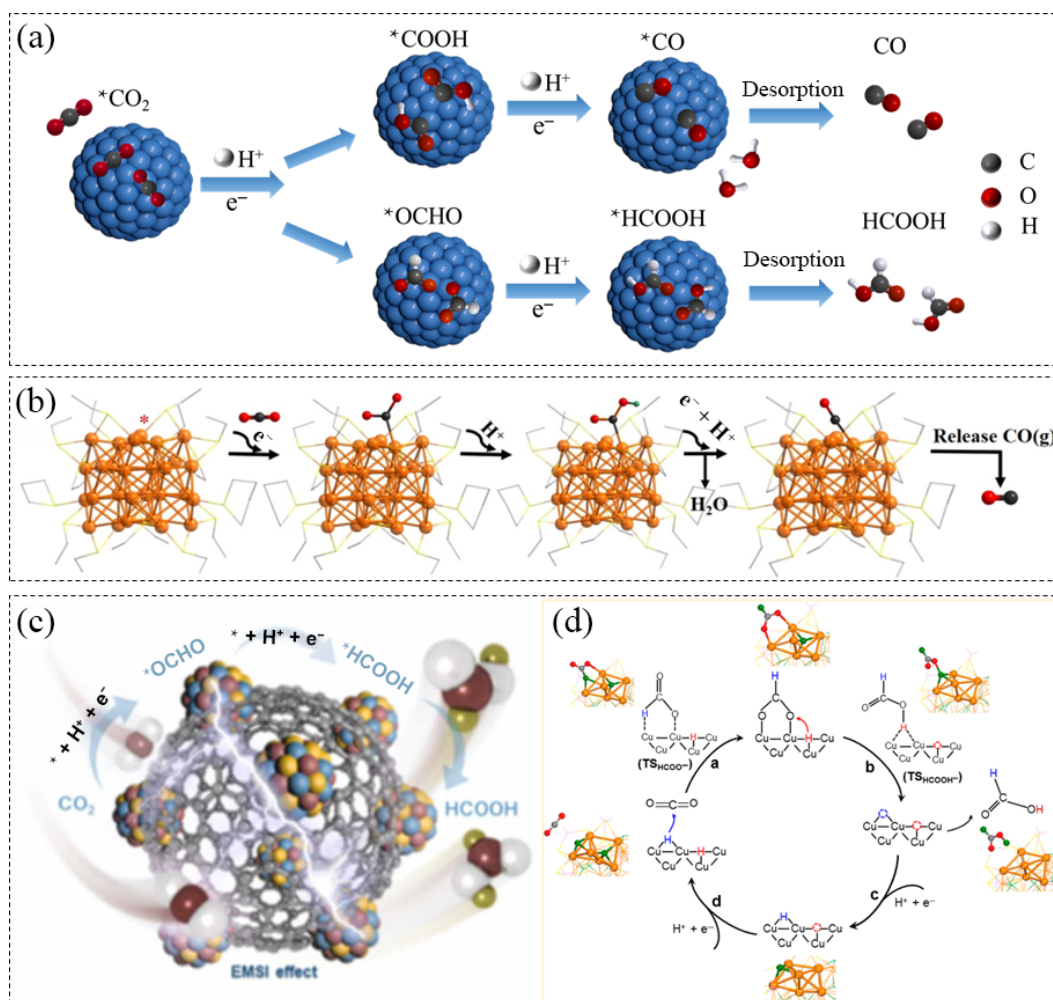


Figure 2 (a) Pathway diagram for the formation of CO and HCOOH. (b) The schematic diagram of the electrocatalytic carbon dioxide reaction process on Au₃₈-S. Au: orange, S: yellow, C: black and grey, and O: red. Hydrogen atoms are omitted for clarity. Reproduced with permission from Ref. [27], © Wiley-VCH GmbH 2022. (c) Schematic diagram of formate formation on BiOI-C. Reproduced with permission from Ref. [34], © Sui, P. F. et al. 2025. (d) Overall mechanism of HCOOH formation from CO₂ reduction on Cu₃₂H₂₀L₁₂ via the lattice-hydride channel; the structures of the key intermediates and transition states are shown. Color code: orange, Cu; green, hydride; red, oxygen; gray, carbon; and L = S₂PH₃, not shown. Reproduced with permission from Ref. [41], © American Chemical Society 2017.

stabilize *OCHO, fundamentally distinguishing formate-selective catalysts from Au or Ag nanoclusters that favor CO production.

Benefiting from partially filled p-orbitals and intrinsic oxophilicity, p-block metal NCs (e.g., Bi, In, and Sn) preferentially anchor and stabilize the key *OCHO intermediate through O-binding, thereby steering CO₂RR selectivity toward HCOOH or formate [34–37]. Hybrid catalysts Bi₃/Bi₂O₂CO₃ and In-C₆₀ effectively facilitate the formation of the key *OCHO intermediate, optimize its adsorption energy, and lower the energy barrier for proton migration to generate *HCOOH via charge redistribution and modulation of In–O antibonding orbital occupation, respectively, thus achieving outstanding formate selectivity. Meanwhile, Bi₃/Bi₂O₂CO₃ catalysts further enhance CO₂ activation, making the elementary reaction spontaneous and exothermic [38, 39].

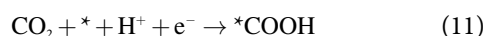
It is noted that Cu-based nanoclusters preferentially produce C₂₊ products under most conditions, yet core-structure modulation enables reaction switching toward the formate pathway. Liu et al. synthesized two structural isomers of Cu₈ clusters with cubic and bitetrahedral configurations [40]. Compared with cubic Cu₈, the core-exposed bitetrahedral counterpart features uniquely distorted

corner-site coordination, which reduces the Gibbs free energy for CO₂ activation to form HCOO*. This free-energy value is markedly lower than that for *COOH formation and facilitates moderate adsorption of HCOO*. Meanwhile, such distinctive coordination raises the energy barrier of HER to suppress the competing side reaction, steering the catalytic pathway selectively toward formate formation. Unlike the electroreduction pathway of Cu₈ nanoclusters, Cu₃₂H₂₀L₁₂ catalysts produce formate via a lattice hydride-mediated mechanism without additional coupled proton-electron transfer (Fig. 2(d)) [41]. Negatively charged intrinsic lattice hydride (H⁻) inside the cluster performs nucleophilic attack on the electropositive carbon atom of CO₂ to activate and convert CO₂. Specifically, a surface μ₃-H lattice hydride initially transfers to the carbon atom of CO₂ to form an adsorbed *HCOO intermediate; Subsequently, a structural μ₄-H hydride further adds onto *HCOO and triggers product desorption, affording efficient HCOOH production.

2.3 Reaction pathway for deep-reduction C₁ and C₂₊ products

Beyond two-electron products such as CO and formate, deep CO₂

reduction toward CH_4 and C_{2+} products requires additional proton/electron-transfer steps and, for C_{2+} products, C–C coupling between adsorbed carbonaceous intermediates. Given the extensive literature on CO_2 conversion to multicarbon products, this section briefly summarizes the reaction pathways most relevant to nanocluster-based catalytic systems [42–44]. The formation of multicarbon products mainly relies on Cu-based nanocluster catalytic systems. With moderate *CO adsorption affinity, Cu-based nanoclusters enable efficient and continuous electron and proton transfer. The adsorbed CO intermediates on these catalyst surfaces can be well stabilized, and further converted into diverse multi-electron reduction products via hydrogenation and/or C–C coupling (Figs. 3(a) and 3(b)) [45–47]. Taking the deep CO_2 reduction to methane (CH_4 , C_1) and ethylene (C_2H_4 , C_2) as model reactions, we systematically analyze their respective elementary steps.



Equation (13) corresponds to the RDS for CH_4 formation, and the resultant intermediate undergoes successive hydrogenation to form CH_4 ($\text{*CHO} \rightarrow \text{*CH}_2\text{O} \rightarrow \text{*CH}_3\text{O} \rightarrow \text{*CH}_2\text{OH} \rightarrow \text{*CH}_3 \rightarrow \text{CH}_4$) (Fig. 3(c)) [48]. For C_2H_4 production, the dimerization process in

Eq. (14) usually acts as the RDS, followed by sequential proton–electron-coupled transfers to complete the reaction ($\text{*OCCO} \rightarrow \text{*OCCOH} \rightarrow \text{*CCH}_2\text{O} \rightarrow \text{*CCH}_2\text{OH} \rightarrow \text{*CHCH}_2\text{OH} \rightarrow \text{*CHCH}_2 \rightarrow \text{C}_2\text{H}_4$).

Catalysts $\text{Cu}_6(\text{MBD})_6$ and $\text{NHCH}^{\text{H}}\text{-Cu}_7$ can effectively stabilize the *CO intermediates derived from *COOH conversion by regulating the coordination environment and electronic structure of Cu active sites [49, 50]. In this catalytic system, the energy barrier for *CHO formation is lower than that for *CO desorption, which drives the subsequent hydrogenation of intermediates to form CH_4 or C–C coupling to produce C_2H_4 . Both catalysts preferentially produce CH_4 , where the conversion of *CO to *CHO acts as the core reaction bottleneck. Nevertheless, Ge et al. demonstrated that the interfacial synergy between Cu sites and nitrogen-containing supports can overcome this limitation by strengthening CO_2 adsorption and suppressing the HER, thereby boosting the selectivity toward the CH_4 pathway [51].

The intermediates *CHO and $(\text{*CO})_2$ act as pivotal species governing the product selectivity between C_1 and C_{2+} products during CO_2RR . For Cu-based nanoclusters (Cu_{45} and Cu_8), the exposed Cu–Cu dual-active sites and moderate CO coverage effectively stabilize the $(\text{*CO})_2$ dimer [52, 53]. This favors the C–C coupling of adsorbed *CO intermediates and consequently drives the reaction toward C_{2+} product formation. Meanwhile, Cu_8 exhibits a high activation energy for water dissociation, which maintains a low surface coverage of *H and further suppresses the generation of *CHO species. Therefore, promoting C_{2+} formation requires the coordinated regulation of *CO adsorption, local *CO coverage, adjacent metal ensembles for C–C coupling, and proton availability.

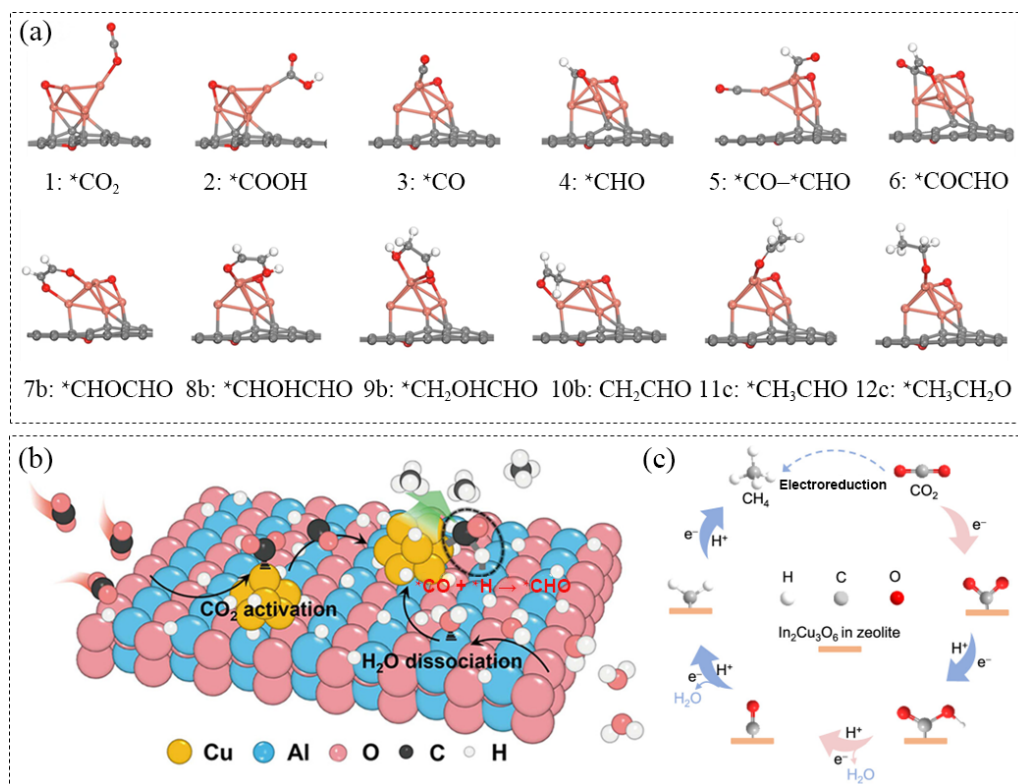


Figure 3 (a) The optimized configurations of $\text{CH}_3\text{CH}_2\text{OH}$ intermediates. Reproduced with permission from Ref. [46], © Liu, K. Y. et al. 2025. (b) A proposed multi-site reaction mechanism for the CO_2RR to CH_4 on the $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalysts. Reproduced with permission from Ref. [47], © Zeng, X. K. et al. 2026. (c) Proposed reaction pathway of the electrochemical conversion of CO_2 to methane on the $\text{In}_2\text{Cu}_3\text{O}_6/\text{zeolite}$ electrode. Reproduced with permission from Ref. [48], © American Chemical Society 2025.

These mechanistic insights directly guide ligand and support engineering strategies for nanocluster catalysts. Ligands can tune the electronic structure of metal cores, regulate CO binding, suppress excessive proton access through hydrophobic microenvironments, and modulate steric accessibility of neighboring active sites. Meanwhile, supports can stabilize low-coordination metal ensembles, facilitate interfacial charge transfer, enrich CO₂/CO intermediates, and regulate local pH or water activation. In this context, the mechanistic differences among CO, formate, and C₂₊ pathways provide a rational framework for understanding how ligand shells and support interfaces steer CO₂RR product selectivity. Therefore, modulating the binding strength of *CO intermediates on the catalyst surface to facilitate the C–C coupling process is a core strategy for developing nanocluster electrocatalysts toward selective C₂₊ production. Thus, the mechanistic distinction among CO, formate, and C₂₊ pathways provides the basis for understanding how ligand and support environments regulate product selectivity.

3 Ligand-protected metal nanoclusters for CO₂RR

Ligand-protected metal NCs bridge molecular catalysts and heterogeneous electrocatalysts, providing a structurally well-defined platforms for mechanistic investigation. The metal core and ligand shell collectively determine cluster stability, electronic structure, active-site accessibility, and the local reaction environment. For CO₂RR, this cooperation is especially important since the reaction occurs at a gas–liquid–solid interface, where CO₂ activation, proton-coupled electron transfer, intermediate stabilization, and product desorption are all sensitive to the outer coordination sphere. Accordingly, ligand-protected NCs are discussed here in terms of three interconnected strategies: conventional ligand protection, functional ligand-shell engineering, and controlled ligand removal or ligand-shell reconstruction [5]. This framework emphasizes that ligands can function not only as stabilizers but also as regulators of the catalytic microenvironment.

3.1 Conventional ligand-protected nanoclusters: Stabilization and intrinsic ligand effects

Atomically precise ligand-protected NCs are generally denoted as [M_n(L)_m]^q, where M denotes the metal atoms in the metal core and surface coordination units, L refers to the protecting ligands, and *q* is the overall charge state of the cluster [54]. Conventional ligands, including thiolates, glutathione (GSH), phosphines, alkynyls, halides, and N-heterocyclic carbenes (NHCs), play a vital role in stabilizing ultrasmall metal cores and maintaining their molecule-like electronic structures [55–57]. Through strong metal–ligand coordination, these ligands determine the metal-atom nuclearity, surface structure, and charge state of nanoclusters, while preventing aggregation and structural degradation under reaction conditions. Although conventional ligands primarily serve to stabilize atomically precise nanoclusters, their chemical identity, surface coverage, and binding configuration may also affect catalytic behavior. These catalytic effects are discussed separately in Section 3.2 according to their dominant mechanistic roles, including electronic, microenvironmental, and steric regulation. Therefore, in this section, we mainly focus on conventional ligand-protected nanoclusters as structurally stabilized model systems, while also highlighting their intrinsic catalytic influence and

limitations in CO₂RR. Beyond their stabilizing role, conventional ligands can also influence CO₂RR by regulating the electronic structure of surface metal atoms, suppressing the competing HER, and regulating the local reaction environment at the metal–ligand interface. Therefore, conventional ligands should be regarded as active components of nanocluster electrocatalysts rather than merely protective agents [58].

The catalytic performance of ligand-protected nanoclusters in CO₂RR was first demonstrated by Kauffman and co-workers in 2012, who used phenylethyl-thiolate-protected Au₂₅(SR)₁₈ as an atomically precise model catalyst for electrochemical CO₂-to-CO conversion [57]. Their work showed that a well-defined Au₂₅ structure can promote CO₂ electroreduction in aqueous media. It also provided an early example of correlating catalytic behavior with a specific metal core and ligand environment, and the catalyst delivered peak CO conversion at –1.0 V vs. reversible hydrogen electrode (RHE) with a Faradaic efficiency (FE) of approximately 100%. Compared with conventional nanoparticles, whose active sites are often structurally heterogeneous, ligand-protected nanoclusters offer a more defined platform for identifying active-site structures and understanding structure–performance relationships at the molecular level. The development of NHC-protected nanoclusters further demonstrates the importance of ligands in controlling cluster stability and surface reactivity. Compared with thiolates and phosphines, NHCs are strong σ-donor ligands that form robust metal–carbon bonds, providing enhanced structural stability and electronic tunability. Narouz et al. achieved the stabilization of magic-number Au(0) nanoclusters through NHC ligand substitution, expanding the ligand chemistry of atomically precise nanoclusters beyond typical thiolate- and phosphine-protected systems [59].

Nevertheless, the introduction of conventional organic ligands requires a balance between structural stability and catalytic activity. Dense ligand shells may block exposed metal sites, which subsequently increases interfacial charge-transfer resistance and restricts mass transport. In addition, ligand shells also introduce steric constraints on the adsorption and transformation of reaction intermediates [60, 61]. Therefore, the central issue is not simply whether ligands should be retained or removed, but how the metal–ligand interface can be rationally regulated to balance cluster stability, electronic conductivity, substrate accessibility, and active-site exposure. This consideration provides the basis for functional ligand-shell engineering and controlled ligand-removal strategies, which will be discussed in Section 3.3. The following section therefore focuses on functional ligand design, where the ligand shell is retained but chemically tailored to improve catalytic function.

3.2 Functional ligand engineering: Electronic, microenvironmental, and spatial regulation

Ligand functionalization is a key strategy for regulating the catalytic performance of metal clusters in CO₂RR. By tailoring ligand functional groups and metal–ligand binding configurations, ligand engineering can precisely modulate the electron density distribution, intermediate adsorption energetics, substrate transport, and active sites exposure of metal NCs. Accordingly, functional ligand engineering can be broadly classified into three major regulatory modes, including electronic regulation, microenvironmental regulation, and spatial regulation.

Electronic regulation represents one of the most direct ways by which ligands influence CO₂RR activity and selectivity. The

modification of electronic properties for metal centers, particularly the d-band center, can optimize intermediate adsorption energetics and reaction pathways [43]. This strategy has been widely applied in various nanocluster catalytic systems [27, 50, 62, 63]. For example, Dai et al. designed a series of stable Cu_8 nanoclusters (Cu_8 -1 to Cu_8 -4) via precise ligand engineering. Among them, Cu_8 -2 and Cu_8 -3 were functionalized with electron-donating ligands [62]. Experimental and density functional theory (DFT) results revealed that these ligands induce electron accumulation on Cu sites (Fig. 4(a)), upshift the d-band center toward the Fermi level, and

promote proton-coupled electron transfer. This ligand-induced electronic redistribution strengthens both van der Waals and covalent interactions between Cu clusters and reaction intermediates, increasing the total adsorption binding energy of intermediates, and thereby thermodynamically favoring the selective formation of C_{2+} products (Fig. 4(b)). The tert-butyl group in Cu_8 -3 possesses stronger electron-donating capability than the phenyl group in Cu_8 -1 (Fig. 4(c)), which effectively modulates product selectivity (Fig. 4(d)) with an impressive $\text{FE}_{\text{C}_{2+}}$ of 64.9% at -1.3 V (vs. RHE). Moreover, n-propanol, a C_3 product, was also

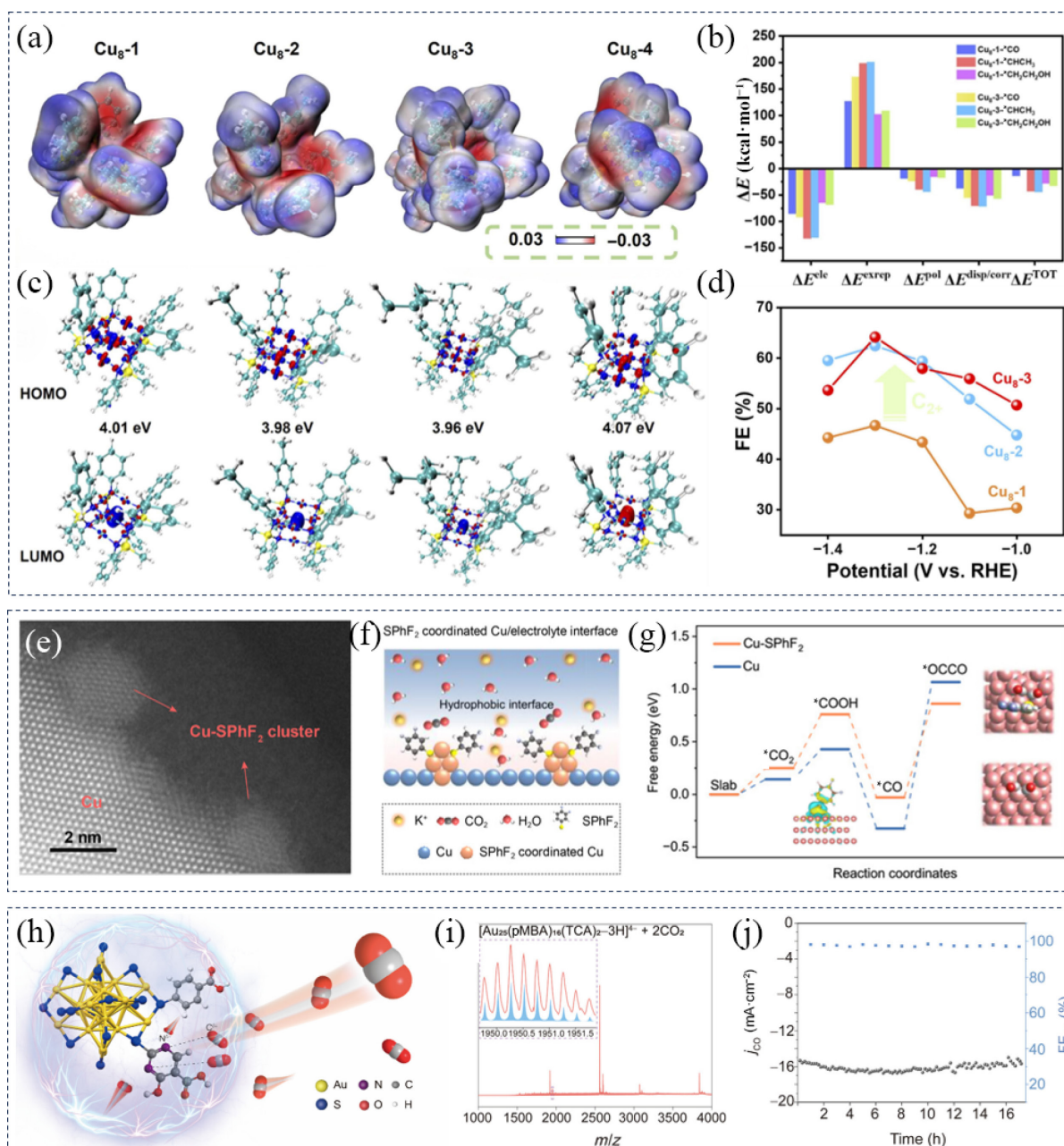


Figure 4 (a) Plots of electrostatic potential of Cu_8 -1–4. (b) Calculated energy decomposition analyses (EDA) of Cu_8 -1 and Cu_8 -3. (c) Charge density patterns of Cu_8 -1–4. (d) product Faradaic efficiency for Cu_8 -1–3. Reproduced with permission from Ref. [62], © Elsevier B.V. 2025. (e) Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of thiophenol-ligand-modified Cu nanosheet. (f) Schematic illustration of the proposed thiophenol ligand-regulated local electrolyte microenvironment on Cu-SPhF₂ NS. (g) Free energy diagram of the reaction for CO_2 adsorption to $^*\text{OCCO}$ intermediate, insert is the electron density difference plots. Reproduced with permission from Ref. [70], © Wiley-VCH GmbH 2026. (h) Schematic illustration of $[\text{Au}_{25}(\text{pMBA})_{18-x}(\text{TCA})_x]^-$ NCs. (i) ESI-MS spectra of $[\text{Au}_{25}(\text{pMBA})_{18-x}(\text{TCA})_x]^-$ after bubbling CO_2 (the inset shows the isotope patterns of cluster ions). (j) Electrochemical stability test of $[\text{Au}_{25}(\text{pMBA})_{18-x}(\text{TCA})_x]^-$ at -0.9 V. Reproduced with permission from Ref. [7], © American Chemical Society 2024.

detected in the reaction system. Notably, the Cu₈-3 nanocluster represents a rare example of an atomically precise copper cluster capable of catalyzing CO₂ reduction toward C₃ product formation. This work demonstrates the potential of ligand-induced electronic modulation for extending nanocluster-based CO₂RR beyond conventional C₁ and C₂ products.

Surface ligands can regulate CO₂RR performance of nanoclusters by constructing interfacial microenvironments. Two representative microenvironmental strategies include the construction of hydrophobic interfaces and the local enrichment of CO₂ molecules. These two strategies operate through different mechanisms. Hydrophobic ligand shells mainly suppress the competing HER by reducing interfacial water density and restricting proton accessibility, while maintaining CO₂ transport toward catalytic active sites [31, 64, 65]. In contrast, CO₂-enriching ligands enhance the local concentration of CO₂ near active sites, thereby accelerating CO₂ adsorption, mass transfer, and subsequent reduction kinetics [66, 67]. For hydrophobic microenvironment regulation, Luo et al. adopted hydrophobic ethylthiolate (–SCH₂CH₃)-protected Au₂₅ nanoclusters as a theoretical model. Theoretical calculations reveal that the hydrophobic microenvironment stabilizes the *COOH intermediate by mitigating aqueous interference, thereby lowering the energy barrier for CO₂RR [68]. This mechanistic insight is supported by experimental results, offering theoretical and practical guidance for the microenvironment engineering in nanoclusters electrocatalysts toward enhanced electrocatalytic performance [31, 69, 70]. In addition, Yoo et al. synthesized hydrophobic Ag₂₅(IPBT)₁₈ nanoclusters through interfacial ligand exchange, using hydrophilic Ag₂₅(Capt)₁₈ as a reference [31]. The bulky alkyl groups create a local hydrophobic microenvironment that modulates water arrangement and intermediate adsorption. The synergistic effect of the optimized γ-type water structure and weakened *CO adsorption enables Ag₂₅(IPBT)₁₈ to exhibit superior CO₂RR performance, with a Faradaic efficiency of CO (FE_{CO}) of 90.5% and long-term stability over 120 h at a cell potential of –3.2 V in a membrane electrode assembly (MEA).

Zhang et al. further demonstrated that hydrophobic ligands can simultaneously regulate interfacial water structure and metal-site electronics [70]. They employed an *in situ* growth strategy to construct high-density organic ligand (SPhF₂)-modified Cu nanoclusters on two-dimensional (2D) Cu nanosheets (Cu-SPhF₂ NS) (Fig. 4(e)). *In situ* spectroscopy and multiscale simulations revealed that the thiophenol ligand creates a hydrophobic microenvironment and electronically modulates Cu active sites, reducing surface H₂O density, increasing K⁺ concentration, and moderately downshifting the electron density of Cu sites (Fig. 4(f)). These effects stabilize the *CO intermediate and lower the C–C coupling barrier (Fig. 4(g)).

Distinct from hydrophobic regulation, local CO₂ enrichment relies on specific ligand–CO₂ interactions to increase the effective CO₂ concentration around catalytic sites. Inspired by enzymatic catalytic mechanisms, Liu et al. developed TCA-doped nanoclusters with the formula of [Au₂₅(pMBA)_{18–x}(TCA)_x][–] (Fig. 4(h)) [7]. The nucleophilic N^{δ–} sites within the pyrimidine ring of TCA ligands engage in supramolecular interactions with the electrophilic C^{δ+} center of CO₂ (Fig. 4(i)). Such interaction locally accumulates CO₂ around Au active sites, accelerates mass transfer, and substantially improves the reaction kinetics and product selectivity of CO₂RR with a FE_{CO} of 98.6% and long-term stability over 16 h at –0.9 V (vs. RHE) (Fig. 4(j)). This ligand-assisted CO₂ enrichment strategy is particularly promising for CO₂RR under low CO₂ partial pressure,

where limited CO₂ availability often constrains catalytic performance.

Beyond electronic and microenvironmental regulation, the spatial configuration of ligand shells also plays a crucial role in determining substrate accessibility and intermediate transformation. Ligand steric effects can either expose or shield metal active sites, thereby influencing the adsorption and transformation of CO₂ molecules and their reaction intermediates. Han et al. successfully synthesized structurally stable Cu17a and Cu17b nanoclusters [71]. Owing to their unique J28 core structure (Fig. 5(a)) and strong ligand coordination interactions, these nanoclusters can remain stable in solution for more than three months (Fig. 5(b)). Electrochemical measurements demonstrate that Cu17a exhibits excellent selectivity toward CO and C₂H₄, with Faradaic efficiencies reaching 91% and 39%, respectively. The selectivity of the two products varies distinctively with applied potential. DFT calculations reveal that NHC ligands in Cu17a possess low steric hindrance, allowing CO₂ and key intermediates such as *COOH and *CO to approach the Cu active sites and form thermodynamically favorable adsorption geometries (Fig. 5(c)). Meanwhile, these less hindered NHC ligands fully expose neighboring Cu atoms to provide bimetallic binding sites for adsorbed *CO, which lowers the energy barrier of *CO intermediate coupling (Fig. 5(d)). In contrast, the larger steric hindrance caused by the benzene ring substituents in Cu17b compromises its catalytic activity. Huang et al. further confirmed that the steric effect of ligand terminal groups can regulate reactant diffusion and catalytic performance [72]. These studies demonstrate that rational control of ligand steric is essential for balancing cluster stability with active-site accessibility.

In certain cases, structural reconstruction triggered by ligand rearrangement can effectively expose abundant metallic active sites. Zhu et al. proposed a ligand interface reorganization strategy based on guanidinium cations (GuH⁺) (Fig. 5(e)) [60]. Through the synergistic effect of hydrogen bonding and ion-pair interactions (Fig. 5(f)), this strategy precisely modulates the spatial orientation and arrangement of surface ligands on Au nanoclusters. While fully preserving the original metal–ligand coordination framework (Au–S bonds), this approach constructs highly efficient mass-transport pathways. The optimized spatial arrangement of ligands substantially improves the accessibility of metallic active sites toward CO₂ molecules (Fig. 5(g)), ultimately achieving a maximum FE_{CO} of 96.5% and durable stability (> 12 h) under a potential of –0.9 V (vs. RHE) (Figs. 5(h) and 5(i)). Collectively, these studies demonstrate that functional ligand engineering is not limited to stabilizing metal nanoclusters. Instead, ligand shells act as active regulatory components that govern electronic structure, interfacial solvation, cation distribution, CO₂ enrichment, substrate accessibility, and intermediate binding. Rational integration of electronic, microenvironmental, and spatial ligand effects provides a powerful design principle for developing high-performance nanocluster electrocatalysts for CO₂RR.

3.3 Controlled ligand removal: Exposure of active sites

While ligands are critical for stabilizing metal clusters and modulating their electronic structures, controlled or selective ligand stripping (e.g., thiolate [33, 73–75], phosphines [23, 76], and alkynyl groups [77–79]) can expose additional metal active sites to further enhance CO₂RR performance. For instance, Seong et al. employed atomically precise Au₂₅, Au₃₈, and Au₁₄₄ nanoclusters as model

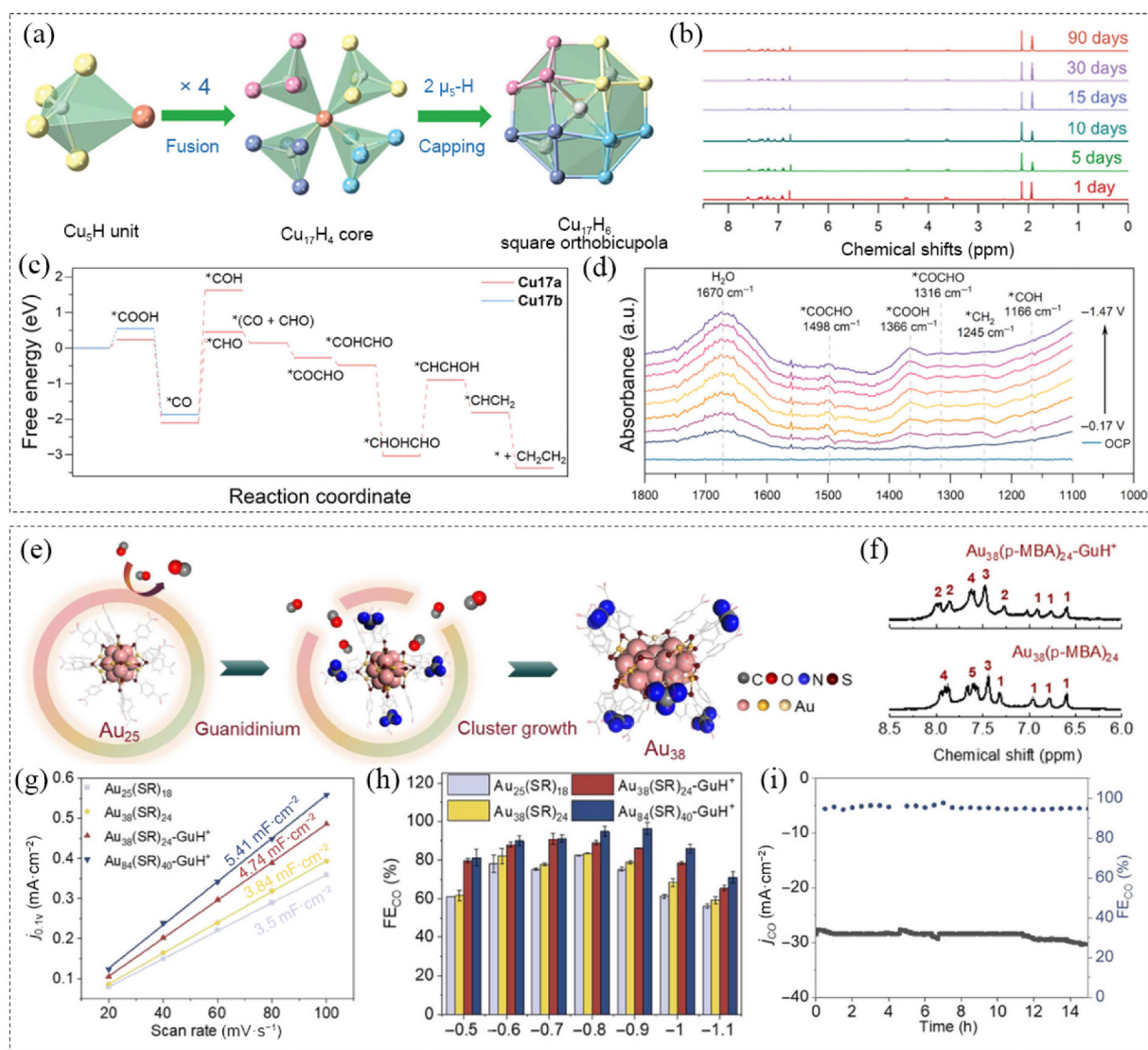


Figure 5 (a) The formation of the Cu_{17}H_6 square orthobicupola (J28). (b) Time-dependent ^1H nuclear magnetic resonance (NMR) spectra of **Cu17a** in CD_3CN . (c) Free energy diagrams of CO_2RR on **Cu17a** and **Cu17b**. (d) Attenuated total reflection surface-enhanced IR absorption spectra recorded of **Cu17a** (OCP: open circuit potential). Reproduced with permission from Ref. [71], © Wiley-VCH GmbH 2025. (e) Schematic illustration of size-growth reaction from $\text{Au}_{25}(\text{p-MBA})_{18}$ to $\text{Au}_{38}(\text{p-MBA})_{24}$ by GuH^+ -assisted surface regulation. (f) ^1H NMR spectra of $\text{Au}_{38}(\text{p-MBA})_{24}\text{-GuH}^+$ and $\text{Au}_{38}(\text{p-MBA})_{24}$ NCs, respectively. (g) Electrochemical surface-active area (ECSA) of different Au NCs. (h) FE_{CO} during CO_2RR . (i) Electrochemical stability test of $\text{Au}_{38}(\text{p-MBA})_{40}\text{-GuH}^+$ at -0.9 V. Reproduced with permission from Ref. [60], © Zhu, M. S. Q. et al. 2025.

catalysts, which delivered CO selectivity above 90% [33]. The results reveal that gold nanoclusters undergo *in situ* activation at the initial stage of CO_2RR , where each staple motif on the cluster surface loses one thiolate ligand to generate exposed Au active sites. These thiol-free Au sites possess enhanced surface charge density and an upshifted d-band level (Fig. 6(a)), which can effectively stabilize the key $^*\text{COOH}$ intermediate and substantially reduce the reaction energy barrier (Figure. 6(b)). Meanwhile, the CO_2RR activity is governed by the number of surface active sites (Fig. 6(c)), showing a positive size-dependence with increasing nanocluster diameter. Deng et al. reported that partial removal of alkynyl ligands from alkynyl/diphosphine dual-ligand-protected $\text{Ag}_{15}\text{Cu}_6$ nanoclusters exposes bimetallic Ag–Cu active sites, which optimizes the adsorption geometries of various key intermediates during CO_2RR (Fig. 6(d)) [77]. Such ligand modulation substantially lowers the reaction energy barrier and suppresses the competing HER.

Consequently, the optimized nanocluster catalyst achieves a maximum FE_{CO} of 91.3% (Fig. 6(e)) and outstanding long-term stability over 145 h (Fig. 6(f)) at a -3.25 V cell potential in an MEA, offering an atomic-level design principle for modulating the catalytic performance of bimetallic nanoclusters.

Meanwhile, by achieving partial removal rather than complete stripping of the halogen-atom ligand, the residual ligand can be utilized to isolate and selectively regulate the active site. Wang and co-workers synthesized pure Ag_{19} nanoclusters as well as $\text{Ag}_{19}\text{Cu}_2$ and $\text{Ag}_{12}\text{Cu}_7$ bimetallic alloy nanoclusters via a photochemical approach (Fig. 6(g)) [80]. The Cu-rich $\text{Ag}_{12}\text{Cu}_7$ nanocluster exhibits a broader highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO) band gap and exposes more Ag active sites (Fig. 6(h)). Experimental investigations demonstrate that ligand desorption enables precise regulation of the CO_2RR reaction pathway. Specifically, Cl ligand removal on $\text{Ag}_{12}\text{Cu}_7$ activates Ag

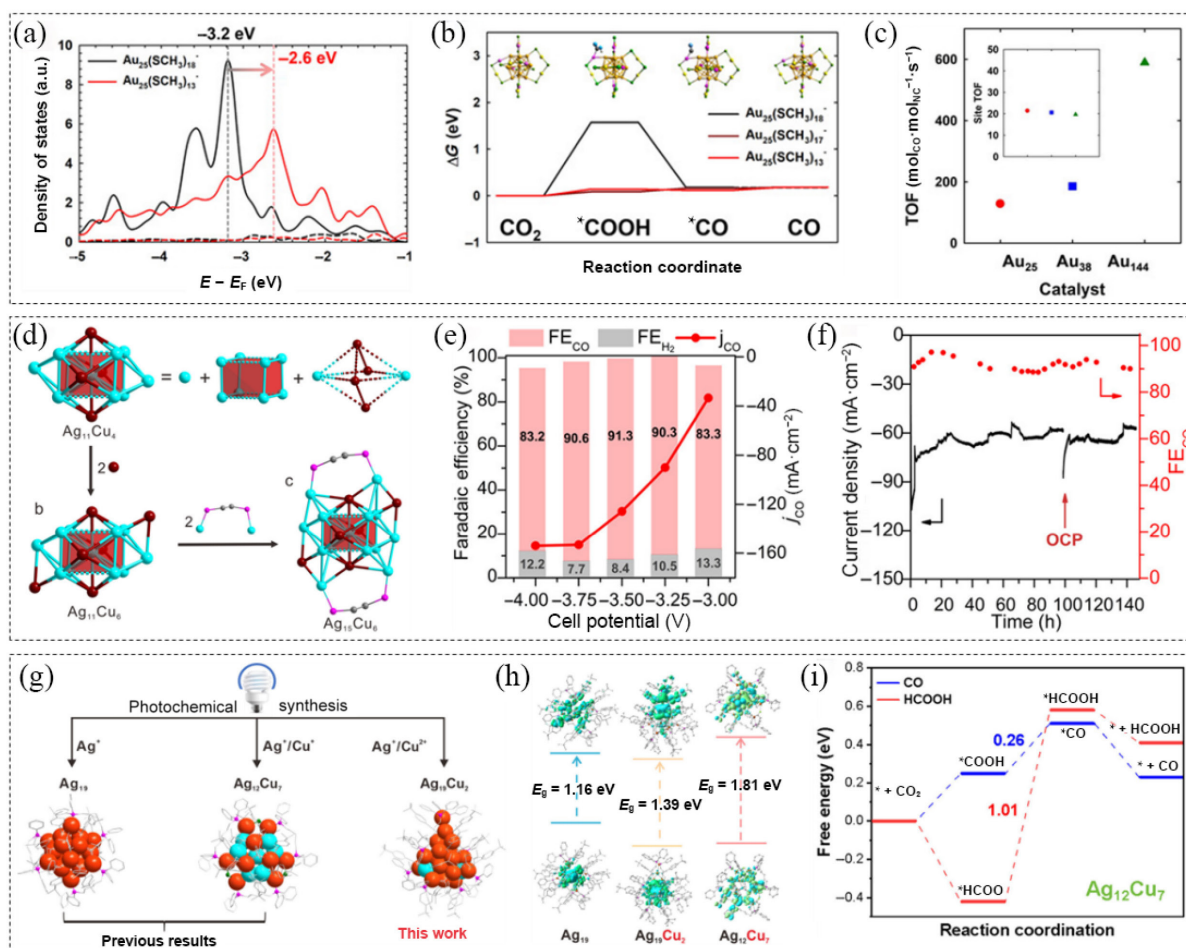


Figure 6 (a) Projected density of states (PDOS) of the sp-states (dashed lines) and d-states (solid lines) of the staple Au in the $\text{Au}_{25}(\text{SCH}_3)_{18}^-$ (black) and $\text{Au}_{25}(\text{SCH}_3)_{13}^-$ (red) NCs. (b) Free energy diagrams describing the CO_2 reduction to CO. (c) TOFs obtained for the Au_{25} (red circle), Au_{38} (blue square), and Au_{44} (green triangle) NC/GDEs. The inset shows the site TOFs ($\text{mol}_{\text{CO}} \cdot \text{mol}_{\text{Au}}^{-1} \cdot \text{s}^{-1}$) determined for each active site of the Au NCs. Reproduced with permission from Ref. [33], © Wiley-VCH GmbH 2021. (d) Structure analysis of the $\text{Ag}_{15}\text{Cu}_6$ cluster. (e) FE_{CO} , FE_{H_2} , and j_{CO} of $\text{Ag}_{15}\text{Cu}_6/\text{C}$ at various cell potentials in the MEA-cell. (f) Long-term operation of $\text{Ag}_{15}\text{Cu}_6/\text{C}$ at a cell potential of -3.25 V in the MEA-cell. Reproduced with permission from Ref. [77], © American Chemical Society 2022. (g) Previous results: photochemical synthesis of Ag_{19} and $\text{Ag}_{12}\text{Cu}_7$ nanoclusters. This work: photochemical synthesis of atomically precise $\text{Ag}_{15}\text{Cu}_6$ nanocluster. (h) Energy level diagrams and topology of HOMO and LUMO orbitals for Ag_{19} , $\text{Ag}_{15}\text{Cu}_2$, and $\text{Ag}_{15}\text{Cu}_6$, respectively. (i) Comparative free energy diagrams for CO and HCOOH production pathways on $\text{Ag}_{12}\text{Cu}_7$. Reproduced with permission from Ref. [80], © Wang, Y. X. et al. 2025.

sites to facilitate the conversion of $^*\text{COOH}$ intermediates toward CO production (Fig. 6(i)), whereas alkynyl ligand desorption on $\text{Ag}_{19}\text{Cu}_2$ modulates Cu sites to preferentially promote formate generation with an FE of 41.9% at -0.77 V (vs. RHE). These findings confirm that ligand desorption serves as a critical mechanism for optimizing the CO_2RR catalytic performance of alloy nanoclusters. Similarly, Deng et al. reported the partial removal of Cl ligand from Au-Cu nanoalloy clusters [81]. These ligand-based strategies highlight how local coordination can regulate activity, whereas practical stabilization often further requires anchoring clusters on conductive or confined supports.

4 Supported metal nanoclusters for CO_2RR

Supported immobilization represents a pivotal strategy for stabilizing metal NCs and enhancing their catalytic performance. In this approach, atomically precise metal NCs are dispersed and anchored on the surface or within the pores of support materials [82]. Support materials typically possess a high specific surface area, superior electrical conductivity, abundant porous architectures,

and/or well-defined surface functional groups. These inherent structural and surface properties play a critical role in stabilizing metal nanoclusters, suppressing their agglomeration, and facilitating the efficient progression of CO_2RR [22, 83]. The following subsections distinguish these effects according to support type, because carbon, doped carbon, oxides, and zeolites stabilize clusters through different interfacial interactions.

4.1 Carbon-based supports

As a support material for nanoclusters, carbon support is not merely a physical scaffold. They possess multiple inherent catalytic functions, including high specific surface area, abundant defect sites, strong metal-support interactions (SMSI), and intrinsic high electrical conductivity, which have attracted extensive research interest and in-depth exploration [82, 84–87]. Shi et al. investigated Cu_{19} clusters supported on graphene (G) and graphyne (GDY) through theoretical calculations [88]. The results demonstrated that the carbon support could significantly optimize catalytic activity and product selectivity by regulating electron transfer at the metal-support interface and CO_2 adsorption activation behavior.

This design strategy has been extensively validated in numerous experimental studies [24, 34, 46]. For example, Liu et al. developed a transient pulse discharge method to fabricate graphene aerogel-supported Cu nanoclusters with asymmetric $\text{Cu}_4\text{O-Cu}_2\text{O}_1$ structure ($\text{Cu}_{1.7}\text{Clu/GAs}$) (Figs. 7(a) and 7(b)) [46]. The Cu clusters are strongly anchored to the support via Cu-C bonds (Fig. 7(c)), and aggregation is effectively suppressed by SMSI. The asymmetric coordination induces lattice distortion and a local polarization field, greatly boosting CO_2 adsorption. Meanwhile, efficient interfacial electron transfer reduces the average partial charge of Cu to $+0.37\text{e}^-$ and decreases the oxidation state to $+0.5$, providing a key driving force for selective C_{2+} production. Experimental results reveal that this system significantly lowers the $^*\text{CO-CHO}$ coupling barrier and steers the reaction toward ethanol by stabilizing key intermediates (e.g., $^*\text{CO}$ and CH_3) (Figs. 7(d) and 7(e)), thus delivering high FE_{EtOH} (75.3%) and high selectivity of C_{2+} production (90.5%) at -1.1V (vs. RHE).

Abundant carbon defects in the support serve as another key advantage for enhancing catalytic performance. They can act as anchoring sites by forming metal-carbon bonds with clusters to suppress aggregation, or optimize cluster structure and boost activity via interfacial electron transfer. Su et al. constructed $\text{Fe}_2\text{C-}$

Cs@DC in 2023. By leveraging carbon topological defects, the metal clusters were efficiently anchored and dispersed [89]. The synergy between carbon dangling bonds and Fe_2C nanoclusters enabled precise modulation of the electronic structure of Fe active centers, leading to a downshift of the d-band center and effectively weakened adsorption of the $^*\text{CO}$ intermediate. Similarly, Yang et al. synthesized bismuth nanoclusters supported on activated carbon (Bi NCs/AC) via a two-step thermal annealing approach, where the micropore confinement effect of activated carbon effectively suppresses cluster aggregation [90]. The catalyst exhibits a high current density ($58.1\text{ mA}\cdot\text{cm}^{-2}$), outstanding $\text{FE}_{\text{formate}}$ of 98.8% at -0.8 V (vs. RHE), and excellent long-term stability ($> 60\text{ h}$) (Figs. 7(f) and 7(g)). Its superior catalytic activity originates from the local electron redistribution induced by carbon defects, which optimizes the electronic structure of Bi NCs and facilitates the formation of the key $^*\text{OCHO}$ intermediate (Fig. 7(h)), thereby enabling highly efficient CO_2 conversion to formate; even under diluted CO_2 conditions, the catalyst retains excellent reduction performance. These examples suggest that carbon supports contribute to CO_2RR not only by dispersing NCs but also by mediating interfacial charge transfer and stabilizing catalytically relevant coordination environments.

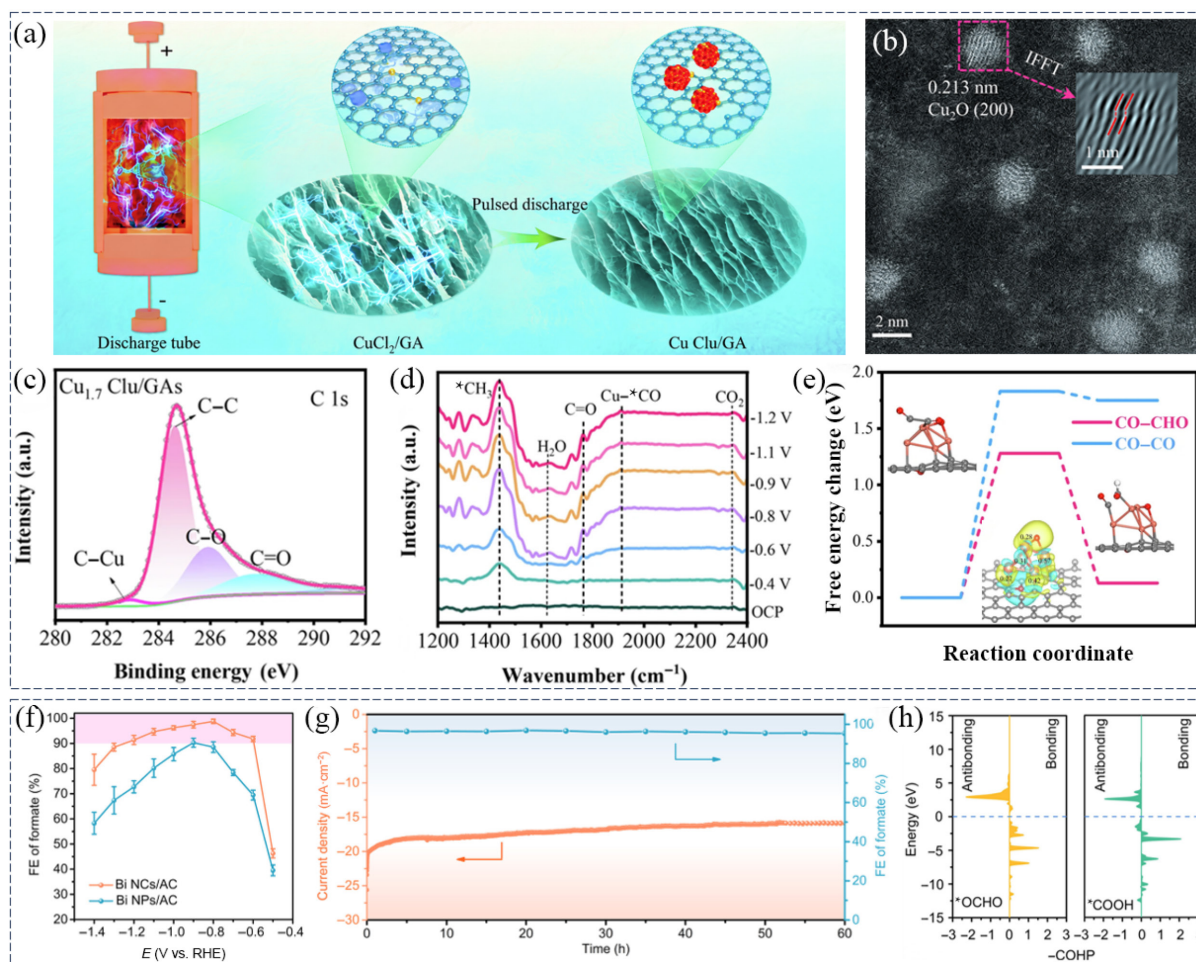


Figure 7 (a) A schematic plot of the preparation strategy by the transient pulsed discharge. (b) The local magnified image of $\text{Cu}_{1.7}\text{Clu/GAs}$. Inset is a locally enlarged inverse fast Fourier transform (IFFT) image of a marked single cluster. (c) The C 1s X-ray photoelectron spectroscopy (XPS) spectra of $\text{Cu}_{1.7}\text{Clu/GAs}$. (d) *In situ* attenuated total reflection-fourier transform infrared (ATR-FTIR) results of $\text{Cu}_{1.7}\text{Clu/GAs}$ at different potentials. (e) The energy barrier of C-C coupling through CO-CO and CO-CHO dimerization, and insets are the transition state and bader charge. Reproduced with permission from Ref. [46], © Liu, K. Y. et al. 2025. (f) FE of formate. (g) Long-term stability test of Bi NCs/AC catalyst acquired at -0.8 V . (h) COHP for Bi NCs/C- $^*\text{COOH}$ and Bi NCs/C- $^*\text{OCHO}$ systems. Reproduced with permission from Ref. [90], © Yang, F. Q. et al. 2025.

nitridation of the Ni cluster structure precisely optimizes the adsorption energy of the $^*\text{COOH}$ intermediate. The catalyst achieved a record-low overpotential (16 mV) and an outstanding FE_{CO} above 99.0% at a potential of as low as -0.272 V (vs. RHE) (Fig. 8(c)), enabling highly efficient CO_2 -to-CO conversion (Fig. 8(d)). Furthermore, Liu's group synthesized a nanotube-structured $\text{Ni}_6@(\text{Ni}-\text{N}_3)$ catalyst via low-temperature pyrolysis, which successfully integrates Ni nanoclusters with unsaturated Ni-N₃ single-atom sites [100]. Nickel nanoclusters were used to stabilize unsaturated Ni-N₃ single-atom sites, achieving a high FE_{CO} of 99.7% at $500 \text{ mA}\cdot\text{cm}^{-2}$ under -1.15 V (vs. RHE), along with significantly enhanced turnover frequency and structural stability (Fig. 8(e)). DFT calculations and experiments demonstrated that Ni nanoclusters regulate the electronic structure and strengthen $^*\text{COOH}$ adsorption, providing an effective strategy for the stable design of unsaturated single-atom catalysts. Additionally, the ability of nanoclusters to boost catalytic activity holds valid across a broad range of nanocluster sizes (Fig. 8(f)). In the same year, Liu's group reported a similar nitrogen-doped carbon-supported Ni nanocluster catalyst. Precise modulation of the asymmetric $\text{Ni}_3\text{-N-C}$ coordination microenvironment substantially lowered the protonation energy barrier and boosted the kinetics of CO_2 -to-CO electroreduction [102]. N-doped carbon supports are also employed for theoretical investigations. Zhu et al. investigated subnanometer Cu_8 clusters supported on $\text{g-C}_3\text{N}_4$ using GCMC and GCDFT simulations [53]. It was found that under negative potentials, CO adsorption is significantly enhanced, whereas formate adsorption is suppressed. $\text{g-C}_3\text{N}_4$ can stably anchor the Cu_8 cluster via Cu-N bonds and construct low-coordination Cu active sites on the cluster surface. This coordination structure elevates the Fermi level and shifts the U_{PZC} value positively, enabling higher electron accumulation at identical applied potentials. This stabilizes the $^*\text{OCCO}$ intermediate through orbital hybridization and electrostatic interactions, thereby remarkably improving the selectivity to C_{2+} products.

The co-doping of S and N heteroatoms is also widely employed in carbon supports. Hua et al. devised an atomic coordination engineering strategy to fabricate a subnanometer Cu cluster catalyst co-coordinated by sulfur and nitrogen (Cu/SNC) [97]. The N and S atoms in the support form Cu-N and Cu-S coordination bonds with Cu sites, respectively, enabling robust anchoring of Cu clusters on the carbon framework and effectively suppressing cluster aggregation. DFT calculations reveal that S doping tailors the electronic structure of Cu subnanoclusters, upshifting the d-band center of Cu active sites to stabilize key intermediates such as $^*\text{CO}$ and $^*\text{OCHCH}_2$ (Figs. 8(g) and 8(h)). Meanwhile, the synergistic coordination of S and N weakens the Cu-O bond and strengthens the C-O bond, rationally regulating the reaction pathway. As a result, the catalyst exhibited a high selectivity of 59.1% toward C_{2+} alcohol products and satisfactory stability (> 20 h) at $200 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 8(i)). Liu et al. loaded Cu-Zn bimetallic clusters onto S/N-codoped carbon supports and successfully constructed charge-asymmetric active centers [96]. The synergy between Cu and Zn, together with S doping, collectively modulates the electronic structure of active sites, stabilizes $\text{Cu}^+/\text{Zn}^{2+}$ species, and enhances the adsorption and conversion of the $^*\text{COOH}$ intermediate. This design finally achieves high CO selectivity, clearly revealing the crucial role of sulfur atoms in stabilizing metal active species and promoting the transformation of key intermediates.

4.3 Metal oxide- and zeolite-based supports: Charge transfer, oxygen vacancies, and spatial confinement

Metal oxides (e.g., Al_2O_3 , CeO_2 , and CuO) serve as essential materials for supported catalysts [103–106]. The SMSI at the metal-metal oxide interface can effectively modulate the electronic structure of nanoclusters, shift the d-band center of metal active sites, and optimize the adsorption energies of key intermediates (e.g., $^*\text{COOH}$ and $^*\text{CO}$), which has therefore been extensively investigated. Compared with carbon supports, oxide and zeolite supports more strongly tune local coordination and spatial confinement, making them especially useful for product-selectivity control.

For example, Zeng et al. fabricated a multi-active-site catalyst by anchoring atomically dispersed Cu nanoclusters on $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ supports ($\text{Cu}/\gamma\text{-Al}_2\text{O}_3$) (Fig. 9(a)) [47]. Lewis acidic Al^{3+} sites polarize and anchor water molecules, thereby weakening O-H bonds and promoting water dissociation. In contrast, surface hydroxyl groups function mainly as hydrogen-bonding/stabilization sites for adsorbed H species, assisting subsequent hydrogenation steps. Together with Cu nanoclusters that activate CO_2 and CO-derived intermediates, these support-derived functions lower the energetic penalty for $^*\text{CO}$ hydrogenation toward $^*\text{CHO}$ (Fig. 9(b)). DFT results confirm that metal-support interactions induce interfacial electron transfer, endowing Cu active sites with electron enrichment (Fig. 9(c)) and an upshifted d-band center (Fig. 9(d)). This strengthens the adsorption of key intermediates (CO) and drastically lowers the energy barrier for CHO formation (Fig. 9(e)), thereby achieving efficient CH_4 electrosynthesis with a FE of 72% at a high current density ($500 \text{ mA}\cdot\text{cm}^{-2}$). Different from the excellent water dissociation capability of $\gamma\text{-Al}_2\text{O}_3$ supports, Tang et al. anchored Ag nanoclusters on oxygen-vacancy-rich CeO_2 nanorods ($\text{O}_v\text{-CeO}_2$) to fabricate an $\text{Ag}/\text{O}_v\text{-CeO}_2$ heterointerface catalyst [107]. The abundant oxygen vacancies on CeO_2 can drive interfacial charge spillover and effectively modulate the electronic structure of Ag active sites. Moreover, these vacancies serve as exclusive adsorption sites for $^*\text{COOH}$ intermediates, which strengthen $^*\text{COOH}$ adsorption without impeding $^*\text{CO}$ desorption. Such a feature breaks the linear scaling relationship between key reaction intermediates, thereby realizing the highly selective electroreduction of CO_2 to CO. The switching of products from C_1 to C_2 species can be achieved by modulating metal oxide supports for anchored Ag clusters. Wang et al. embedded Ag nanoclusters into mesoporous Cu_2O nanospheres to construct a semi-enclosed tandem heterointerface catalyst ($\text{Ag NCs}@P\text{-Cu}_2\text{O NSs}$) [103]. The mesoporous Cu_2O structure efficiently enriches $^*\text{CO}$ intermediates via the spatial confinement effect, increasing the local CO concentration. Meanwhile, the electronic reconstruction at the Ag-Cu interface further optimizes the CO adsorption strength of Cu sites and lowers the C-C coupling energy barrier, achieving a high $\text{FE}_{\text{C}_{2+}}$ of 66.9% at -1.3 V (vs. RHE).

Zeolite-supported nanoclusters can stabilize key reaction intermediates via their unique confinement effect, thereby effectively improving product selectivity. Zhu et al. developed a one-pot method to prepare $\text{SnCu}_x\text{O}_{2+x}$ nanoclusters encapsulated in pure-silica MFI zeolite ($\text{SnCu}_x\text{O}_{2+x}@MFI$) as an electrocatalyst (Fig. 9(f)) [108]. The catalyst delivered a maximum $\text{FE}_{\text{methane}}$ of $66.3\% \pm 3.2\%$ and retained catalytic stability for up to 25 h at -1.55 V (vs. RHE) (Figs. 9(g) and 9(h)). The spatial confinement effect of zeolite stabilizes the $^*\text{CO}$ intermediate, facilitating its stepwise protonation into CH_x ($x = 1, 2$, and 3) species over the nanocluster active sites

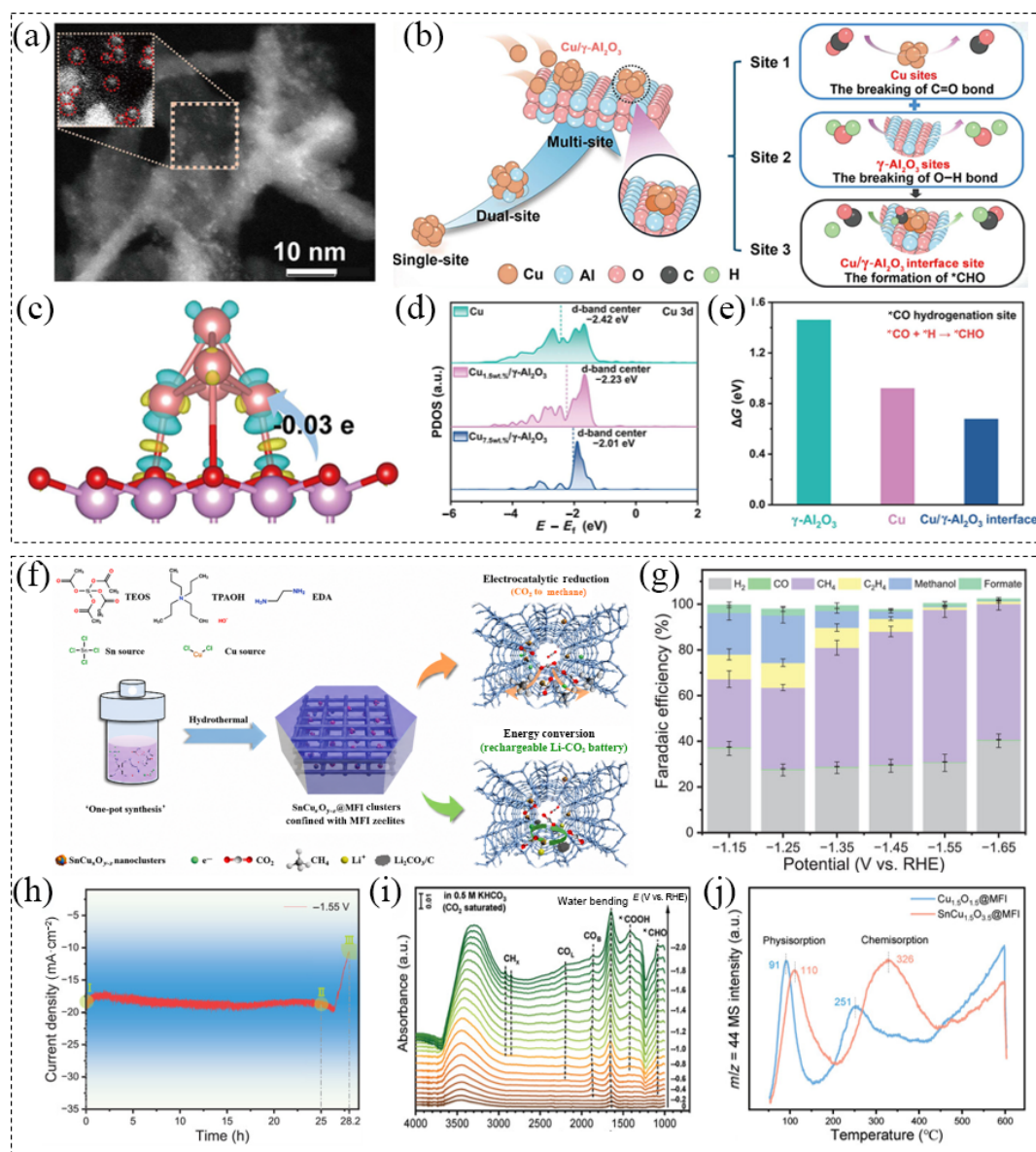


Figure 9 (a) High-resolution transmission electron microscopy (HRTEM) dark field images of $\text{Cu}_{1.5\text{wt}\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst. (b) Schematic illustration for the preparation of $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ and multi-site tandem mechanism for electrocatalytic CO_2 methanation. (c) Differential charge densities and Bader charge transfer of $\text{Cu}_{1.5\text{wt}\%}/\gamma\text{-Al}_2\text{O}_3$. (d) PDOS diagrams for different structures. (e) $^*\text{CO}$ hydrogenation to $^*\text{CHO}$ at the Cu, $\gamma\text{-Al}_2\text{O}_3$, and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ interfacial sites in $\text{Cu}_{1.5\text{wt}\%}/\gamma\text{-Al}_2\text{O}_3$. Reproduced with permission from Ref. [47], © Zeng, X. K. et al. 2026. (f) Material synthesis. (g) Faradaic efficiencies of reduction products for the $\text{SnCu}_{1.5}\text{O}_{3.5}@\text{MFI}$. (h) I - t curve for stability test of the $\text{SnCu}_{1.5}\text{O}_{3.5}@\text{MFI}$ catalyst at -1.55 V (vs. RHE) in a CO_2 -saturated 0.1 M KHCO_3 electrolyte. (i) *In situ* surface-enhanced infrared absorption spectroscopy (SEIRAS) spectra with the $\text{SnCu}_{1.5}\text{O}_{3.5}@\text{MFI}$ electrode reaction at 0.0 to -2.0 V (vs. RHE). (j) CO_2 -temperature programmed desorption (TPD) spectra of $\text{Cu}_{1.5}\text{O}_{1.5}@\text{MFI}$ and $\text{SnCu}_{1.5}\text{O}_{3.5}@\text{MFI}$ catalysts. Reproduced with permission from Ref. [108], © Wiley-VCH GmbH 2023.

and ultimately yielding methane (Fig. 9(i)). In contrast, bare nanoclusters without zeolite confinement predominantly produce formate. Furthermore, tuning the Sn/Cu ratio modulates the electron-unsaturated configuration of Cu sites, strengthens the adsorption capability toward reductive intermediates (Fig. 9(j)), and promotes the protonation process during CO_2 reduction. Similarly, Zhu et al. further synthesized the $\text{In}_2\text{Cu}_3\text{O}_6@\text{zeolite}$ catalyst, where $\text{In}_2\text{Cu}_3\text{O}_6$ nanoclusters were encapsulated within siliceous MFI zeolites [48]. The spatial confinement effect of zeolites enables the enrichment and activation of CO_2 as well as the confinement of intermediates to facilitate multistep protonation. Meanwhile, the buffer capacity neutralizes byproduct OH^- , stabilizes the interfacial pH, and continuously supplies protons to raise the concentration of

active species, thereby effectively suppressing the HER. Consequently, it achieved a high $\text{FE}_{\text{methane}}$ up to $74.1\% \pm 4.7\%$ and maintained a long-term operational durability of over 40 hours under an applied potential of -1.15 V (vs. RHE). Such investigations offer a feasible strategy for the application of zeolite-based catalysts in electrocatalysis. Therefore, oxide and zeolite supports provide complementary routes for regulating charge transfer and spatial confinement, which are particularly important for controlling product selectivity in deep CO_2 reduction.

5 Conclusions and perspective

This review summarizes recent advances in ligand-protected and

supported metal nanoclusters for electrochemical CO₂RR, with emphasis on reaction mechanisms, structure–performance relationships, and catalyst-design principles. Atomically precise metal NCs provide well-defined platforms for correlating cluster size, composition, coordination environment, electronic structure, and interfacial microenvironment with catalytic activity and product selectivity [109–118]. In ligand-protected NCs, the ligand shell not only stabilizes the metal core but also regulates active-site accessibility, electronic structures, local solvation, cation enrichment, proton transfer, and intermediate adsorption. In supported NCs, conductive, defective, doped, oxide, and zeolite-based supports improve cluster dispersion and stability, promote interfacial charge redistribution, and create confined reaction environments that modulate reaction pathways. These advances indicate that nanocluster-based CO₂RR catalysis should be viewed as an integrated metal–core/ligand/support system rather than as isolated metal clusters. Despite substantial progress, several critical challenges remain.

The structural stability of metal NCs under electrochemical operating conditions remains a central issue. Owing to their high surface energy, metal NCs are susceptible to aggregation, Ostwald ripening, ligand loss, oxidation-state variation, and potential-induced reconstruction during long-term electrolysis. Although ligand protection can stabilize cluster frameworks, dense ligand shells may block active sites, increase charge-transfer resistance, and restrict mass transport. Conversely, excessive ligand removal may expose active sites but accelerate cluster aggregation or structural collapse. Therefore, future catalyst design should establish a delicate balance among structural stability, active-site exposure, electronic conductivity, and reactant accessibility. Robust yet catalytically functional ligands, dynamic ligand-shell regulation, and strong anchoring interactions with conductive or confined supports are promising directions for improving operational durability.

The precise identification of active sites and real catalytic structures remains insufficient. Although atomically precise NCs possess well-defined initial structures, their working states under applied potentials, electrolytes, local pH gradients, and gas–liquid–solid interfaces may differ substantially from their pristine structures. Active sites may arise from partially ligand-deficient motifs, reconstructed metal atoms, metal–support interfacial sites, or transient oxidation-state configurations. Advanced *operando* characterization techniques, including X-ray absorption spectroscopy, surface-enhanced infrared (IR) spectroscopy, Raman spectroscopy, electrochemical transmission electron microscopy, and isotope-labeling studies, should be combined with density functional theory, constant-potential modeling, and microkinetic analysis to reveal dynamic structure evolution, intermediate formation, charge redistribution, and selectivity-determining steps under realistic CO₂RR conditions.

Product-selectivity control, especially toward high-value C₂₊ products, remains challenging. Most reported metal NC catalysts preferentially produce C₁ products such as CO and formate, whereas efficient C–C coupling requires suitable *CO coverage, adjacent active sites, balanced proton/electron transfer, and suppressed hydrogen evolution. Cu-based NCs offer unique opportunities for C₂₊ production because of their moderate binding strength toward carbonaceous intermediates and tunable Cu–Cu ensembles. However, maintaining atomically precise Cu-based clusters under reductive conditions remains difficult. Future efforts should focus on constructing stable Cu-containing NCs, alloy NCs,

cluster–cluster interfaces, and tandem catalytic architectures that promote *CO generation, retention, and coupling while controlling local proton availability and water activation. In addition, the modulation effect of local microenvironments (e.g., elevated interfacial pH and high CO₂ coverage) on C₂₊ selectivity deserves particular attention. Notably, identical metal clusters supported on mesoporous carbon substrates with different pore sizes exhibit distinct mass transfer limitations, which can substantially alter the selectivity toward C₂₊ products. Without effective decoupling of intrinsic catalytic activity and macroscopic mass transfer effects via *in situ* characterization techniques, the prevalent understanding of “structure-dominated selectivity” merely reflects the indirect modulation originating from support engineering. In this case, the genuine structure–performance correlation of cluster-based catalysts cannot be fully elucidated.

Scalable synthesis and device-level evaluation require greater attention. Many atomically precise NCs are still synthesized through complex procedures with limited yield, high cost, and demanding purification processes. Developing scalable synthetic routes with controllable nuclearity, ligand environment, oxidation state, and support interaction is essential for practical implementation. In addition, catalyst evaluation should move beyond conventional H-cell measurements toward flow cells, gas-diffusion electrodes, and membrane-electrode assemblies operated at industrially relevant current densities. Standardized reporting of partial current density, energy efficiency, carbon efficiency, stability, product crossover, and structural evolution after long-term operation will be crucial for comparing nanocluster catalysts across different systems.

Establishing a multidimensional catalytic evaluation system is critical to objectively and comprehensively assess the intrinsic catalytic performance of catalysts. Most existing studies solely concentrate on Faradaic efficiency while overlooking core evaluation metrics such as energy efficiency and mass activity, which leads to one-sided performance assessment. Some metal cluster catalysts deliver a CO selectivity of 90% at –0.6 V, yet their current density only reaches 0.1 mA·cm^{–2}, far below the industrial threshold of 200 mA·cm^{–2}. Furthermore, thiol and phosphine organic ligands widely adopted to stabilize cluster structures can effectively suppress cluster agglomeration. Nevertheless, these ligands cover active sites and raise the interfacial charge transfer resistance, thereby increasing the reaction overpotential. Such a trade-off effect, where structural stability is achieved at the cost of reaction kinetics, drastically reduces the full-cell energy efficiency of cluster catalysts and severely hinders their prospects for practical implementation.

Overall, ligand and support engineering provide powerful and complementary strategies for translating the structural precision of metal NCs into controllable CO₂RR performance. By integrating atomically precise synthesis, rational ligand design, interfacial support engineering, *operando* characterization, and advanced theoretical modeling, metal NCs are expected to evolve from model catalysts for mechanistic studies into practical electrocatalysts for selective CO₂ conversion. Continued progress in this direction will not only deepen the fundamental understanding of nanocluster catalysis but also contribute to the development of next-generation electrocatalytic systems for carbon–neutral energy conversion.

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. C.: Conceptualization, framework construction, writing – original draft. F. Z., H. T., X. Y. Z., M. I., and J. H. K.: Supervision and investigation. X. X. S.: Supervision, investigation, and funding acquisition. P. L. and B. X. Z.: Supervision, investigation, and writing – review. X. Y. Z.: Conceptualization, supervision, writing – review and editing, funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

During the preparation of this work, the authors used ChatGPT in order to polish the language. After using this tool or service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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