Cu-based catalyst designs in CO₂ electroreduction: precise modulation of reaction intermediates for high-value chemical generation

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The massive emission of excess greenhouse gases (mainly CO₂) have an irreversible impact on the Earth’s ecology. Electrocatalytic CO₂ reduction (ECR), a technique that utilizes renewable energy sources to create highly reduced chemicals (e.g. C₂H₄, C₂H₅OH), has attracted significant attention in the science community. Cu-based catalysts have emerged as promising candidates for ECR, particularly in producing multi-carbon products that hold substantial value in modern industries. The formation of multi-carbon products involves a range of transient intermediates, the behaviour of which critically influences the reaction pathway and product distribution. Consequently, achieving desirable products necessitates precise regulation of these intermediates. This review explores state-of-the-art designs of Cu-based catalysts, classified into three categories based on the different prospects of the intermediates’ modulation: heteroatom doping, morphological structure engineering, and local catalytic environment engineering. These catalyst designs enable efficient multi-carbon generation in ECR by effectively modulating reaction intermediates.

1. Introduction

The excessive emission of greenhouse gases has resulted in various environmental degradations, posing a significant threat to the delicate balance of Earth’s ecosystem.²⁻⁴ Among these greenhouse gases, CO₂ is the primary constituent responsible for the majority of environmental issues.⁵⁻⁷ Consequently, the scientific community has set its sights on reducing CO₂ emissions and transforming excessive CO₂ into high-value chemicals.⁸⁻¹⁰ Over the past few decades, scientists have diligently pursued the development of advanced technologies that enable the environmentally friendly conversion of CO₂ into...
valuable chemical products.\textsuperscript{18–28} With the utilization of renewable energy sources, ECR has emerged as a promising avenue for converting CO\textsubscript{2} into value-added multi-carbon products, facilitating the attainment of carbon neutrality (Fig. 1).\textsuperscript{29–35}

Conventional ECR experiments typically involve an electrolytic cell divided into two primary sections: the working electrode section (cathode) where CO\textsubscript{2} is reduced, and the counter electrode section (anode) where the O\textsubscript{2} oxidation reaction occurs. These sections are separated by an ion exchange membrane, which effectively prevents the cathode products from migrating to the anode and undergoing oxidation. Moreover, the ion exchange membrane facilitates the charge balance of the electrolytic system.\textsuperscript{36} One commonly employed ECR device is the H-cell, where CO\textsubscript{2} gas must traverse the cathode electrolyte. In this configuration, CO\textsubscript{2} gas exists as carbonate and other ionic forms, migrating toward the cathode surface. However, the solubility of CO\textsubscript{2} in typical aqueous electrolytes is approximately 10\textsuperscript{-3}–10\textsuperscript{-2} M; such low CO\textsubscript{2} concentrations restrict the reaction rate within the H-cell and hinder efficient CO\textsubscript{2} conversion. To address this limitation, a Kenis-type structured electrolytic device has been developed to mitigate the hindering effect of the electrolyte on CO\textsubscript{2}. These electrolyser devices comprise an anode, a gas diffusion electrode (GDE) serving as the cathode, and an ion exchange membrane (Fig. 2a). In these electrolyser systems, CO\textsubscript{2} gas rapidly diffuses through a thin GDE layer and undergoes reduction at the gas–liquid–solid three-phase interface.\textsuperscript{37}

The liquid-phase electrolyser, also known as the flow cell, enhances CO\textsubscript{2} conversion efficiency by adjusting the flow rate of the electrolyte fluids (Fig. 2b). The gas-phase electrolyser prevents electrolyte penetration into the GDE and improves the stability of the catalytic system (Fig. 2c). Notably, the diffusion distance of CO\textsubscript{2} from the GDE to the catalyst surface in the flow cell (50 nm) is approximately three orders of magnitude shorter than that in the H-cell (30–60 \mu m).\textsuperscript{38–40} This reduced distance reduces CO\textsubscript{2} solubility in the aqueous electrolyte, enabling greater absorption of CO\textsubscript{2} into the catalyst and subsequent reduction into multi-carbon products. Moreover, incorporating the GDE layer significantly enhances the catalytic current density, which surpasses 100 mA cm\textsuperscript{-2} at the surface level compared to using the H-cell. Various methods, such as airbrushing, drop casting, or electrodeposition, can be used to

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apply the catalyst onto the GDE layer. Gas phase products are analysed by Gas Chromatography (GC), while the liquid phase products obtained from the cathode layer can be analysed via techniques such as Nuclear Magnetic Resonance (NMR) or Liquid Chromatography-Mass Spectrometry (LC-MS).

However, the high energy input, intense competition from the hydrogen evolution reaction (HER), and poor product selectivity significantly hinder the efficiency of CO₂ conversion in the ECR process. Therefore, researchers consistently tried to seek high-performance electrocatalysts that can enhance catalyst activity and selectivity. In 1985, Hori and colleagues made a ground-breaking discovery by demonstrating that metal electrodes can efficiently reduce CO₂ to various products, including CO and hydrocarbons. Since then, extensive investigations have been conducted to explore the properties of different catalysts and optimize their performance. Currently, Cu-based catalysts stand out as prominent candidates due to their moderate absorption capability for *C₁ intermediates and their ability to couple two adjacent *C₁. Moreover, they hold greater application potential compared to other C₁-produced catalysts such as Au and Ag, which primarily yield CO. Over the past three decades, significant research efforts have been dedicated to Cu-based catalysts in ECR, leading to innovative developments in catalytic devices, product monitoring methods, and optimal catalyst design.

The CO₂ electroreduction process is a complex surface chemical process that involves multiple intermediates whose behavior cannot be fully described through theoretical calculations or simulations alone.

As a result, an increasing variety of in situ characterization instruments are being employed to monitor these intermediates visually. Techniques such as time-resolved Attenuated Total Reflectance-Surface Enhanced Infrared Absorption Spectroscopy (ATR-SEIRAS), in situ Raman Spectroscopy, in situ X-ray Absorption Spectroscopy (XAS), operando Electrochemical Scanning Transmission Electron Microscopy (EC-
2. Basic outline of electrocatalytic CO\textsubscript{2} reduction

2.1. Evaluation parameters for electrocatalytic CO\textsubscript{2} reduction

The electrocatalytic reduction of CO\textsubscript{2} to fuels and feedstocks presents a promising avenue for converting renewable electricity into chemical energy for storage. However, the catalytic performance of ECR can be influenced by various factors, including the catalyst type, electrolyte selection, reactant delivery method, and catalytic equipment design. Among these factors, the catalyst properties play a paramount role. To comprehensively evaluate the performance of an electrocatalytic system, several experimental parameters are commonly employed. Key parameters encompassing overpotential, current density, faradaic efficiency, Tafel slope, and others hold significant importance and are widely utilized.

2.1.1 Overpotential. The onset potential refers to the experimentally determined potential at which the formation of a product initiates during electrocatalytic CO\textsubscript{2} reduction (ECR). Typically, it is lower than the standard reduction potential of CO\textsubscript{2} due to kinetic hysteresis in the reaction. The disparity between these values is known as the overpotential, denoted as \( \eta \), and can be mathematically expressed as follows (eqn (1)):

\[
\eta = E - E_{\text{eq}}
\]  

Here, \( E \) represents the onset potential of the product measured in the experiment, while \( E_{\text{eq}} \) denotes the standard reduction potential of that product under the given experimental conditions. The Cu\textsubscript{2}S\textsubscript{1−x} catalyst with abundant Cu\textsuperscript{+} (0 < \( \delta \) < 1) species exhibited an exceptionally low overpotential (\( \eta \)) of 0.19 V. This overpotential represents the disparity between the theoretical potential for ethanol electrolysis (0.09 V vs. RHE) and the onset potential (−0.1 V vs. RHE). The diminutive overpotential further illustrates the catalyst’s ability to facilitate C\textsubscript{2}H\textsubscript{5}OH production from CO\textsubscript{2} with minimal energy input.\textsuperscript{75}

2.1.2 Current density. Current density (\( j \)) is a pivotal parameter in CO\textsubscript{2} electrocatalysis, signifying the number of electrons that traverse the electrode surface within a given time frame. Typically, \( j \) is normalized to the catalyst’s surface area or mass. Additionally, \( j \) provides insights into the rate of CO\textsubscript{2} reduction.

2.1.3 Faradaic efficiency (FE). Faradaic efficiency (FE) serves as a direct indicator of product selectivity in CO\textsubscript{2} electrocatalysis and can be mathematically expressed through eqn (2):

\[
\varepsilon_{\text{faradaic}} = \frac{\alpha n F}{Q}
\]  

In this equation, \( \alpha \) represents the number of electrons transferred to produce a specific product. For instance, when reducing CO\textsubscript{2} to CO, 2 electrons are required, thus \( \alpha = 2 \). Meanwhile, \( n \) denotes the molar amount of the obtained product, \( F \) represents the faradaic constant with a value of 96 485 C mol\textsuperscript{−1}, and \( Q \) signifies the total amount of charge transferred.

Moreover, a relationship exists between the partial current density of a product and its corresponding FE, as depicted by eqn (3):

\[
I_{\text{partial}} = \varepsilon_{\text{faradaic}} \times j
\]
Here, \( j_{\text{partial}} \) refers to the partial current density of the product, which is obtained by multiplying the total current \( j \) by the respective FE.

### 2.1.4 Tafel slope

The Tafel slope \( (b) \) serves as an empirical parameter derived from the Butler–Volmer equation, which characterizes the kinetics of electron transfer in electrocatalysis. It can be determined by plotting the reaction potential against the logarithm of the partial current density of a product, with \( b \) representing the slope of the linear region. The Tafel slope indicates the increase in overpotential required to achieve a specific current density. Generally, a smaller Tafel slope implies faster electrocatalytic reaction kinetics and superior catalytic performance. Furthermore, the Tafel slope reflects the rate-determining step in the formation of desired products. For instance, a Tafel slope of 59 mV dec\(^{-1}\) suggests that the rate-determining step does not involve electron transfer, and only one electron is transferred in all preceding steps. Conversely, a Tafel slope of 116 mV dec\(^{-1}\) indicates that the rate-determining step is a single electron transfer, with no electron transfer occurring before this step. The Tafel equation can be expressed as follows:

\[
\eta = a + b \log |j|
\]

In this equation, \( \eta \) represents the overpotential, \( a \) is a constant, and \( j \) signifies the current density. Zheng \textit{et al.} demonstrated a progressive decrease in the CO Tafel slope (from 244 to 116 mV dec\(^{-1}\)) and C\(_2\)H\(_4\) Tafel slope (from 104 to 35 mV dec\(^{-1}\)), indicating a gradual slowdown in CO\(_2\)RR electrocatalytic kinetics.\(^{76}\) Moreover, as Tafel slope values reveal the rate-determining step of the catalytic reaction, we can discern the evolution of the reaction mechanism through these changing slopes. In contrast, Surendranath \textit{et al.} observed a C\(_2\)H\(_4\) Tafel slope of 27 mV dec\(^{-1}\) in aprotic solvents, signifying a markedly distinct reaction mechanism characterized by a quasi-equilibrium PCET step compared to that in protic solvents.\(^{77}\)

### 2.1.5 Other parameters

In addition to the previously mentioned parameters, there exist other parameters that are not extensively utilized but can be used to assess catalytic systems from unconventional perspectives. For instance, the electrochemically active surface area (ECSA) reflects the surface structural characteristics of the catalyst, and is derived from double-layer capacitance \( (C_{dl}) \) measurements. Typically, ECSA serves as a metric for assessing the exposure of active sites on the catalyst surface. Consequently, ECSA values within an appropriate range tend to exhibit a positive correlation with CO\(_2\) electrocatalytic performance.\(^{76,77}\) The construction of a highly porous and rough catalyst surface morphology can lead to an increase in ECSA.\(^{76,77}\) Occasionally, to investigate the specific influence of a non-electrochemically active area factor, the ECSA values of both the experimental and control groups are adjusted in a manner nearly identical to control the active site variables.\(^{78,79}\) The turnover number (TON), representing the product yield per unit catalyst, and turnover frequency (TOF), representing the product yield per unit catalyst over a specific time period, are additional parameters that can offer insights into catalyst utilization and stability. These two physical parameters are commonly employed to assess both the catalytic performance and the visible light harvesting capacity of catalysts in photocatalytic systems.\(^{82}\) Han \textit{et al.} developed an effective photosensitizer for CO\(_2\) reduction by directly coordinating redox-active metal centers with natural organic dyes. For instance, the CuPP/FeTDHPP system achieves more than 16 100 turnovers of CO with a maximum TOF of 7650 h\(^{-1}\), surpassing a reported Ir(ppy)\(_3\)/FeTDHPP system (TON = 140 in 55 h) by two orders of magnitude, demonstrating exceptional photocatalytic activity in CO\(_2\) reduction.\(^{82}\) TON/TOF is also employed to assess product formation rates in specific electrocatalytic systems utilizing molecular catalysts. Buonsanti \textit{et al.} developed a tandem catalyst, Cu\(_{cys}\)/Fe-Por, consisting of the CO-producing component iron porphyrin (Fe-Por) and Cu nanocubes (Cu\(_{cub}\)).. This tandem catalyst displayed an approximately 22-fold increase in C\(_2\)H\(_4\) selectivity compared to pristine Cu\(_{cub}\), which was attributed to the integration of molecular catalysts with tuneable TOF\(_{CO}\).\(^{84}\) It is crucial to apply diverse evaluation parameters judiciously, considering various aspects, to comprehensively characterize the catalytic effect of the catalyst from different dimensions.

### 2.2. Possible mechanisms in CO\(_2\) electroreduction

Chemical reactions occurring on the metal surface involve three fundamental steps: (1) the physical or chemical adsorption of reactants onto the surface; (2) the catalytic transformation on the surface; and (3) the desorption from the surface and formation of the product.\(^{85}\) In the case of multi-carbon products derived from CO\(_2\) electrocatalysis, the reactions taking place on the catalyst surface are highly intricate and diverse. The resulting reaction intermediates span from common C\(_1\) intermediates like *CO, *CHO, and *COOH to recognized C\(_2\) intermediates such as*C\(_2\)O\(_2\), *COOH, *CH\(_2\)OH* and others. These intermediates evolve from the fundamental *CO generated during the earlier electrolysis of CO\(_2\). Metals such as Au or Ag exhibit weak adsorption towards *CO and *H, favouring the desorption of *CO and consequently promoting the generation of CO rather than multi-carbon products. In contrast, metals like Pt or Fe, which excessively adsorb *CO and *H, tend to compete with CO\(_2\) electroreduction through intense HER. Therefore, when compared to other metals, only Cu exhibits the ability to produce a wide array of hydrocarbon products. This is due to its affinity for *CO and *H adsorption, striking a balance between preserving active site functionality and enabling the intermediates’ facile desorption from the catalyst surface.\(^{85}\) Based on the preceding analysis, controlling the quantity and distribution of catalytic active sites that can enrich *CO can significantly enhance the catalyst's selectivity for the desired products.

#### 2.2.1 Reaction mechanism of C\(_1\) products

The initial stage in the generation of C\(_1\) products involves the adsorption and activation of a CO\(_2\) molecule on the catalyst surface, resulting in a bent state denoted as *CO\(_2\)*. Subsequently, *CO\(_2\)* can undergo hydrogenation to yield either *COOH or *OOCR, which can further convert to HCOOH or CO, respectively. The
latter transformation entails the dehydrogenation of \(^*\text{COOH}\). These products, namely \(\text{H}_2\), \(\text{HCOOH}\), and \(\text{CO}\), dominate at lower negative potentials due to the simplicity of the reduction process and the small number of electron transfers required. According to the Computational Hydrogen Electrode (CHE) model proposed by the Nørskov group, the crucial step for the formation of \(\text{CH}_4\) and other higher-order hydrocarbons is the hydrogenation of \(^*\text{CO}\) to \(^*\text{CHO}\), which occurs at \(-0.74\ \text{V vs. RHE}\). This suggests that a more negative potential favours the production of products derived from \(^*\text{CHO}\). Subsequently, \(^*\text{CHO}\) can be further reduced to \(\text{CH}_3\text{O}\) and \(\text{CH}_3\text{OH}\), leading to the production of \(\text{CH}_4\). Notably, a small amount of \(\text{CH}_3\text{OH}\) is also generated during this process, however, its thermodynamic stability is comparatively lower than that of other \(\text{C}_1\) products.

### 2.2.2 Reaction mechanism of \(\text{C}_2\) products

The generation of \(\text{C}_2\) products involves the coupling of adsorbed \(^*\text{CO}\) species on the catalyst surface. Comprehending the mechanisms and factors influencing the \(\text{C}-\text{C}\) coupling and hydrogenation processes is pivotal for the rational design of highly active and selective catalysts. Hwang \textit{et al.}, using time-resolved Attenuated Total Reflectance-Surface Enhanced Infrared Absorption Spectroscopy (ATR-SEIRAS), observed a kinetically linked dimer intermediate denoted as \(^*\text{OCOCO}\), which they identified as the key intermediate for the generation of \(\text{C}_2\) products. Wang \textit{et al.} proposed a hydrogen-assisted \(\text{C}-\text{C}\) coupling mechanism, wherein adsorbed \(^*\text{CHO}\) couples to form \(\text{OCHCHO}\) over a Cu catalyst modified with fluorine. Head-Gordon \textit{et al.} suggested \(\text{COCH}\) as another possible intermediate resulting from the coupling of \(^*\text{CO}\) and \(^*\text{CHO}\), which determines the selectivity between \(\text{CH}_3\text{H}_4\) and \(\text{CH}_3\text{OH}\). Additionally, aside from these conventional intermediates, certain studies have investigated the role of \(\text{CO(g)}\) in the \(\text{C}-\text{C}\) coupling reaction under specific conditions. It has been proposed that \(\text{CO(g)}\) could form unconventional intermediates with \(^*\text{COOH}\) or \(^*\text{CO/CO(g)}\), potentially competing with the \(^*\text{OCOCO}\) dimerization pathway.

The selectivity of \(\text{C}_2\) products relies on the involvement of intermediates in the \(\text{C}-\text{C}\) coupling and hydrogenation reactions. Various studies have proposed different intermediates, including \(^*\text{OCOCO}\), \(^*\text{OCHCHO}\), and \(^*\text{CO/CHO}\). These intermediates originate from proton and electron transfers of \(^*\text{CO}\) or \(^*\text{OCOCO}\), resulting in various \(\text{C}_2\) products such as \(\text{C}_2\text{H}_4\) and \(\text{C}_2\text{H}_5\text{OH}\). The formation barriers for these products are closely situated, leading to varied production tendencies under different conditions. Another potential intermediate is \(^*\text{CHOH}\), derived from the hydrogenation of \(\text{OC/COH}\). Goddard \textit{et al.} suggested that this intermediate is the crucial determinant of the selectivity of \(\text{C}_2\) products. It can either undergo dehydrogenation to form \(\text{CH}_2\text{O}\) and \(\text{CH}_4\) or hydrogenation to produce \(^*\text{CHCHO}\) and form \(\text{C}_2\text{H}_5\text{OH}\) (Fig. 3).

The selectivity between \(\text{C}_2\text{H}_4\) and oxygenated products is influenced by the reaction pathways of different intermediates involved in the \(\text{C}-\text{C}\) coupling and hydrogenation reactions, as well as the microenvironment of the catalyst surface, such as substrate coverage and alkaline conditions in the electrolyte. For instance, Sargent \textit{et al.} discovered that a lower \(\text{CO}\) coverage favoured the dehydrogenation of \(^*\text{OCOCO}\) or \(^*\text{OCHCHO}\) to form \(\text{C}_2\text{H}_4\). Meanwhile, the formation of \(\text{C}_3\) products has been observed on Cu-based catalysts. The mechanism of \(\text{C}_3\) formation remains elusive as no \(\text{C}_2\) intermediates have been detected through various characterizations. Theoretical calculations have proposed several potential pathways for \(\text{C}_3\) formation. For example, Zheng \textit{et al.} demonstrated that double sulphur vacancies on hexagonal CuS (100) planes could serve as active sites for ECR, enabling the stabilization of \(^*\text{CO}\) and \(^*\text{OCOCO}\), leading to the coupling of \(^*\text{CO}\) and \(^*\text{OCOCO}\) and the formation of the crucial \(\text{C}_3\) intermediate \(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\). The double sulphur vacancy-rich CuS catalyst they synthesized exhibited a faradic efficiency of 15.4 ± 1% for \(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\) production. Therefore, a plausible hypothesis for generating \(\text{C}_3\) products is that an absorbed \(^*\text{CO}\) couples with an adjacent \(^*\text{OCOCO}\) to form a \(\text{C}_3\) intermediate, which then undergoes proton and electron transfer to yield the final \(\text{C}_3\) product.

The synthesis of a wide range of chemicals and fuels from \(\text{CO}_2\) is a complex process, influenced by several factors, such as the electrolyte environment, applied potential, and, most significantly, the properties of the catalyst. Therefore, the precise and systematic design of catalysts that can effectively manipulate crucial intermediates by extending their residence time or modifying their structural conformation is essential for enhancing selectivity toward desired products. Frequently employed approaches for catalyst modification to control critical carbon-based intermediates encompass, but are not restricted to, the following: (1) fine-tuning the electronic properties of the catalytic active site. (2) Creating unique spatial structures to enhance the concentration of key intermediates. (3) Enhancing microenvironment alkalinity to suppress competition for hydrogen precipitation. (4) Adjusting the local \(\text{CO}\) concentration by varying the reactant concentration. These approaches correspond to the modification of specific

![Fig. 3 Possible C–C coupling mechanisms in the electrocatalytic CO₂ reduction (above). Mechanisms of forming C₂H₄ and C₂H₅OH after C–C coupling (below). Reproduced from ref. 92. Copyright 2021 Royal Society of Chemistry.](https://doi.org/10.1039/D1SC00309A)
intermediates in the aforementioned reaction mechanisms, either directly or indirectly, resulting in improved selectivity for multi-carbon target compounds.

3. Heteroatom doping engineering

Among the current state-of-the-art approaches for designing Cu-based catalysts capable of modulating intermediates, heteroatom doping stands out as the most effective strategy. Heteroatom doping brings about selective alterations in the electronic and geometrical structure of the catalyst surface. These modifications in the electronic structure impact the binding strength of reaction intermediates, while changes in the geometrical structure influence the exposure of active sites to intermediates. Consequently, composite catalysts exhibit distinct catalytic properties when compared to their monometallic counterparts. This section classifies heteroatom doping into two subcategories based on the type of heteroatom: metallic heteroatom doping and non-metallic heteroatom doping (Table 1).

3.1. Metallic heteroatom doping

Alloying, the practice of introducing an additional metal atom into a Cu-based catalyst, is a commonly employed strategy for designing catalysts that can harness the synergistic effects of multiple metals. The lattice mismatches between Cu and the alloying metal can induce strain at the interface, consequently influencing the binding energy barriers of carbonate intermediates on the catalyst surface. The geometric and electronic properties of the catalyst are contingent upon the type and quantity of doped metal atoms, making alloying one of the most direct and widespread catalyst design approaches for modulating intermediates.

Through metallic heteroatom doping, electron transfer occurs at the interface due to the difference in electronegativity between the two metals. This leads to varied binding energies for essential intermediates involved in the formation of C2+ products. For instance, Xiong et al. successfully doped amorphous CuTi alloy (a-CuTi@Cu) with coordinatively unsaturated Cu to produce C2–4 products. Theoretical simulations and in situ characterization demonstrated that subsurface Ti transfers electrons to Cu, enhancing the affinity for *CO and lowering the reaction barrier energies of *CO dimerization and trimerization (Fig. 4a). Metallic heteroatom doping not only facilitates electron transfer but also modifies the electronic environment of the entire catalyst. For instance, doping mesopore-rich Cu oxide nanofibers (Cu–Al MONFs) with Al significantly improved the electrocatalytic performance in CO2 electroreduction to...
generate C₂+, products. The Cu–Al MONFs achieved a remarkable C₂+, faradaic efficiency of 76.4%, surpassing CuO nanofibers (with an FE of only ~10%) under the same conditions (Fig. 4b). Further investigation revealed that Al reconstructed the surface charge distribution of Cu, optimizing the energy barrier of *CO–*COH coupling.¹⁰⁷ Doping Pb into Cu (Pb,Co) alters the electronic environment of Cu active sites. These activated Cu sites modulate the adsorption free energy of HCOO*, diverting the CO₂RR toward the HCOO* pathway rather than the COOH* pathway and enhancing the selectivity of HCOOH with a high activity exceeding 1 A cm⁻² (Fig. 4c).¹⁰⁸ Furthermore, the improved performance in ECR can be attributed to the direct adsorption of crucial intermediates at distinct atomic interfaces. For example, when Cu is doped with a second metal Sb (Sb₃Cu), it stimulates a surface promotion effect for intermediates. Computational simulations indicate that Sb doping promotes CO₂ adsorption and activation while facilitating the desorption of *CO during the reaction, significantly improving CO selectivity.⁵⁹ Introducing Pd to Cu creates a strong affinity for CO* and effectively inhibits hydrogen precipitation, resulting in a single-pass carbon efficiency of 60% for CO₂ to C₂*, at 500 mA cm⁻² under acidic conditions.¹⁰⁹ Dopping Cu with another metal atom can impact not only the charge distribution of the Cu surface but also other aspects like the catalyst’s morphology. For instance, Cao et al. synthesized Cu nanowires decorated with a small quantity of Au nanoparticles (Cu–Au NWs) via a homonuclear method. The presence of Au nanoparticles increased the surface roughness of the catalyst, exposing more active sites, which enhances the adsorption of *CO on the electron-deficient Cu surface. This in turn improved the selectivity towards C₂+, products, resulting in an increase in faradaic efficiency from 39.7% (Cu NWs) to 65.3% (Cu–Au NWs).¹¹⁰ Dopping with other metals can also reduce the formation energy barrier of certain rare intermediates, enabling their production and even altering the reaction pathway towards desired products.⁶¹,¹¹⁰ For example, CuAg thin films with nonequilibrium Cu/Ag alloying were fabricated via physical vapor deposition. This approach surpassed the limitations of thermodynamic miscibility and enhanced the interphase mixing of Ag into the Cu-rich catalyst. The improved miscibility optimized the binding energies of adsorbates and reaction intermediates on the catalyst surface, thereby increasing the selectivity for liquid carbonyl products such as CH₃CHO and CH₂COOH compared to bare Cu.¹¹¹ Expanding on the discovery of interphase miscibility, Jaramillo et al. investigated the impact of Ag doping on Cu (CuAg-NF) and its influence on the selectivity between CH₃CHO and C₂H₅OH in electrochemical CO reduction. Utilizing density functional theory calculations, they attributed the higher selectivity towards CH₃CHO rather than C₂H₅OH to the reduced formation energy barriers of relevant intermediates induced by Ag doping.¹¹² Cu, being the most promising metal for polycarbonate production, can experience CO “spillover” at the interface when doped with metals that predominantly produce C₁ products. This leads to further C–C coupling on Cu. For instance, the doping of Cu with Pd reduces the average d-band of the CuPd bimetallic catalyst below the Fermi level, facilitating CO spillover at the CuPd interface for subsequent coupling (Fig. 4d).¹¹³ Similarly, doping Cu with Au, another metal that primarily produces CO, can also result in CO spillover.¹¹⁴ In addition, the presence of Zn in Cu₁₋ₓZnₓ alloys has been observed to facilitate the spillover of CO. The introduction of Zn alters the catalyst’s electronic structure by shifting the position of the d-band center, making *CO desorption from the surface easier and promoting the formation of *COCH and even *COCOCH. This “CO insertion process” enhances the selectivity for CH₃COCH₃ (Fig. 4e).¹³ Doping Cu-based catalysts with a second metal is a straightforward strategy to selectively modify the electronic distribution by varying the type and amount of dopant. However, since metallic heteroatom doping is often costly, this approach is not economically feasible for large-scale industrial applications. There is a need to develop more cost-effective design strategies for non-precious metals.

### 3.2. Non-metallic heteroatom doping

Doping Cu-based catalysts with non-metallic elements induces interfacial strain and alters the electronic structure of the catalyst. This modification impacts the oxidation state of Cu, particularly when the electronegativity of the dopant exceeds that of Cu. As a result, the selectivity towards C₂+ products is significantly enhanced. Compared to metallic heteroatom doping, non-metallic heteroatom doping reduces the overall costs of catalyst preparation due to the abundance of non-metallic elements. Consequently, non-metallic heteroatom doping has gained widespread application in recent years.¹¹⁵–¹¹⁸

By doping Cu-based catalysts with non-metallic heteroatoms, particularly halogen elements with higher...
electron negativity than Cu, the regulation of the d-band center of Cu can be achieved, thereby enhancing the absorption of key intermidiates. For instance, fluorine-doped Cu-based catalysts exhibit enhanced capabilities in water dissociation, *CO adsorption, and hydrogenation of *CO to *CHO (Fig. 5a). Notably, this fluorine-modified Cu catalyst achieved an impressive faradaic efficiency of approximately 80% for C₂ products (primarily C₂H₄ and C₂H₂OH), with a remarkable current density of 1.6 A cm⁻². Similarly, iodide-derived copper (ID-Cu) benefits from high-density defects and surface roughness, which enhance *CO adsorption by elevating the d-band center of Cu and facilitating C-C coupling on ID-Cu. The doping of halogen elements induces the formation of the Cu oxidation states while preserving the phase structure, resulting in strong adsorption of *CO and other carbonate intermediates on Cu²⁺. Cui et al. demonstrated that Cu²⁺ can be dynamically stabilized by I⁻ in HCO₃⁻ electrolytes through the formation of CuI, leading to the formation of atypical Cu(O)²⁻ complexes with strong binding of in situ formed *CO. This system achieved a remarkable 3.0-fold increase in faradaic efficiency towards C₂ compared to the system without I⁻. Moreover, introducing halogen elements into Cu creates a synergistic effect that impacts the coordination microenvironment on active catalytic centers, thereby influencing the behavior of intermediates. Lan et al. constructed a stable crystalline single-chain catalyst model system consisting of four homomorphic one-dimensional chain-like compounds (Cu-PzH, Cu-PzCl, Cu-PzBr, and Cu-PzI). The difference in Pz ligands' electronegativity originates from the substituents of halogen atoms. This variation in the coordination microenvironment results in different δCu-Cu distances and βCu-Cu dihedral angles between neighboring Cu active sites, leading to linear regulation of catalyst selectivity for CH₄ and C₂H₄.

Non-halogen heteroatom doping is another effective method to promote Cu oxidation states, leading to enhanced selectivity for C₂⁺ products. For example, Cu-based compounds with heteroatoms (N, P, S, O) underwent significant structural reconstruction to form heteroatom-derived Cu under CO₂RR conditions. The N-engineered Cu (N-Cu) catalyst achieved the best CO₂-to-C₂⁺ production rate at ~1100 mA cm⁻² with a faradaic efficiency of 73.7%, outperforming most reported Cu-based catalysts. Cubic copper nitrite (Cu₃N₄) with high-density nitrogen vacancies exhibits improved *CO adsorption and subsequent *CO- *CO coupling, facilitating the enrichment of key C₂ intermediates (Fig. 5b). The Cu₃N₄ catalyst, abundant in nitrogen vacancies, achieves an impressive faradaic efficiency of 81.7 ± 2.3% for C₂ products at 307 ± 9 mA cm⁻². In a similar vein, Oh et al. doped boron in copper oxide (B-CuO) to create multiple Cu⁺⁺ sites for electrochemical CO reduction. ATR-SEIRAS measurements directly revealed stronger *CO adsorption on B-CuO compared to CuO, thereby promoting the C-C coupling of CO and resulting in a C₂⁺ faradaic efficiency of 62.1% at ~0.62 V vs. RHE, a significant improvement over CuO with 48% faradaic efficiency. The incorporation of non-metallic elements through heteroatom doping presents new opportunities for enhancing CO₂ to C₂⁺ conversion efficiency by modifying the local electronic environment on the catalyst surface. Non-metallic heteroatom doping is a widely adopted catalyst design strategy that allows easy regulation of the d-band center of Cu and the occurrence of Cu²⁺, thereby modulating the efficiency towards C₂⁺ conversion.

Table 1: Summary of the ECR performance of various Cu-based electrocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Cell type</th>
<th>E (V vs. RHE)</th>
<th>j (mA cm⁻²)</th>
<th>Main C₂⁺ product</th>
<th>FE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic heteroatom doping</td>
<td>Cu₃Ag₁</td>
<td>0.5 M KHCO₃</td>
<td>H-Cell</td>
<td>-0.95</td>
<td>25</td>
<td>C₂H₂OH</td>
<td>63</td>
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<tr>
<td>Cu₂Smₓ</td>
<td>0.1 M KHCO₃</td>
<td>H-Cell</td>
<td>-1.4</td>
<td>15.05</td>
<td>C₂H₂OH</td>
<td>25.93</td>
<td>69</td>
</tr>
<tr>
<td>Cuₓ–Znₓ</td>
<td>0.1 M NaHCO₃</td>
<td>Flow cell</td>
<td>-0.4</td>
<td>48</td>
<td>C₂H₂OH</td>
<td>19</td>
<td>71</td>
</tr>
<tr>
<td>a-CuTi@Cu</td>
<td>0.1 M KHCO₃</td>
<td>H-Cell</td>
<td>-0.8</td>
<td>485</td>
<td>C₂H₂OH</td>
<td>48.82</td>
<td>106</td>
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<tr>
<td>Cu–Al MONFs</td>
<td>1 M KOH</td>
<td>Flow cell</td>
<td>-1.7</td>
<td>485</td>
<td>C₂H₂OH</td>
<td>76.4</td>
<td>107</td>
</tr>
<tr>
<td>PbₓCu</td>
<td>0.5 M KHCO₃</td>
<td>H-Cell</td>
<td>-0.8</td>
<td>800</td>
<td>HCOOH</td>
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<td>124</td>
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<tr>
<td>SbₓCu–5</td>
<td>0.5 M KHCO₃</td>
<td>Flow cell</td>
<td>-1.6</td>
<td>452</td>
<td>CO</td>
<td>91</td>
<td>59</td>
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<tr>
<td>Pd–Cu catalyst</td>
<td>0.5 M K₂SO₄ (pH adjusted to 2.0 with H₂SO₄)</td>
<td>Flow cell</td>
<td>-1.2</td>
<td>500</td>
<td>C₂H₂OH</td>
<td>89 ± 4</td>
<td>109</td>
</tr>
</tbody>
</table>

| Non-metallic heteroatom doping | Cu–Au NWs | 0.1 M KHCO₃ & 0.1 M KCl | H-Cell | -1.25 | 12.1 | C₂⁺ | 65.3 | 114 |
| BaO/Cu | 1 M KOH | Flow cell | -0.75 | 244 | C₂⁺ alcohol | 61 | 110 |
| CuAg thin film | 0.1 M KHCO₃ | H-Cell | -1 | 16 | Carbonyl products | 8.1 | 111 |
| CuAg | 0.1 M KOH | Flow cell | -0.536 | 20 | CH₂CHO | 50 | 112 |
| CuOHCl NSs | 0.1 M KHCO₃ | H-Cell | -1 | 53 | C₂⁺ | 53.8 | 125 |
| Sputtered Cu | 0.1 M KHCO₃ & 0.1 M KI | H-Cell | -0.95 | 13 | C₂⁺ | 55 | 120 |
| ID-Cu | 0.1 M KHCO₃ | Flow cell | -1.1 | 290 | C₂⁺ | 71.16 | 119 |
| Cu-PzX | 1 M KOH | Flow cell | -0.9 | 346.46 | CH₄ | 39.4 | 121 |
| N-Cu | 1 M KOH | Flow cell | -1.15 | 287.52 | CH₄ | 25.35 | 122 |
| CuₓNₓ | 1 M KOH | Flow cell | -1.15 | 1100 | C₂⁺ | 73.7 | 116 |
| B–CuO | 1 M KOH & 1 M KHCO₃ | Flow cell | -0.62 | 135 | C₂⁺ | 81.7 ± 2.3 | 122 |

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adsorption strength of intermediates, particularly enhancing CO adsorption. Non-metallic heteroatom doping provides valuable insights into the low-cost preparation of catalysts that can achieve electrocatalytic activity comparable to that of catalysts prepared via metallic heteroatom doping.

4. Morphological structure engineering

Among the current cutting-edge designs for Cu-based catalysts aimed at regulating intermediates, the second major category is morphological structure engineering, which is equally prevalent as heteroatom doping. The manipulation of catalyst morphologies can significantly influence the exposure configuration and abundance of active sites on the catalyst surface, thereby exerting a critical and complex impact on the behaviour of key intermediates and even the distribution of products. Particularly, the geometric confinement effect plays a significant role in enhancing the localized retention of key intermediates, effectively promoting the formation of multi-carbon products and deepening the extent of product reduction. Considering these advantages, morphological structure engineering holds greater promise for practical applications than heteroatom doping. The reported works in this field can be categorized as follows: grain boundary effect, geometric confinement through pores and hierarchical structures, facet engineering, defect engineering, and the influence of chemical state (Table 2).

4.1. Grain boundary effect

In general, the activity of catalysts in CO2 and CO reduction is proportional to the abundance of grain boundaries (Fig. 6a). Therefore, it is widely accepted that grain boundaries play a crucial role in modulating the absorption energy barriers of intermediates, thereby promoting the formation of multi-carbon products. Grain boundaries typically form between different crystalline phases of copper with the same valence state. Gong et al. fabricated copper catalysts rich in grain boundaries (GB-Cu) via additive-controlled electrodeposition. In situ attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) demonstrated that the presence of enriched grain boundaries enhanced the adsorption of the key intermediate CO on copper surfaces, enabling GB-Cu to achieve a C2 faradaic efficiency of up to 70% over a wide potential range (Fig. 6b and c). Similarly, Zheng et al. created a CuO electrocatalyst with high-density grain boundaries and micron-strains by rapidly cooling in liquid nitrogen (Fig. 6d). With an increased cooling rate, the CuO catalyst exhibited remarkable faradaic efficiency for C2 products, mainly C2H5OH, with partial current densities reaching up to 300 mA cm⁻². Grain boundaries can also exist between different facets of Cu with the same valence state and between Cu with different valence states. Through the simple reduction of Cu(OH)2 and carbonization, Han et al. prepared a series of Cu-based composites with a range of gradient grain boundary densities and Cu⁷/Cu⁹ ratios. The enhanced adsorption of CO* on Cu⁺ and the high density of grain boundaries resulted in a faradaic efficiency of 64.5% for C2 products at 26.2 mA cm⁻².

An effective approach to enhance the production of C2 products is the construction of electrocatalysts with abundant grain boundaries, which directly facilitate the adsorption of CO* on the surface. However, control over the construction and density of grain boundaries is challenging due to the uncertainty of in situ catalyst growth and the difficulty of characterization. This presents a significant challenge in developing catalysts rich in grain boundaries.

4.2. Geometric confinement of pore and hierarchical structure

The design of catalysts with abundant pores and hierarchical structures offers two key advantages: it increases the surface area-to-volume ratio, exposes more active sites for the reaction,
and enhances the mass transport of reactants.\textsuperscript{144-146} The porosity of catalysts can be classified into three types: macropores (\textgtr 50 nm), mesopores (2-50 nm), and micropores (<2 nm). Macropores expand the specific surface area of the catalyst and facilitate the diffusion of electrolyte and reactant molecules. Mesopores and micropores both configure the intermediates and prevent their leakage,\textsuperscript{147-150} while creating an OH-rich microenvironment that promotes C-C coupling.\textsuperscript{151-153} In summary, constructing porous catalysts is a straightforward approach to control the concentration and residence time of intermediates.\textsuperscript{154-158}

One effective approach to enhance the performance of ECR is to design catalysts with a high degree of porosity, which increases the concentration of CO and facilitates their coupling. Ma \textit{et al.} successfully synthesized a series of uniform hollow oxide-derived Cu (OD-Cu-H) catalysts with varying degrees of porosity by a simple method. They observed a positive correlation between porosity density and C\textsubscript{2} selectivity, while C\textsubscript{1} products and H\textsubscript{2} formation showed a negative correlation. This phenomenon was attributed to the localization of CO\textsuperscript{*} and the promotion of C-C coupling on the porous surface (Fig. 7a).\textsuperscript{159} Similarly, Deng \textit{et al.} utilized mechanically polished Cu foils to expose highly reactive Cu sites that effectively confined CO and other intermediates for the subsequent generation of C\textsubscript{2} products.\textsuperscript{160} In addition, Geng \textit{et al.} investigated the effect of pore size on the regulation of *CO intermediate using core-shell Ag@Cu catalysts. They discovered that moderately sized mesopores (4.9 nm) on the Cu shell provided optimal confinement for *CO (Fig. 7b), leading to an improved catalytic performance for C\textsubscript{2}+ products, with a yield of approximately 73.7% at 300 mA cm\textsuperscript{-2}.\textsuperscript{147} Zeng \textit{et al.} documented a correlation between CO\textsubscript{2}-to-C\textsubscript{2}+ conversion and the nanoc confinement effect of Cu hollow multi-shell structures. Specifically, an increase in the number of shells is positively associated with the selectivity and activity of the C\textsubscript{2} species. Simulations using the finite element method demonstrated that an increase in the number of shells enhances the C-C coupling process by reducing diffusion kinetics, enabling a higher concentration of CO adsorbates to accumulate within the nanovoids.\textsuperscript{153}

In addition to regulating key intermediates associated with the reaction, the porosity of catalysts also plays a crucial role in stabilizing the active species during ECR.\textsuperscript{150,161} For instance, Yu \textit{et al.} successfully constructed Cu\textsubscript{2}O catalysts with nanocavities, effectively preventing the overconsumption of carbon intermediates and maintaining high coverage of easily reduced Cu\textsuperscript{+} species. The high concentration of Cu\textsuperscript{+} species greatly enhanced the selectivity for C\textsubscript{2}+ products, resulting in a remarkable C\textsubscript{2}/C\textsubscript{1} ratio of approximately 7.2 at high reaction rates (Fig. 7c). Raman spectroscopy and X-ray absorption studies confirmed the stability of Cu\textsuperscript{+} species during the catalytic process.\textsuperscript{148} The suitable and
abundant porosity of the catalyst, along with the presence of stable active species, provides geometric confinement for the intermediates. Additionally, the hierarchical structure of the catalyst influences the residence and reaction pathways of intermediates, as well as the kinetics of the protonation process.\textsuperscript{81,146,161} Zhang et al. developed multi-shelled CuO microboxes and investigated the effect of the hierarchical structure on active sites’ exposure and the adsorption of carbonate intermediates.\textsuperscript{242} They discovered that small and uniform multi-shelled CuO microboxes exhibited significantly improved performance in converting CO\textsubscript{2} into C\textsubscript{2}H\textsubscript{4}, which was attributed to the enrichment of *CO.

Constructing moderate pores or hierarchical structures is a promising strategy for regulating the behaviour of key intermediates and promoting the formation of C\textsubscript{2}+ products in ECR. However, the type of intermediate, rather than the retention time, is the primary factor and is influenced by geometric and hierarchical confinement. Therefore, to achieve high selectivity for desirable products, more complex morphological structures are required, which can precisely control the type of reaction intermediate.

4.3. Facet

The facet structure of Cu is an important factor that influences the behaviour of intermediates on its surface. Copper (Cu) is a metallic material that exhibits multiple crystalline facets, typically consisting of low-index facets unless specifically modified. Different crystal facets of Cu exhibit distinct periodic arrangements of atoms and surface electronic structures, leading to varying adsorption strengths for reaction intermediates.\textsuperscript{43,163} Unlike the commonly observed low-index facets, relatively high-index crystal facets such as Cu(511) and Cu(611) possess abundant step-like sites and kinks on their surfaces. These step-like sites and kinks on these facets exhibit low coordination numbers for Cu reaction sites, resulting in higher catalytic activity than Cu reaction sites on low-index facets.\textsuperscript{164}

Different facets of Cu exhibit distinct catalytic orientations in ECR. Extensive research indicates that Cu(100) and Cu(110) facets are preferred for generating C\textsubscript{2}+ products due to their enhanced adsorption of *CO, leading to the formation of *OCCO and *CH\textsubscript{2}CHO.\textsuperscript{165} In contrast, the Cu(111) facet promotes the formation of C\textsubscript{1} products, such as CH\textsubscript{4}, by facilitating the generation of *COOH and *CO.\textsuperscript{43,165,166} Sun et al. investigated the influence of the Cu(100) facet on CO\textsubscript{2} electrodeposition by employing hierarchical micro/nanostructured Cu(100)-rich copper hollow fibers as a gas penetration electrode. Theoretical calculations (Fig. 8a) confirmed a significant enhancement in the adsorption of *CO on the Cu(100) facet, enabling efficient C-C coupling and yielding a remarkable selectivity of 62.8% towards C\textsubscript{2}+ products at an ultra-high current of 2.3 A cm\textsuperscript{-2}, surpassing that of existing Cu-based catalysts.\textsuperscript{168} Several recent studies have reported the enhanced adsorption of *CO on Cu(100) and Cu(110) crystalline surfaces.\textsuperscript{169–171}

The synergistic effect of different crystalline sites is worth considering to modulate the behaviour of reaction intermediates. Through investigating the edge-to-surface ratio of Cu NC catalysts, Wang et al. demonstrated the significance of the Cu(100) facet in combination with step-like sites along the edge to improve the selectivity of acetic acid production (Fig. 8b).\textsuperscript{172} Similarly, Sargent et al. investigated the synergistic effect of Cu\textsubscript{1} and Cu\textsubscript{2} sites on highly fragmented Cu, which facilitated the coupling of Cu\textsubscript{1} and Cu\textsubscript{2} intermediates to promote the formation of CH\textsubscript{3}CH\textsubscript{2}CHO (Fig. 8c and d). They achieved a selectivity of 20% at a high reaction rate, corresponding to a partial current density of 8.5 mA cm\textsuperscript{-2}.\textsuperscript{24} In addition to facet orientation, the surface orderliness of Cu also impacts the behaviour of reaction intermediates during ECR. Roldan Cuenya et al. observed that highly clean, atomically ordered Cu(111) and Cu(100) single crystal facets predominantly yield H\textsubscript{2} instead of the expected hydrocarbon products. Hydrocarbon products from CO\textsubscript{2} conversion are primarily achieved when there are adequate defects and high-index crystal surfaces.\textsuperscript{173} Therefore, constructing non-planar sites and high-energy crystal surfaces is crucial to enhance the catalysts’ ability to regulate intermediates. For instance, Huang et al. activated Cu nanowires and introduced a highly stepped surface morphology. Experimental findings indicate a positive correlation between the proportion of stepped-surface structure A- \textit{(hkl)} and the faradaic efficiency of C\textsubscript{2}H\textsubscript{4}, which is attributed to the increased adsorption of 2CO* on the stepped surface [3(100) × (111)] (Fig. 8e).\textsuperscript{174} Likewise, Guo et al. explored the nature of CO-CO structures adsorbed on high-index Cu surfaces and reaffirmed their contribution to C\textsubscript{2}+ products.\textsuperscript{175}

Selecting the appropriate crystalline facets is vital in regulating the behaviour of key intermediates, thereby influencing the reaction pathway and product distribution. Additionally, the synergistic effects of specific crystallographic facets should be taken into consideration.\textsuperscript{176} Nevertheless, accurate characterization of the catalyst surface morphology is necessary as the catalytic site may not align with our expectations.

4.4. Defect

Constructing defects on Cu catalysts provides a means to modify the coordination environment and electronic structure of Cu without introducing additional elements. Defects, also referred to as ion vacancies, can enhance CO\textsubscript{2} activation and *C\textsubscript{1} adsorption, thereby promoting the formation of desirable C\textsubscript{2}+ products.\textsuperscript{176,177} For instance, Zheng et al. synthesized a Cu catalyst with abundant defect sites under CO-rich conditions (Cu\textsubscript{DS}), and they demonstrated that the substantial *CO coverage on the Cu\textsubscript{DS} surface activated the CO\textsubscript{2}-C\textsubscript{2}H\textsubscript{4}OH reaction pathway with its strong adsorption, as depicted in Fig. 9a and b.\textsuperscript{178} In certain cases, defects do not act alone as promoters of the CO\textsubscript{2}RR; rather, they synergistically interact with specific crystalline facets like Cu(100), Cu(110), or grain boundaries to precisely modulate the surface intermediates. Cuenya et al. achieved oxidation state and morphology tuning of the copper catalysts via pulsed CO\textsubscript{2} electrolysis, revealing that the optimal arrangement of Cu(100) domains, defect sites, and surface CuO promoted the CO\textsubscript{2}RR pathway towards C\textsubscript{2}+ products. Specifically, they observed that the enhanced C\textsubscript{2}H\textsubscript{4}OH selectivity correlated with the coexistence of Cu(i) and Cu\textsuperscript{0} species,
while the extent of the Cu(100) gradient predominantly influenced C$_2$H$_4$ production, as depicted in Fig. 9c.\textsuperscript{179}

Achieving precise control over the construction of defects on Cu has posed a longstanding challenge for scientists due to the inherent difficulty in precise defect manipulation. In recent years, several studies have documented the introduction and subsequent removal of heteroatoms in Cu-based catalysts as a method to create defects.\textsuperscript{98,180} For instance, Zheng et al. devised a straightforward lithium electrochemical modulation strategy, which not only generates a high density of double sulphur vacancies but also reduces the Cu–Cu distance, as illustrated in Fig. 9d. Their investigation revealed that the bisulphide vacancies formed within the hexagonal CuS (100) plane served as active electrocatalytic centers for CO$_2$ electro-reduction, promoting the stability of CO* and OCCO* dimers and facilitating the *CO–OCCO* coupling, leading to the formation of the crucial *C$_3$ intermediate in CH$_3$CH$_2$CH$_2$OH production. As a result, the catalytic performance of CH$_3$CH$_2$:CH$_2$OH, quantified by its faradaic efficiency, can reach as high as 15.4% in the H-cell along with a partial current density of 9.9 mA cm$^{-2}$ in the flow cell.\textsuperscript{98}

Defects can also be created by removing other highly electronegative elements, such as halogens. Palmore et al. documented a practical and scalable anodic halogenation method for fabricating Cu-based catalysts with a significant defect density. They also explored the correlation between defect density, surface roughness, and the anodic halogenation conditions of the catalysts. The investigation revealed that the Cu(I)X-derived catalysts (where X = Cl, Br, or I) exhibited exceptional performance in ECR, which can be attributed to the enhanced adsorption of carbonate intermediates on the catalyst surface. The experimental results and characterization data strongly indicate that the abundant defects greatly promote the production of polycarbonate products, while reducing
roughness mitigates the competition from hydrogen precipitation (Fig. 9e and f). Consequently, this offers a novel avenue for the meticulous design of catalyst defect structures.

Engineering defects enables precise control of reaction intermediates, particularly \(^*\)CO, and can significantly impact the reaction pathway. Defects can synergistically interact with specific sites like facets and grain boundaries in certain cases. Moreover, there is growing documentation on the precise incorporation of defects into Cu-based catalysts, establishing defect engineering as a strategy capable of precisely modulating the concentration and reaction behaviour of intermediates.

### 4.5. Chemical state effect

The oxidation state of an atom represents the electron gain or loss in a chemical bond, providing insights into the nature and strength of its covalent or ionic interactions.\(^{182}\) Oxide-derived copper (OD-Cu) catalysts primarily consist of Cu\(^+\) and Cu\(^2+\) species and are synthesized by incompletely reducing copper oxide precursors.\(^{183–185}\) Following Kanan et al.’s groundbreaking work on the exceptional catalytic performance of annealed Cu for ECR (Fig. 10a),\(^{186}\) numerous studies have investigated the mechanism and performance of OD-Cu catalysts for electrocatalytic \(\text{CO}_2\) reduction.\(^{137,179,187}\) Jung et al. developed a novel porous Cu/Cu\(_2\)O aerogel with remarkable \(\text{C}_2\text{H}_5\text{OH}\) productivity in ECR (Fig. 10b–d). They attributed this to the presence of abundant Cu\(^{0–}\text{–Cu}\)\(^{1+}\) interfaces and the elevated local pH within the confined porous aerogel network structure, resulting in a high faradaic efficiency (\(\text{FE}_{\text{CHOH}}\)) of 41.2\% and a partial current density (\(I_{\text{CHOH}}\)) of 32.55 mA cm\(^{-2}\).\(^{188}\) The valence effect often synergizes with other factors to modulate the behaviour of intermediates and enhance the performance of Cu-based catalysts in ECR. An exemplary case of this synergy is the unique and stable OD-Cu (Cu\(_x\)O) catalyst, characterized by a hierarchical pore and nanograin-boundary structure. Systematic characterization analysis and theoretical calculations demonstrated that the atypical OD-Cu enables highly sensitive modulation towards \(^*\)CO adsorption and boosts further C–C dimerization, eventually achieving an outstanding faradaic efficiency of 45\% towards \(\text{C}_2\text{H}_4\) at a partial current density of 44.7 mA cm\(^{-2}\) in neutral media (Fig. 10e).\(^{189}\)

Non-zero-valent Cu in its single-atom form demonstrates exceptional control over carbon intermediates, distinct from bulk-scale OD-Cu. Li et al. introduced a novel atom-pair catalyst strategy, demonstrating the stabilization of Cu atom-pair sites (Cu\(_{10}\)–Cu\(_{11}\)) on Te surface defects of Pd\(_{20}\)Te\(_3\) alloy nanowires. The authors investigated the mechanism of these catalysts, referred to as the “bi-atomic activating bimolecular"
mechanism. Experimental results and density functional theory (DFT) simulations reveal that Cu$_{1+x}^{+}$ improves H$_2$O adsorption and stabilizes chemisorbed CO$_2$ molecules on adjacent Cu$_{10}$, facilitating protonation and subsequent reduction of the absorbed CO$_2$. The kinetics and thermodynamic favourability of Cu atom-pair sites enable the catalyst to attain a faradaic efficiency of over 92% for CO while negligibly impacting the hydrogen evolution reaction.

Despite the extensive research highlighting the exceptional performance of OD-Cu surfaces, single-atom pairs of Cu in CO$_2$ electrolysis, certain questions remain unanswered: can oxidized Cu be sustained under highly negative voltages? Moreover, is oxidized Cu the true catalytic site for CO$_2$ reduction? Addressing these questions is crucial since they have implications for designing and optimizing Cu-based catalysts in ECR. While a consensus on these questions has yet to be reached, further research and discussions are anticipated to provide insights.

5. Local catalytic environment engineering

In addition to catalyst structure construction, another approach to catalyst design for CO$_2$ electrolysis is the modulation of the local catalytic environment, which pertains to the specific conditions of active sites. This strategy encompasses several principles, including the substrate effect, co-catalyst effect, surface additive effect, reactant coverage effect, and local electrolyte microenvironment effect (Table 3). These factors impact the adsorption, activation, and reaction of multiple intermediates on the catalyst surface, therefore influencing the selectivity and efficiency of CO$_2$ electrolysis.

5.1. Substrate effect

The substrate on which the metal nanoparticles are loaded is one of the factors that can modulate the local catalytic environment of active sites in ECR. The substrate can influence the catalytic performance of metal nanoparticles in multiple ways. First, the substrate can facilitate efficient electron transfer, thereby modulating the electronic structure of the catalyst surface. Second, highly porous substrates can restrict the domain of metal nanoparticles, preventing their reduction or agglomeration. These characteristics significantly impact the modulation of intermediates’ behaviour, thus influencing the selectivity and efficiency of CO$_2$ electrolysis.
Table 2  Summary of the ECR performance of various Cu-based electrocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Cell type</th>
<th>(E) (V vs. RHE)</th>
<th>(j) (mA cm(^{-2}))</th>
<th>Main C(_2) product</th>
<th>FE (%)</th>
<th>Ref.</th>
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<tr>
<td><strong>Grain boundary</strong></td>
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<td>Cu/CNT</td>
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<td>(\text{C}_2\text{H}_5\text{OH}, \text{CH}_3\text{COOH})</td>
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<td>131</td>
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<td>CuO nanosheets</td>
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<td>(\text{C}_2)</td>
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<td>(\text{C}_2\text{H}_4, \text{C}_2\text{H}_5\text{OH})</td>
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<td>136</td>
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<td>(\text{C}_2)</td>
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<td>R-Cu-5</td>
<td>0.1 M KHCO(_3)</td>
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<td>(\text{C}_2)</td>
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<td><strong>Geometric confinement of pore and hierarchical structure</strong></td>
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<tr>
<td>Ag–Cu nanoenzyme</td>
<td>0.1 M KHCO(_3)</td>
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<td>−0.65</td>
<td>5(^a)</td>
<td>(\text{C}_2)</td>
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<tr>
<td>Multi-hollow Cu(_2)O</td>
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<td>−0.61</td>
<td>267 ± 13</td>
<td>(\text{C}_2)</td>
<td>75.2 ± 2.7</td>
<td>148</td>
</tr>
<tr>
<td>Cu mesopore electrode</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1.7</td>
<td>5.7</td>
<td>(\text{C}_2\text{H}_4)</td>
<td>38</td>
<td>151</td>
</tr>
<tr>
<td>Cu mesopore electrode</td>
<td>(30 nm/40 nm)</td>
<td></td>
<td></td>
<td>4.0</td>
<td>(\text{C}_2\text{H}_6)</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Cu mesopore electrode</td>
<td>(30 nm/70 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoporous Cu</td>
<td>1 M KOH</td>
<td>Flow cell</td>
<td>−0.67</td>
<td>653</td>
<td>(\text{C}_2)</td>
<td>62</td>
<td>156</td>
</tr>
<tr>
<td>Hollow OD-Cu(_2)O</td>
<td>0.1 M KHCO(_3)</td>
<td>Flow cell</td>
<td>−1.4</td>
<td>14.5</td>
<td>(\text{C}_2)</td>
<td>71.1</td>
<td>159</td>
</tr>
<tr>
<td>Cu-12.5 nm</td>
<td>0.4 M KI</td>
<td>H-Cell</td>
<td>−1.3</td>
<td>17</td>
<td>(\text{C}_2)</td>
<td>65.7</td>
<td>160</td>
</tr>
<tr>
<td>Ag@Cu-p4.9</td>
<td>1 M KHCO(_3)</td>
<td>Flow cell</td>
<td>−1.2</td>
<td>300</td>
<td>(\text{C}_2)</td>
<td>73.7</td>
<td>147</td>
</tr>
<tr>
<td>CuO@Cu-OYSNPs</td>
<td>1 M KOH</td>
<td>Flow cell</td>
<td>−1</td>
<td>50</td>
<td>(\text{C}_2\text{H}_4\text{OH})</td>
<td>22.22 ± 0.38</td>
<td>81</td>
</tr>
<tr>
<td>CuO cavity</td>
<td>1 M KOH</td>
<td>Flow cell</td>
<td>−0.59</td>
<td>605 ± 14</td>
<td>(\text{C}_2)</td>
<td>75.6 ± 1.8</td>
<td>146</td>
</tr>
<tr>
<td>Multi-shelled CuO microboxes</td>
<td>0.1 M K(_2)SO(_4)</td>
<td>H-Cell</td>
<td>−1.05</td>
<td>24.2</td>
<td>(\text{C}_2\text{H}_4)</td>
<td>51.3</td>
<td>197</td>
</tr>
<tr>
<td>3-Shell HoMSs</td>
<td>0.5 M KHCO(_3)</td>
<td>Flow cell</td>
<td>−0.82</td>
<td>513.7 ± 0.7</td>
<td>(\text{C}_2)</td>
<td>77.0 ± 0.3%</td>
<td>153</td>
</tr>
<tr>
<td><strong>Facet</strong></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>HF-Cu</td>
<td>1 M KOH</td>
<td>Flow cell</td>
<td>−0.45</td>
<td>8.5</td>
<td>(\text{CH}_2\text{CH}_2\text{OH})</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>Cu(100)-rich Cu hollow fiber</td>
<td>0.5 M KHCO(_3)</td>
<td>Flow cell</td>
<td>−1.94</td>
<td>2300</td>
<td>(\text{C}_2)</td>
<td>62.8</td>
<td>168</td>
</tr>
<tr>
<td>D-Cu(_2)O/Cu</td>
<td>0.1 M KCl</td>
<td>H-Cell</td>
<td>−1.2</td>
<td>70</td>
<td>(\text{C}_2)</td>
<td>70</td>
<td>170</td>
</tr>
<tr>
<td>HFP-Cu</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1.4</td>
<td>43</td>
<td>(\text{C}_2)</td>
<td>43</td>
<td>171</td>
</tr>
<tr>
<td>Cu NC</td>
<td>0.5 M KHCO(_3)</td>
<td>Flow cell</td>
<td>−1.5</td>
<td>200</td>
<td>(\text{CH}_3\text{COOH})</td>
<td>43</td>
<td>172</td>
</tr>
<tr>
<td>Cu NWs</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1</td>
<td>69.79 ± 1.44</td>
<td>(\text{C}_2\text{H}_4)</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td><strong>Defect</strong></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>CuO(_{10})</td>
<td>0.1 M KHCO(_3)</td>
<td>Flow cell</td>
<td>−1.08</td>
<td>100</td>
<td>(\text{C}_2)</td>
<td>70</td>
<td>178</td>
</tr>
<tr>
<td>Cu(100) electrode</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1</td>
<td>76</td>
<td>(\text{C}_2)</td>
<td>76</td>
<td>179</td>
</tr>
<tr>
<td>CuCl, CuBr, CuI</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1.1</td>
<td>72</td>
<td>(\text{C}_2)</td>
<td>72</td>
<td>181</td>
</tr>
<tr>
<td>Sb/CuO(V(_{0}))</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1</td>
<td>500</td>
<td>(\text{C}_2\text{H}_4)</td>
<td>89.3 ± 1.1</td>
<td>180</td>
</tr>
<tr>
<td>Cu(_2)S-DV</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1.05</td>
<td>3.1 ± 0.2</td>
<td>(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})</td>
<td>15.4 ± 1</td>
<td>98</td>
</tr>
<tr>
<td><strong>Chemical state effect</strong></td>
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</tr>
<tr>
<td>CuSiO(_2)@SiO(_2)</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1</td>
<td>9</td>
<td>(\text{C}_2)</td>
<td>70</td>
<td>183</td>
</tr>
<tr>
<td>OD-Cu-45</td>
<td>0.1 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1.04</td>
<td>0.35</td>
<td>(\text{C}_2)</td>
<td>65</td>
<td>185</td>
</tr>
<tr>
<td>Annealed Cu</td>
<td>0.5 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−0.35</td>
<td>2.1</td>
<td>CO</td>
<td>48</td>
<td>186</td>
</tr>
<tr>
<td>Cu/Cu(_2)O aerogel</td>
<td>0.1 M KCl</td>
<td>H-Cell</td>
<td>−0.58</td>
<td>3.7</td>
<td>HCOOH</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cu(_2)O</td>
<td>0.5 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1</td>
<td>32.55</td>
<td>(\text{C}_2\text{H}_5\text{OH})</td>
<td>41.2</td>
<td>188</td>
</tr>
<tr>
<td>CuO</td>
<td>0.5 M KHCO(_3)</td>
<td>H-Cell</td>
<td>−1</td>
<td>44.7</td>
<td>(\text{C}_2\text{H}_4)</td>
<td>45</td>
<td>192</td>
</tr>
<tr>
<td>Cu-APC</td>
<td>0.2 M NaHCO(_3)</td>
<td>H-Cell</td>
<td>−0.78</td>
<td>7.9</td>
<td>CO</td>
<td>92</td>
<td>190</td>
</tr>
<tr>
<td>CuO@CuO-PC</td>
<td>1 M KOH</td>
<td>Flow cell</td>
<td>−1.38</td>
<td>578</td>
<td>(\text{C}_2\text{H}_4)</td>
<td>65.12</td>
<td>195</td>
</tr>
</tbody>
</table>

\(^a\) Product formation rate (10\(^{-8}\) mol s\(^{-1}\) g\(^{-1}\)).

derived carbon aerogels (CA) doped with trace Cu nanoparticles (SF-Cu/CA-1) through a facile self-assembly strategy. They observed that the carbon aerogel substrate greatly enhanced the catalytic performance by improving the electron transfer efficiency and increasing the active site exposure area of the catalyst. Additionally, it controlled the rapid desorption of \(^*\)CO\(_2\), leading to a selectivity of 83.06% for CO and a notable inhibition of hydrogen precipitation.\(^{29}\)

Specifically designed carbon substrates can synergistically interact with metal nanoparticle catalysts, promoting the formation of multi-carbon products. The synergistic effect between graphitic carbon nitride substrates ([g-C\(_3\)N\(_4\)]) and medium-sized Cu nanoparticles was determined by Han et al. They collectively achieved a faradaic efficiency of up to 62.8% at a partial current density of 188 mA cm\(^{-2}\) for \(\text{CH}_3\text{COOH}\) during the electrochemical reduction of CO. In situ experimental results demonstrated that the Cu\(_3\)C\(_4\)).
interface enhances the hydrogenation of CO, resulting in the formation of *CHO intermediates. The *CHO intermediates migrate smoothly to Cu nanoparticles (NPs) for subsequent coupling and protonation, resulting in the formation of CH2=COOH. The remarkable stability of the substrate enables Cu (25 nm)-CN-3 to steadily reduce CO at 100 mA cm−2 for over 120 h.58 The carbon substrate occasionally acts as an intermediate donor in CO2 electroreduction, enabling the formation of a tandem-like catalyst. Hou et al. developed an *in situ* CO generation and spillover strategy by designing a single Ni atom on a pyridinic N-enriched carbon support with a sodalite (SOD) topology, referred to as Ni-SOD/NC. The substrate serves as a donor, supplying adjacent Cu nanoparticles (NPs) with *CO intermediates. This strategy resulted in a remarkable C2H4 selectivity of 62.5% at an industrial-level partial current density of 160 mA cm−2.58 This study showcases the unusual potential of the substrate to function as a tandem catalyst by regulating the intermediates.58

In addition to carbon materials, covalent frameworks are extensively utilized as substrates due to their exceptional electrical conductivity and ability to stabilize domains. Yang et al. developed a Cu-based catalyst confined within a rationally designed covalent triazine framework (CTF-B), exhibiting a CuN2Cl2 coordination structure. They achieved a faradaic efficiency of 81.3% for overall CO2 reduction towards hydrocarbon (C2H4 up to 30.6%). Direct experimental evidence substantiated that CTF-B significantly enhances the adsorption of *CO* thereby accelerating subsequent C–C coupling on Cu. Additionally, the favourable chemically confined environment of CTF-B plays a crucial role in selectively producing CH2=COOH as the sole liquid product.58 Nonetheless, the intricate fabrication process of covalent frameworks restricts their broader utilization in comparison to carbon materials. Utilizing diverse substrates positively influences active site exposure, modulation of catalyst charge environment, and overall system stability. This approach is an effective strategy to regulate intermediate behaviour and obtain high-value chemicals.

### 5.2. Tandem catalyst design

In the electroreduction of CO2 over Cu to generate multi-carbon products, Cu is frequently hindered by slow thermodynamics or kinetics in specific reaction steps, resulting in inadequate coverage of crucial intermediates and posing challenges in achieving substantial selectivity for desired products. The tandem catalyst strategy offers a solution to this problem by integrating C1-producing Au, Ag, or monoatomic catalysts with Cu-based catalysts that exhibit high activity for C2+ products.7,217 The design of the catalyst structure can significantly influence the direction and duration of intermediate migration, particularly for the crucial CO intermediate.26 Schuhmann et al. mimicked the “substrate channelling effect” of the enzyme by using a nanoparticle catalyst for CO2 electroreduction. The catalyst featured an Ag core surrounded by a porous Cu shell with multiple active sites. In this setup, CO was initially generated on the Ag core and subsequently transferred to the adjacent porous Cu shell for subsequent C–C coupling (Fig. 11a). This catalyst configuration greatly enhanced the production of C2+ products at lower overpotentials.144 Similarly, Huang et al. designed Cu@Ag core–shell nanoparticles with a tuneable shell thickness for ECR. They discovered that an optimal Ag shell thickness significantly enhanced the CO absorption at the Ag/Cu interface, thereby facilitating rapid charge transfer. Consequently, the overall selectivity for CO2 reduction reached 67.6%, and the selectivity for C2H4 reached 32.2% (Fig. 11b and c).207

Another strategy for achieving a tandem catalyst effect is to directly apply the segmented catalyst layer on the GDE using an airbrushing technique. Wu et al. designed segmented gas-diffusion electrodes (s-GDEs), in which the CO selective catalyst layer (CL) Ag NP section at the inlet reduced CO2 to CO, and the subsequent C2+ selective segment coated with Cu NPs converted CO to C2+ products. This segmented structure significantly prolonged the residence time of the crucial CO intermediate and significantly enhanced the CO2 conversion rate, as demonstrated in Fig. 11d and e. They also observed a 250% increase in \( j_{\text{c}} \) compared to pure Cu by optimizing the Cu:Ag area ratio to 1.00:0.05 (Fig. 11f–h). Furthermore, they developed a Cu/Fe–N–C s-GDE demonstrating a tandem effect similar to the Cu/Ag segmented catalyst. The same segmented hypothesis was experimentally confirmed by the work of Zhang.208 These findings underscore the feasibility and advantages of regulating intermediate transport in the design of cascade catalysts.209 The cascade catalyst strategy can effectively break down the complex multi-step ECR process into segmented and simplified steps, enabling precise modulation of the behaviour of key intermediates, particularly CO, during the formation of multi-carbon products. However, selecting and designing the structure of cascade catalysts pose significant challenges in achieving desired products.

### 5.3. Surface additive effect

The surface additive strategy typically involves the introduction of molecules onto the catalyst surface, including immobilized organometallic complex catalysts, MOFs, COFs, and metal-free polymer catalysts, to modify the surface charge environment. This approach is commonly referred to as surface functionalization (Fig. 12a).210 Among the various strategies for surface functionalization, the most common strategy for surface functionalization is introducing the organic molecular polymer due to the flexible and adjustable nature of the preparation. This section will focus on this particular approach.

Applying an organic polymer coating on the catalyst surface enables the modulation of key intermediate coverage at the catalyst–polymer interface during ECR. Zhuang et al. reported a facile method to boost the selectivity of polycrystalline Cu towards C2+ products by coating the Cu surface with a 50 nm thick film of polyaniline (Cu/PANI). This resulted in a remarkable increase in the faradaic efficiency (FE) of C2+ hydrocarbons, from 15% to 60%, at −1.1 V vs. RHE in KHCO3 solutions. *In situ* infrared spectroscopy confirmed that the enhanced coverage of

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*CO at the Cu/polyaniline interface plays a significant role in improving the selectivity towards C2+ hydrocarbons (Fig. 12b and c).\textsuperscript{211} The surface functionalization strategy was used by Sargent et al. to obtain CO from CO\textsubscript{2} electrolysis. They introduced a collaborative catalyst design featuring a molecule–metal catalyst interface through the functionalization of the Cu surface with a series of porphyrin-based metallic complexes. From the \textit{in situ} characterization tests and theoretical calculations, the concentration of *CO was greatly enhanced at the molecule–metal catalyst interface, facilitating C–C coupling and activating the reaction pathway towards C\textsubscript{2}H\textsubscript{5}OH. They achieved a CO\textsubscript{2}-to-C\textsubscript{2}H\textsubscript{5}OH faradaic efficiency of up to 41\% and a partial current density of 124 mA cm\textsuperscript{-2} at \textasciitilde\textasciitilde0.82 V vs. RHE.\textsuperscript{212} This study further highlights the potential of molecular additives to synergistically interact with Cu-based catalysts and modulate the behaviour of intermediates.

The strategy of incorporating molecular additives allows for precise modulation of the local catalytic microenvironment near the surface through the use of organic compounds, thereby enabling the regulation of intermediates and achieving high selectivity for target products.\textsuperscript{213,214} Nevertheless, selecting the appropriate additive molecule to modulate the concentration and reaction tendency of desired intermediates can be a challenging task.

5.4. Coverage effect

The coverage effect is an understudied catalyst design approach that controls the behaviour of key intermediates by manipulating the coverage of the substrate (CO\textsubscript{2} or CO) during CO\textsubscript{2} electroreduction. Cuenya \textit{et al.} employed \textit{operando} Raman spectroscopy and DFT modelling to investigate the structural changes of Cu\textsubscript{2}O nanocubes and the dynamics of surface...
intermediates during the process of ECR. They observed that at high coverage of CO\(_2\), CO molecules adsorb in a mixture of atop and bridge configurations. These configurations, favoured by structural effects, facilitate CO\(_{\text{atop}}\)-CO\(_{\text{atop}}\) and CO\(_{\text{atop}}\)-CO\(_{\text{bridge}}\) coupling while limiting CO\(_{\text{bridge}}\)-CO\(_{\text{bridge}}\) interactions. The weakly bound atop configuration does not interact with CO, thereby inhibiting CO-CO dissociation and promoting OCCO\(^-\) formation. Additionally, they observed a potential-dependent intensity ratio between the Cu-CO stretching band (P2) and the CO rotation band (P1), which exhibits a volcano-like trend similar to the faradaic efficiency of multi-carbon products in CO\(_2\) electroreduction (Fig. 13a and c).

Substrate coverage influences the conformation of reaction intermediates and the reaction pathways leading to target products in ECR. Sargent et al. discovered that when they decreased the concentration of CO in CO electroreduction, the product distribution was more biased towards C\(_2\)H\(_4\) production than oxygenates. Based on density functional theory results, they concluded that a lower CO coverage promotes CO dimerization, resulting in the formation of oxygenates. Through modulating coverage to control local CO availability, they achieved desirable product selectivity, achieving a C\(_2\)H\(_4\) faradaic efficiency of 72% at a partial current density exceeding 800 mA cm\(^{-2}\) (Fig. 13b, d, g and h). In subsequent studies, they employed a *CO\(_2\) modulation strategy to control the behaviour and reaction rate of *CO. Density functional theory calculations showed that a lower *CO\(_2\) coverage on the Cu surface reduces the coverage of *CO, thereby facilitating the production of CH\(_4\) instead of C\(_2\)H\(_4\). Consequently, they achieved a faradaic efficiency of CH\(_4\) of (48 ± 2)% at a partial current density of (108 ± 5) mA cm\(^{-2}\) under a dilute CO\(_2\) gas stream. These studies offer valuable insights into the direct conversion of diluted CO\(_2\) or CO feedstock into target products with high selectivity, while also providing an understanding of how to regulate the local microchemical environment of the catalyst surface to modulate the behaviour of intermediates.

5.5. Local electrolyte microenvironment effect
Manipulating the local catalytic microenvironment constitutes another category of strategies for influencing the behaviours of
reaction intermediates and the selectivity of products. In this section, numerous factors contribute to variations in the microenvironment surrounding catalytic sites. Nonetheless, our primary focus will be on discussing and analysing the electrolyte composition and pH, as they have the most direct and substantial catalytic influence on adsorbed intermediates.

In certain electrocatalytic CO$_2$RR systems employing non-aqueous electrolytes, the inclusion of aprotic solvents like ionic liquids and organic solvents has a substantial impact on specific reactants and intermediates. Yang et al. examined the influence of electrolyte additives on catalyst surface reconstruction and their electrocatalytic performance. Specifically, the electrolyte additive EDTMPA induces atomic rearrangement on the Cu surface, resulting in the formation of Cu(110) facets. Additionally, it creates an adsorption layer that enhances the utilization of both *H and *CO and stabilizes *CHO intermediates during the rate-determining step of CH$_4$ generation.

The solvent environment and proton donors also play pivotal roles in determining the CO$_2$ electroreduction mechanism. Yogesh et al. proposed and reported a novel reaction mechanism, based on the lower C$_2$H$_4$ Tafel slope in the dimethyl sulfoxide electrolyte (27 ± 1 mV dec$^{-1}$) compared to the aqueous electrolyte (119 mV dec$^{-1}$). This mechanism involves multiple quasi-reversible proton- and electron-transfer (PCET) steps preceding a chemical rate-determining step. Moreover, electrolyte molecules serve as carriers for proton donors, such as H$_2$O, facilitating their efficient transport to the electrode surface. This process reduces the overpotential for CO$_2$ reduction to *CO and indirectly promotes the production of key intermediates.

In certain electrocatalytic CO$_2$RR systems using aqueous solution-based electrolytes, elevated electrolyte alkalinity is advantageous for suppressing hydrogen precipitation and enhancing the selectivity of CO$_2$ conversion to multi-carbon products.
products. Sargent et al. determined that within the highly alkaline electrolytic environment (10 M KOH), CO₂ in the electrolyte predominantly localizes at the catalyst layer’s immediate reaction interface, extending to the first 120 nm. This is in contrast to the less alkaline catalytic environment (1 M KOH). The limited presence of H° coverage within this narrow range of catalytic sites results in reduced competition for hydrogen precipitation. Furthermore, even under moderately negative potentials, the localized intensity of the CO₂ reaction enhances the *CO coverage. This hydroxide-mediated transformation significantly enhances the reaction kinetics of CO dimerization, leading to a substantial improvement in electrocatalytic performance. Modulating the concentration and residence time of crucial intermediates over Cu-based catalysts provides new insights into product distributions’ regulation. Guided by a number of previous works, numerous investigations on

### 6. Conclusions

Electrocatalytic reduction of CO₂ to a wide range of high value chemicals is a promising technology for energy storage and conversion. Modulating the concentration and residence time of crucial intermediates over Cu-based catalysts provides new insights into product distributions’ regulation. Guided by a number of previous works, numerous investigations on
catalyst composition engineering, catalyst morphology design, and electrolysis equipment and conditions have been conducted, wherein the synergistic effects of some strategies have also been created. With these efforts, the performance of Cu-based catalysts has taken a qualitative leap forward from decades ago. To promote the practical feasibility of the electrocatalytic CO_{2} reduction, more elaborate characterisation instruments for observing intermediates and catalyst designs should be built upon and improved to suit more realistic catalytic conditions.

This review focuses on catalyst designs that modulate the reaction process of key intermediates on the catalyst surface. We provided a detailed overview of the basic outline of electrocatalytic CO_{2} reduction (ECR) firstly, including the universal reaction apparatus, the commonly used evaluation parameters for electrocatalytic CO_{2} reduction (overpotential, current density, faradaic efficiency, Tafel slope and other parameters), and a comprehensive overview of the ECR experimental mechanism based on a wealth of experimental results and theoretical studies subsequently. Drawing from our observations of intermediate reactions on the catalyst surface, we present an overview of advanced catalyst designs aimed at manipulating intermediate behaviour, encompassing their residence time and inclination to engage in various reaction pathways. Categorizing these designs into three primary groups, we differentiate them based on their ability to finely or comprehensively modulate intermediates through various strategies: heteroatom doping (both metallic and non-metallic), morphological structure engineering (involving grain boundaries, pore confinement, hierarchical structures, facets, defects, and chemical states), and local catalytic environment engineering (encompassing the substrate effect, tandem catalyst strategy, surface additives, coverage effect, and local electrolyte microenvironment effect). Although each strategy presents distinct advantages, the synergistic combination of multiple strategies frequently results in enhanced electrocatalytic performance. As an illustration, co-doping the metallic element Ag with the non-metallic element S serves to not only efficiently adjust the electronic structure of the catalyst in favour of CH_{3}OH generation but also to effectively suppress the hydrogen precipitation reaction. These synergistic interactions significantly enhanced the selectivity and reactivity of the CH_{3}OH product.

Despite the substantial recent enhancements in the electrocatalytic performance of Cu-based catalysts for the CO_{2}RR, the development of competent catalyst designs founded on precise reaction mechanisms and the achievement of large-scale industrial applications still pose formidable challenges. In conclusion, we recognize several impending challenges and anticipate shifts in future research priorities:

1. Firstly, the mechanism underlying CO_{2} electroreduction, particularly the formation of C_{2}H_{4}, products, remains enigmatic and demands rigorous exploration. The current CO_{2}RR mechanism is primarily derived through retroactive extrapolation of the distribution of catalytic products, in conjunction with theoretical calculations. However, this approach raises concerns about objectivity and veracity. Obtaining immediate data on reaction intermediates through in situ catalytic instrumentation can offer genuine and precise insights into the reaction mechanism. Consequently, progress in high-resolution in situ characterization techniques is imperative to discern the nuanced behavioural traits of intricate intermediates and explore their reaction mechanisms. Additionally, it is essential to establish a correlation between the evolution of the catalyst surface and the reaction process, extending beyond the observation of intermediate dynamics alone. This correlation is crucial for identifying the active sites and comprehending the reaction mechanism. Yang et al., based on information about the evolution of AgCu catalysts during the CO_{2}RR obtained through time-sequential electron microscopy and elemental mapping studies, confirm that the catalytically active sites consist of the metallic state of Cu and underscore the importance of AgCu phase boundaries in the CO_{2}RR. Furthermore, operando high-energy-resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) furnishes compelling spectroscopic evidence demonstrating the rupture of chemical bonds between ligands and the surfaces of Cu nanoparticles. This confirms that the true active sites are the undercoordinated metallic Cu nanograins in the CO_{2}RR. Furthermore, while simulating reaction scenarios through theoretical calculations significantly aids in structural design and high-throughput catalyst screening, it is crucial to acknowledge that mechanistic investigations cannot rely solely on theoretical calculations.

2. Secondly, the microenvironment of the electrocatalytic system is still under-researched. The interplay between the catalyst, electrolyte, and gas reactant at the three-phase interface has a complex and significant effect on the dehydrogenation and coupling of the reaction intermediates, which demands further exploration. Investigating the interaction between the local reaction environment and mass/electron transfer within this interface will shed light on the influence of microenvironments on electrocatalytic activity and selectivity.

For example, the CO_{2} concentration in waste gases emitted from modern industrial production is typically low, typically ranging from 6% to 15%. However, the current electrocatalytic system employs highly purified reactant feedstock, which not only significantly reduces the efficiency of CO_{2} feedstock utilization but also increases the cost and energy consumption associated with the purification process. To attain high-performance CO_{2} electroreduction for the production of valuable chemicals at nearly realistic feed concentrations, it becomes imperative to investigate the reaction microenvironment under conditions of dilute CO_{2} feed and develop catalyst designs that enhance crucial intermediates. At present, experimental investigations into low-purity CO_{2} feeds primarily focus on discerning and quantifying variations in the adsorption strength of intermediates under different feedstock coverages, while the evolution of catalytic active sites during the reduction process has received limited attention. Indeed, feedstocks with varying coverages are susceptible to interacting differently with active sites in a complex local catalytic microenvironment, leading to changes or transfers of active sites. Therefore, comprehending the impact of the microenvironment on the catalytic reaction is essential for unravelling the catalytic mechanism and enhancing catalytic performance.
(3) Kinetics studies of electrocatalytic processes have received less attention compared to their thermodynamic counterparts. Product distribution is not solely influenced by thermodynamic energy barriers but also by kinetic factors. However, most existing research has relied on higher-order theoretical calculations and simulations to analyse changes in the thermodynamic energy barriers of reaction steps in electrocatalytic processes. A comprehensive and structured kinetic theory simulation system is still lacking, limiting investigations to a superficial understanding of reaction rates in general. Electrochemical parameters such as reaction rate and Tafel slope which evaluate electrocatalytic kinetics could demonstrate a wealth of potential information about the rate-determining step during the reaction process. Establishing a correlation between the kinetic mechanism underlying these parameters and the thermodynamic DFT simulations is of critical importance for a profound comprehension of the electrocatalytic mechanism. In addition, the study of the kinetics of catalytic reactions can help to increase the rate of catalytic reactions, and thus gradually approach the industrialization requirement of high current or even realize the industrialization of catalytic reactions.

(4) The potential of machine learning and computational chemistry in ECR remains largely untapped. In the realm of ECR, these tools can aid in catalyst screening. Machine learning enables the construction of a robust, large-scale catalyst performance database by swiftly evaluating theoretical studies and facilitating rational catalyst design. This expedites the discovery and optimization of highly efficient and selective catalysts. On the other hand, computational chemistry simulates the electrocatalytic microenvironment, catalyst surface morphology, and reactant adsorption configuration to predict catalyst performance, thus guiding the experimental design and minimizing trial-and-error endeavours. Nevertheless, using machine learning and computational chemistry in ECR guarantees further exploration.

In conclusion, electrocatalytic conversion of CO2 into valuable chemicals and fuels holds promise as an environmentally friendly technology capable of mitigating the greenhouse effect and advancing carbon neutrality. Nevertheless, its advancement continues to face substantial challenges, including the unclear formation mechanism of CO2 electroreduction to C2+ products, the insufficiently studied electrocatalytic microenvironments in these systems, and the relatively uncharted territory of dynamics research and machine learning. Overcoming these challenges requires the application of advanced, synergistic catalyst strategies, improved product analysis techniques, and state-of-the-art in situ characterization technologies. Predictably, a new trend in obtaining higher-order CO2RR products will involve the design of efficient Cu-based catalysts with a focus on modulating the behaviour of reaction intermediates.

Data availability
This review article does not include any experimental or computational data.

Author contributions
L. Xie conceptualized the work, performed the investigations and wrote the manuscript. Y. J., W. Z. and S. D. provided resources and supervised the work. Y. Z. and J. Z. were involved in funding acquisition and project administration. All authors have given approval to the final version of the manuscript.

Conflicts of interest
There are no conflicts to declare.

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